Problèmes mathématiques liés à la modélisation des solides à différentes échelles

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Résumé. Cette thèse présente l'étude de divers problèmes mathématiques en modélisation des solides, tant à l'échelle atomique qu'à l'échelle macroscopique. Les modèles correspondants sont très simplifiés, mais présentent tout de même des comportements qualitatifs acceptables, et permettent, du fait de leur simplicité, de pousser l'analyse mathématique plus loin que dans le cas de modèles plus réalistes.
Une première partie (chapitres 2, 3, 4) est consacrée à l'étude de l'origine de la structure cristalline. Ce problème peut être posé de la façon suivante : les modèles étudiés ici rendent-ils compte du fait qu'à température nulle, la matière est ordonnée ? ou, de façon équivalente, l'état de minimum d'énergie de N atomes identiques ressemble-t-il, pour N grand, à une structure périodique ? Ce type de problème est relié au problème de limite thermodynamique, dont certains aspects sont également étudiés ici.
Dans un deuxième temps, nous étudions au chapitre 5 le cas où précisément, la matière n'est pas ordonnée : dans le cas d'un système périodique, il est possible de définir l'énergie du système pour les modèles utilisés ici par le processus de limite thermodynamique. Nous étudions ce même processus dans un cas non-périodique, donnant des hypothèses générales qui permettent de mener à bien une telle étude.
Les chapitres 6 et 7 sont consacrés à l'étude du lien possible entres des théories macroscopiques des solides et ces modèles microscopiques, le premier dans le cas de comportements mécaniques, le deuxième dans le cas du comportement en présence d'un champ électrique.
Enfin, le dernier chapitre présente une brève introduction à certaines techniques utilisées en numérique des solides, pour des modèles beaucoup plus élaborés que ceux des chapitres précédents.

Abstract. We investigate in this thesis various mathematical problems in solid-state modelling, at the atomic scale as well as the macroscopic one. The models we use here are highly simplified (compared to standard quantum models), but exhibit acceptable qualitative behaviours. In addition, their simplicity allows one to go further in their rigourous mathematical analysis.
The first part (chapters 2, 3, 4) is devoted to the study of the origin of crystalline symmetry. This problem may be stated as follows: do the models we study here account for the fact that at zero temperature, matter is ordered? or, equivalently, does the ground state of N identical atoms converge to some periodic structure as N goes to infinity? This kind of problem is related to the problem of thermodynamic limit, which is studied here in some particular cases.
In a second part, we study the case when matter does not show any order: if the system is periodic, the definition of its energy for the models we use here is possible through the thermodynamic limit process. We study it in the case when the system is not periodic, and give general hypotheses allowing to carry out the corresponding study.
In chapters 6 and 7, we study the possible link between these microscopic models and macroscopic solid-state theories, for mechanical features in the first case, and for electrostatic ones in the second. Finally, the last chapter presents numerical technics in use in the modelling of electronic structure in solids.

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Chapitre 1

Introduction et présentation des résultats

Depuis une vingtaine d'années, les problèmes mathématiques de la chimie quantique ont fait une entrée (d'abord timide, mais qui prend progressivement de l'ampleur) dans le paysage des mathématiques appliquées françaises. En témoignent diverses thèses soutenues sur ce type de sujet [3, 5, 13, 18, 19, 35].

Cette thèse se situe dans le prolongement de ces dernières, avec une dominante théorique, bien que certains aspects numériques soient étudiés au chapitre 8. Une deuxième spécificité consiste dans le fait que nous nous intéresserons ici exclusivement à des modèles de chimie quantique des *solides*, donc en particulier à des systèmes comportant une infinité de particules.

Les problèmes évoqués ici sont essentiellement de deux types : d'une part, dans les chapitres 2, 3, 4, nous nous intéressons à l'origine de la structure cristalline : pourquoi les solides observés dans la nature sont-ils le plus souvent ordonnés ? Le mot "ordonné" sera traduit ici par "périodique", bien que ce dernier ne recouvre pas la même généralité. D'autre part, le deuxième type de questions, évoquées aux chapitres 6, 7, peut se poser sous la forme suivante : de ces modèles de chimie quantique, donc *microscopiques*, peut-on déduire pour les solides considérés des propriétés *macroscopiques*, telles que le comportement mécanique ou électrique d'un échantillon cristallin ? Ce type de problème est intimement lié à la notion de *limite thermodynamique*, qui consiste en un passage à la limite pour déduire d'un modèle comportant un nombre fini de particules le modèle équivalent pour un nombre infini de particules. Ce procédé est (relativement) aisé dans le cas où la périodicité de cette infinité de particules est supposée. Toutefois, celle-ci n'est pas toujours démontrée, ni même physiquement acceptable. C'est pourquoi le chapitre 5 est consacré à l'étude de ce problème de limite thermodynamique dans un cadre non périodique.

Avant de présenter les résultats de cette thèse dans les sections qui suivent, nous définissons dans la section 1 les modèles que nous utiliserons dans la suite. Notons que ces modèles, bien que très rudimentaires du point de vue physique, présentent l'avantage de permettre un traitement mathématique plus complet, tout en gardant certaines propriétés qualitatives acceptables.

1 Description des modèles : Thomas-Fermi et Thomas-Fermi-von Weizsäcker

Nous donnons dans cette section un bref aperçu des modèles que nous utilisons dans la suite, et de leur lien avec des modèles plus élaborés, tels que par exemple l'équation de Schrödinger. Pour plus de détails sur ces liens, nous renvoyons à [5] et aux références qui y sont citées, ainsi qu'aux ouvrages de référence de chimie, tels que [23, 29, 28, 24].

1.1 Une approximation de l'équation de Schrödinger

1.1.1 L'équation de Schrödinger

Considérons un système composé de N électrons de positions x_j, et M noyaux, de positions X_k. La mécanique quantique décrit ce système par sa fonction d'onde $\varphi = \varphi(x_1, \dots x_N, X_1, \dots, X_M)$. Nous négligeons ici les variables de spin par souci de clarté, bien qu'il soit facile d'adapter ce qui va suivre pour prendre en compte ces variables supplémentaires. En ne considérant que les interactions électrostatiques, ce qui constitue une bonne approximation à l'échelle moléculaire, l'hamiltonien du système est alors :

$$\begin{aligned} H &= -\sum_{k=1}^{M} \frac{1}{2m_k}\Delta_{X_k} - \sum_{i=1}^{N} \frac{1}{2}\Delta_{x_i} - \sum_{i=1}^{N}\sum_{k=1}^{M} \frac{Z_k}{|x_i - X_k|} \\ &\quad + \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i} \frac{1}{|x_i - x_j|} + \frac{1}{2}\sum_{k=1}^{M}\sum_{l\neq k} \frac{Z_k Z_l}{|X_k - X_l|}, \end{aligned} \tag{1}$$

où m_k est la masse du noyau k et Z_k sa charge, dans un système d'unités dit **atomique**, qui vérifie en particulier :

$$\hbar = 1, \quad \frac{1}{4\pi\varepsilon_0} = 1, \quad m_e = 1, \quad e = 1$$

m_e et e étant respectivement la masse et la charge d'un électron, et ε_0 la permittivité diélectrique du vide. Notons que dans le cas où le système n'est pas isolé, vient s'ajouter dans (1) un terme traduisant l'interaction du système moléculaire avec son environnement, par exemple un potentiel extérieur V_{ext}. Les électrons étant des fermions, la fonction d'onde est supposée antisymétrique par rapport aux variables x_j, ce qui signifie que pour toute permutation σ de l'ensemble $\{1, \dots, N\}$,

$$\varphi(x_{\sigma(1)}, \dots x_{\sigma(N)}, X_1, \dots, X_M) = \varepsilon(\sigma)\varphi(x_1, \dots x_N, X_1, \dots, X_M),$$

$\varepsilon(\sigma)$ étant la signature de σ. De plus, la fonction d'onde φ est supposée être de carré sommable, car la fonction $|\varphi|^2$ est interprétée comme une densité de probabilité de présence, donc doit être normalisable. Ceci se traduit par le fait que l'espace fonctionnel auquel appartient φ est donc :

$$\mathcal{H} = \bigwedge_{i=1}^{N} L^2(\mathbf{R}^3, \mathbf{C}) \otimes L^2(\mathbf{R}^{3M}, \mathbf{C}).$$

Nous nous intéresserons à *l'état fondamental* du système (bien entendu, il est possible d'étudier la *dynamique* d'un tel système, mais ce n'est pas notre propos), c'est-à-dire la solution du problème :

$$\inf\Big\{\langle\varphi, H\varphi\rangle, \quad \varphi\in\mathcal{H}, \quad \|\varphi\|_{\mathcal{H}}=1\Big\}. \tag{2}$$

La quantité $\langle\varphi, H\varphi\rangle$ est physiquement interprétée comme l'énergie du système. Le problème de minimisation (2) revient donc à trouver l'état de minimum d'énergie. On peut également s'intéresser (nous ne le ferons pas ici) aux états stationnaires de cette fonctionnelle d'énergie, c'est-à-dire aux vecteurs propres de H :

$$H\varphi = E\varphi. \tag{3}$$

Les solutions de (2) sont en particulier des solutions de (3), avec E le plus petit possible. Les autres états stationnaires sont dits *excités*.

En fait, le problème (2) n'admet pas de solution dans le cas d'un système isolé, du fait de l'invariance par translation de H (voir [34]). Il faut donc briser cette invariance par translation, par exemple en fixant le centre de masse du système. L'approximation de Born-Oppenheimer, que nous détaillons ci-dessous, est également un moyen de briser cette invariance.

1.1.2 L'approximation de Born-Oppenheimer

Le problème (2) est posé sur un espace difficile à décrire, et il est parfois nécessaire de le simplifier. C'est le cas en particulier quand on désire calculer numériquement les solutions de (2), mais également dans certains cas d'étude théorique où une description très précise des solutions est nécessaire.

Une première simplification consiste à considérer que, comme les noyaux sont nettement plus lourds que les électrons (de trois ordres de grandeur au moins), ils peuvent être traités comme des particules classiques. C'est ce qu'on appelle l'approximation de Born-Oppenheimer. Cette intuition peut être justifiée rigoureusement, au sens où quand le quotient $\frac{m_e}{m_n}$ des deux masses tend vers 0, la dynamique associée à l'hamiltonien H converge en un certain sens vers celle où l'on a remplacé les noyaux par des particules classiques [17]. Dans ce cas, on obtient un *hamiltonien électronique*, qui s'écrit :

$$H_e = -\sum_{i=1}^{N}\frac{1}{2}\Delta_{x_i} - \sum_{i=1}^{N}\sum_{k=1}^{M}\frac{Z_k}{|x_i-X_k|} + \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}\frac{1}{|x_i-x_j|}, \tag{4}$$

et le système est décrit, dans son état fondamental[1], par $(X_1,\dots X_M)\in(\mathbf{R}^3)^M$ et $\psi\in\bigwedge_{i=1}^{N}L^2(\mathbf{R}^3,\mathbf{C})$, l'énergie totale s'écrivant :

$$E\big(\{X_k\}_{1\leq k\leq M},\psi\big) = \langle\psi, H_e\psi\rangle + \frac{1}{2}\sum_{k\neq l}\frac{Z_kZ_l}{|X_k-X_l|}. \tag{5}$$

[1] dans le cas dynamique, on doit rajouter la vitesse des noyaux.

On peut alors séparer la recherche du fondamental en deux étapes : le *problème électronique* d'une part, qui consiste à minimiser (5) par rapport à ψ, les X_k étant fixés (notons que dans ce cas, l'hamiltonien électronique a effectivement un fondamental, tout au moins pour les systèmes neutres ou chargés positivement, car le potentiel engendré par les noyaux brise l'invariance par translation, et qu'il est en fait confinant [33]). La fonction qui aux X_k associe ce minimum constitue alors une fonctionnelle d'énergie dont on peut chercher un éventuel minimum : c'est le problème de l'*optimisation de géométrie*.

Cette première approximation simplifie le problème, mais l'espace $\mathcal{H}_e = \bigwedge_{i=1}^N L^2(\mathbf{R}^3, \mathbf{C})$ reste très complexe, et le problème électronique doit encore être approximé. Pour cela, deux approches sont essentiellement utilisées. La première, dite de *Hartree-Fock*, consiste à utiliser un sous-espace de $\mathcal{H}_e$ que l'on espère représentatif, plutôt que $\mathcal{H}_e$ lui-même. La seconde, appelée *fonctionnelle de la densité*, consiste tout simplement à changer d'inconnue : au lieu de considérer l'énergie comme une fonction de ψ, on la considère comme une fonction de la densité d'électrons $\rho_\psi(x)$, définie par

$$\rho_\psi(x) = N \int_{(\mathbf{R}^3)^{N-1}} |\psi(x, x_2, \ldots, x_N)|^2 dx_2 dx_3 \ldots dx_N. \tag{6}$$

1.1.3 Le modèle de Hartree-Fock

Le modèle de Hartree-Fock consiste à construire la plus simple fonction d'onde électronique antisymétrique (i.e appartenant à $\mathcal{H}_e$) à partir de N fonctions d'ondes individuelles $\phi_i \in L^2(\mathbf{R}^3)$. Ceci consiste à écrire le produit antisymétrisé des ϕ_i, c'est-à-dire :

$$\psi(x_1, x_2, \ldots x_N) = \frac{1}{\sqrt{N!}} \sum_{\sigma \in \mathcal{S}_N} \varepsilon(\sigma) \prod_{i=1}^N \phi_i(x_{\sigma(i)}) = \frac{1}{\sqrt{N!}} \det(\phi_i(x_j)), \tag{7}$$

où $\mathcal{S}_N$ est le groupe symétrique d'ordre N. Le facteur $\frac{1}{\sqrt{N!}}$ est présent pour assurer la normalisation de ψ, dans la mesure où les ϕ_i sont également normalisées. L'expression (7) est appelée *déterminant de Slater*. Elle est invariante si l'on multiplie le vecteur $(\phi_1, \ldots \phi_N)$ par une matrice unitaire, et l'on peut donc se restreindre au cas où ces fonctions sont orthonormées, donc à l'espace

$$\mathcal{H}_F = \left\{ (\phi_i)_{1 \le i \le N}, \quad \phi_i \in L^2(\mathbf{R}^3), \quad \langle \phi_i, \phi_j \rangle = \delta_{ij} \right\}. \tag{8}$$

L'énergie électronique devient alors :

$$\begin{aligned} \langle \psi, H_e \psi \rangle \;=\; & \frac{1}{2} \sum_{i=1}^N \int_{\mathbf{R}^3} |\nabla \phi_i|^2 - \sum_{i=1}^N \sum_{k=1}^M \int_{\mathbf{R}^3} \frac{Z_k |\phi_i(x)|^2}{|x - \overline{x}_k|} dx \\ & + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \int_{\mathbf{R}^3} \int_{\mathbf{R}^3} \frac{|\phi_i(x)|^2 |\phi_j(y)|^2}{|x-y|} dx dy \\ & - \frac{1}{2} \int_{\mathbf{R}^3} \int_{\mathbf{R}^3} \frac{|\sum_{i=1}^N \phi_i(x) \phi_i(y)^*|^2}{|x-y|} dx dy, \end{aligned}$$

où ϕ^* désigne le complexe conjugué de ϕ. Le problème électronique consiste alors à minimiser cette énergie sur l'espace $\mathcal{H}_F$. Ceci conduit à une système de N équations d'Euler-Lagrange qui s'écrit :

$$F\phi_i = \sum_{j=1}^{N} \lambda_{ij}\phi_j,$$

où la matrice $\lambda = (\lambda_{ij})$ est le multiplicateur associé aux contraintes d'orthogonalité présentes dans la définition de $\mathcal{H}_F$, et est donc hermitienne. L'opérateur F est l'opérateur de Fock :

$$\begin{aligned}(F\phi)(x) &= -\frac{1}{2}\Delta\phi(x) - \sum_{k=1}^{M} \frac{Z_k}{|x - X_k|}\phi(x) + \sum_{i=1}^{N} \int_{\mathbf{R}^3} \frac{|\phi_i|^2(y)\phi(x)}{|x-y|}dy \\ &\quad - \sum_{i=1}^{N} \int_{\mathbf{R}^3} \frac{\phi_i(x)\phi_i(y)^*\phi(y)}{|x-y|}dy. \end{aligned} \tag{9}$$

En diagonalisant la matrice λ des multiplicateurs, et en notant U la matrice de passage correspondante, on obtient alors, en posant $(\psi_i) = U(\phi_i)$, les équations de *Hartree-Fock* :

$$F\psi_i = \varepsilon_i\psi_i.$$

Ces équations sont non-linéaires, non locales, et fortement couplées, ce qui implique un traitement mathématique difficile (voir [5, 22, 20]). Notons que les quantités ε_i sont les N plus petites valeurs propres de l'opérateur de Fock F.

Ce modèle est beaucoup utilisé dans les simulations numériques actuellement, éventuellement amélioré (par exemple en élargissant l'espace grâce à l'utilisation d'une combinaison linéaire de déterminants plutôt qu'un seul, mais ce n'est pas la seule méthode). Le chapitre 8 donne un aperçu rapide des méthodes correspondantes dans le cas de solides.

1.1.4 La théorie de la fonctionnelle de la densité

L'approximation de type fonctionnelle de la densité (en anglais DFT, pour *Density Functional Theory*), consiste à utiliser comme inconnue, non plus la fonction d'onde électronique ψ, mais la densité ρ définie par (6). Bien entendu, il n'est pas clair que l'énergie s'écrive comme une fonction de ρ. C'est l'objet du théorème qui suit, établi par Hohenberg et Kohn en 1964 :

Théorème 1.1 (Hohenberg et Kohn, [16])

(a) Soient deux potentiels extérieurs V_1 et V_2, et soient H_1 et H_2 les hamiltoniens de N électrons respectivement dans ces deux potentiels ($H_p = -\frac{1}{2}\sum \Delta_{x_i} + \sum_{i\neq j} \frac{1}{|x_i - x_j|} + V_p$), dont on suppose qu'ils admettent des états fondamentaux ψ_1 et ψ_2. Soient $\rho_j = \rho_{\psi_j}$ les densités électroniques correspondantes, définies par (6). Si $\rho_1 = \rho_2$, alors $V_1 - V_2$ est constant.

(b) Il existe une fonctionnelle $\mathcal{F}$, définie sur l'ensemble des densités électroniques possibles, et indépendante de V_1, *telle que la densité de l'état fondamental de l'hamiltonien H_1 ci-dessus soit solution de :*

$$\inf\left\{\mathcal{F}(\rho)+\int_{\mathbf{R}^3}\rho V_1,\quad \rho\in L^1(\mathbf{R}^3),\quad \rho\geq 0,\quad \int_{\mathbf{R}^3}\rho=N\right\}.$$

Ce théorème donne une justification théorique à la stratégie de la fonctionnelle de la densité, dans le cas de la recherche du fondamental. Ce n'est pas le cas en revanche pour la recherche des états excités ou *a fortiori* la dynamique, bien que les résultats correspondants soient en général physiquement acceptables [29, 24]. De plus, la valeur de ce théorème n'est que théorique. En effet, elle assure l'existence d'une fonctionnelle $\mathcal{F}$, mais sans donner le moindre moyen de la calculer ni de l'approcher. Ainsi, tous les calculs correspondant à cette théorie utilisent une fonctionnelle $\mathcal{F}$ plus ou moins empirique. Nous ne détaillerons pas ici les fonctionnelles standard, renvoyant à [5] et aux références qui y sont citées pour plus de détails.

Un cas particulier de fonctionnelle $\mathcal{F}$ est la fonctionnelle de Thomas-Fermi, qui, bien qu'antérieure au théorème de Hohenberg et Kohn, procède d'une démarche similaire. Elle contient un terme d'approximation de l'énergie cinétique d'une part, et un terme d'interaction électrostatique des électrons avec eux-mêmes d'autre part :

$$\mathcal{F}(\rho)=C_{\mathrm{TF}}\int_{\mathbf{R}^3}\rho^{5/3}+\frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3}\frac{\rho(x)\rho(y)}{|x-y|}dxdy, \tag{10}$$

où C_{TF} est une constante strictement positive. Cette approximation de l'énergie cinétique est valable dans le cas de densités ρ imporantes, mais ne variant pas trop vite (ceci peut être justifié mathématiquement dans certains cas [21, 4]). Certaines améliorations peuvent être apportées, en particulier l'ajout du terme de von Weizsäcker, donnant la fonctionnelle de Thomas-Fermi-von Weizsäcker :

$$\mathcal{F}(\rho)=C_{\mathrm{TF}}\int_{\mathbf{R}^3}\rho^{5/3}+a\int_{\mathbf{R}^3}|\nabla\sqrt{\rho}|^2+\frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3}\frac{\rho(x)\rho(y)}{|x-y|}dxdy, \tag{11}$$

où $a>0$. Notons que ce modèle peut également être vu comme le premier ordre du développement en puissances de $\hbar$ (qui vaut 1 dans notre système d'unité, mais qui est en fait présent en facteur de l'énergie cinétique) de l'énergie cinétique d'origine. En fait, le terme en puissance est une approximation valable pour N grand (à volume fixé), et le terme en gradient est *exact* dans le cas contraire, c'est-à-dire $N=1$. Ces modèles de type Thomas-Fermi sont très peu utilisés pour les calculs, car trop rudimentaires. Néanmoins, une forme corrigée de la fonctionnelle TFW peut donner des résultats relativement satisfaisants [6]. Les constantes a et C_{TF} n'ont pas ici beaucoup d'importance, et nous les fixerons égales à 1.

1.2 Notations

Dans la suite, nous nommerons *énergie TF* l'énergie totale de Thomas-Fermi, c'est-à-dire

$$E^{\mathrm{TF}}(\rho,\{X_i\}) = \int_{\mathbf{R}^3}\rho^{5/3} - \sum_{i=1}^{M}\int_{\mathbf{R}^3}\frac{Z_i\rho(x)}{|x-X_i|}dx + \frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3}\frac{\rho(x)\rho(y)}{|x-y|}dxdy + \frac{1}{2}\sum_{i\neq j}\frac{Z_iZ_j}{|X_i-X_j|}, \tag{12}$$

et *énergie TFW* l'énergie totale de Thomas-Fermi-von Weizsäcker :

$$E^{\mathrm{TFW}}(\rho,\{X_i\}) = \int_{\mathbf{R}^3}\rho^{5/3} + \int_{\mathbf{R}^3}|\nabla\sqrt{\rho}|^2 - \sum_{i=1}^{M}\int_{\mathbf{R}^3}\frac{Z_i\rho(x)}{|x-X_i|}dx + \frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3}\frac{\rho(x)\rho(y)}{|x-y|}dxdy + \frac{1}{2}\sum_{i\neq j}\frac{Z_iZ_j}{|X_i-X_j|}, \tag{13}$$

Dans (12) et (13), X_i et Z_i désignent respectivement la position et la charge du noyau i. Dans les deux cas, on note $E^{\mathrm{TF(W)}}(\{X_i\})$ l'énergie minimale par rapport à ρ, i.e l'énergie de la solution du problème électronique :

$$E^{\mathrm{TF}}(\{X_i\}) = \inf\Big\{E^{\mathrm{TF}}(\rho,\{X_i\}),\ \rho\geq 0,\ \rho\in L^1\cap L^{5/3}(\mathbf{R}^3),\ \int_{\mathbf{R}^3}\rho = N\Big\}, \tag{14}$$

$$E^{\mathrm{TFW}}(\{X_i\}) = \inf\Big\{E^{\mathrm{TFW}}(\rho,\{X_i\}),\ \rho\geq 0,\ \rho\in H^1(\mathbf{R}^3),\ \int_{\mathbf{R}^3}\rho = N\Big\}. \tag{15}$$

Enfin, nous noterons $I_M^{\mathrm{TF(W)}}$ les problèmes d'optimisation de géométrie correspondants :

$$I_M^{\mathrm{TF}} = \inf\Big\{E^{\mathrm{TF}}(\{X_i\}),\ X_i\in\mathbf{R}^3\Big\}, \tag{16}$$

$$I_M^{\mathrm{TFW}} = \inf\Big\{E^{\mathrm{TFW}}(\{X_i\}),\ X_i\in\mathbf{R}^3\Big\}, \tag{17}$$

1.3 Propriétés mathématiques

1.3.1 Le cas moléculaire

Nous rappelons ici les propriétés mathématiques connues des modèles TF et TFW. La première chose est que sous une condition liant la charge totale des noyaux $Z=\sum Z_i$ et le nombre N d'électrons, les problèmes électroniques admettent une unique solution. Ceci est essentiellement dû à la stricte convexité (par rapport à ρ) de ces modèles. Ces résultats sont démontrés dans [21] pour le cas TF, et dans [2] pour le cas TFW. Nous regroupons ces deux résultats dans les théorèmes suivants :

Théorème 1.2 (État fondamental TF, Lieb et Simon [21])
(i) Soient $\{X_i\}_{1\leq i\leq M}$ M vecteurs de $\mathbf{R}^3$ deux à deux distincts, et soient $\{Z_i\}_{1\leq i\leq M}$ des entiers positifs. Alors, si $N \leq \sum_{i=1}^{M} Z_i$, le problème électronique TF (14) admet une unique solution $\rho \geq 0$. Cette solution est à support compact, sauf dans le cas neutre $N = \sum_{i=1}^{M} Z_i$. Si $N > \sum_{i=1}^{M} Z_i$, ce problème n'a pas de solution.

(ii) Dans le cas neutre ($N = \sum_{i=1}^{M} Z_i$), le problème d'optimisation de géométrie TF (16) n'admet pas de solution. Plus précisément, ce minimum n'est atteint que lorsque les X_i sont à l'infini les uns des autres.

La partie (ii) de ce théorème est connue sous le nom de lemme de Teller, ou propriété de "no binding". Elle affirme en particulier que les molécules ne sont pas stables pour le modèle TF. À ce premier aspect non physique du modèle s'ajoute le fait que la densité devient infinie au voisinage des noyaux (ρ se comporte comme $\frac{1}{|x-X_i|^{3/2}}$), alors qu'elle reste finie dans le cas de solutions de l'équation de Schrödinger, et le fait qu'elle décroît (dans le cas neutre) comme une puissance à l'infini, alors que la décroissance devrait être exponentielle. Notons également que la propriété (i) implique la non-existence d'ions négatifs. Ces aspects non physiques sont (au moins qualitativement) corrigés par la présence du terme de von Weizsäcker. Nous avons en particulier :

Théorème 1.3 (Problème électronique TFW, Benguria, Brézis et Lieb, [2])
Soient $\{X_i\}_{1\leq i\leq M}$ M vecteurs de $\mathbf{R}^3$ deux à deux distincts, et soient $\{Z_i\}_{1\leq i\leq M}$ des entiers positifs. Alors il existe $\lambda_c > \sum_{i=1}^{M} Z_i$ tel que :

- *Si $N \leq \lambda_c$, alors le problème électronique TFW (15) admet une unique solution. Cette solution est strictement positive.*
- *si $N > \lambda_c$, alors ce problème n'a pas de solution.*

Le problème d'optimisation de géométrie TFW a été étudié dans [10] :

Théorème 1.4 (Optimisation de géométrie TFW, Catto et Lions [10]) *Dans le cas neutre $N = \sum_{i=1}^{M} Z_i$, le problème d'optimisation de géométrie TFW (17) admet au moins une solution.*

Les équations d'Euler-Lagrange des problèmes électroniques TF et TFW s'écrivent :

$$-\Delta\phi + \left(\frac{3}{5}(\phi-\theta)^+\right)^{3/2} = 4\pi \sum_{j=1}^{M} Z_j \delta_{X_j}$$

dans le cas TF, où $\rho = \left(\frac{3}{5}(\phi-\theta)^+\right)^{3/2}$, θ est le multiplicateur associé à la contrainte de masse, et la partie positive traduit la contrainte $\rho \geq 0$. Dans le cas TFW, posant $u = \sqrt{\rho}$,

nous avons

$$-\Delta u + \frac{5}{3}u^{7/3} - \Big(\sum_{j=1}^{M} \frac{Z_j}{|x - X_j|} - u^2 * \frac{1}{|x|} + \theta\Big)u = 0,$$

où θ est le multiplicateur associé à la contrainte de masse. Cette équation peut également se réécrire comme

$$\begin{cases} -\Delta u + \dfrac{5}{3}u^{7/3} - \phi u = 0, \\ -\Delta \phi = 4\pi\Big(\displaystyle\sum_{j=1}^{M} Z_j \delta_{X_j} - u^2\Big). \end{cases}$$

1.3.2 Le problème de limite thermodynamique

Les propriétés rappelées ci-dessus concernent des modèles *moléculaires*. Nous allons maintenant voir comment de tels modèles peuvent être généralisés au cas de solides cristallins. Pour toute la suite nous ne considérerons que des systèmes *neutres*.

Nous supposerons que le solide considéré est un cristal parfait, c'est-à-dire que les noyaux atomiques sont répartis sur un réseau périodique ℓ. Une méthode pour déduire du modèle moléculaire le modèle des solides correspondant est de considérer un nombre *fini* N d'atomes, dont les noyaux sont répartis sur un sous-ensemble Λ du réseau ℓ, de résoudre le problème électronique (neutre) correspondant, puis de passer à la limite $N \longrightarrow +\infty$, avec la contrainte que Λ remplisse (en un certain sens) le réseau ℓ.

Pour simplifier, nous supposons que tous les atomes sont identiques, bien qu'il soit possible de généraliser au cas de plusieurs types d'atomes ; également par souci de clarté, nous supposons que leur charge est égale à $+1$, la généralisation étant là aussi facile. En termes mathématiques, ceci se traduit comme suit : soit une suite d'ensembles $\Lambda_n \subset \ell$ telle que $\bigcup_{n\in\mathbf{N}} \Lambda_n = \ell$. Considérons la densité électronique correspondante ρ_{Λ_n}, solution de (14) dans le cas TF, de (15) dans le cas TFW, avec $N = |\Lambda_n|$ égal au cardinal de Λ_n (cas neutre). La question est alors :

(i) l'énergie par particule $\frac{E^{\mathrm{TF(W)}}(\Lambda_n)}{|\Lambda_n|}$ a-t-elle une limite $E^{\mathrm{TF(W)}}(\ell)$ quand $\Lambda_n \to \ell$ (autrement dit quand $n \to \infty$) ?

(ii) la densité ρ_{Λ_n} converge-t-elle également vers un certain ρ_ℓ ?

(iii) la densité ρ_ℓ est-elle ℓ-périodique, et peut-elle être caractérisée comme solution d'un problème variationnel ℓ-périodique du même type que le modèle moléculaire d'origine ?

Ces questions ont été étudiées dans [21] pour le cas TF, et dans [8, 9] pour le cas TFW. Dans les deux cas, sous réserve d'hypothèses techniques naturelles sur la convergence de Λ vers ℓ (revenant à supposer essentiellement que le "bord" de Λ est négligeable devant sa partie intérieure), nous avons :

Théorème 1.5 (Limite thermodynamique TF et TFW, [21, 9]) *Les questions (i)-(ii)-(iii) ci-dessus admettent des réponses positives dans le cadre TF et dans le cadre TFW.*

De plus, l'énergie $E^{\mathrm{TF(W)}}(\ell)$ admet la forme suivante :

$$E^{\mathrm{TF(W)}}(\ell) = \inf\Big\{E^{\mathrm{TF(W)}}(\rho,\ell), \quad \rho \in \mathcal{H}_\ell^{\mathrm{TF(W)}}, \quad \rho \geq 0, \quad \int_{Q(\ell)} \rho = 1\Big\}, \tag{18}$$

avec $\mathcal{H}_\ell^{\mathrm{TF}} = L^{5/3}(Q(\ell))$, $\mathcal{H}_\ell^{\mathrm{TFW}} = H^1_{\mathrm{per}}(Q(\ell))$ (ensemble des fonctions de $H^1(Q(\ell))$ ℓ-périodiques), $Q(\ell)$ étant une cellule unité du réseau ℓ. L'énergie $E^{\mathrm{TF(W)}}(\cdot,\ell)$ s'écrit :

$$\begin{aligned} E^{\mathrm{TF(W)}}(\rho,\ell) &= \int_{Q(\ell)} \rho^{5/3} \quad \Big(+\int_{Q(\ell)} |\nabla\sqrt{\rho}|^2\Big) - \int_{Q(\ell)} G_\ell \rho \\ &\quad + \frac{1}{2}\int_{Q(\ell)}\int_{Q(\ell)} \rho(x) G_\ell(x-y)\rho(y)dxdy, \end{aligned} \tag{19}$$

le potentiel d'interaction G_ℓ étant une version ℓ-périodique du potentiel Coulombien $\frac{1}{|x|}$, à savoir la solution de

$$\begin{cases} -\Delta G_\ell = \Big(\sum_{k\in\ell}\delta_k\Big) - \frac{1}{|Q(\ell)|}, \\ \lim_{x\to 0}\Big(G_\ell(x) - \frac{1}{|x|}\Big) = 0. \end{cases} \tag{20}$$

Il est à noter que ce résultat consiste essentiellement à passer à la limite dans l'équation d'Euler-Lagrange du problème électronique et à démontrer l'unicité de la solution de l'équation limite à savoir ($u = \sqrt{\rho}$) :

$$\begin{cases} -\Delta u + \frac{5}{3}u^{7/3} - u\phi = 0, \\ -\Delta\phi = 4\pi\Big(\sum_{j\in\ell}\delta_j - u^2\Big), \\ u \geq 0. \end{cases} \tag{21}$$

2 Optimisation de géométrie et "Crystal problem"

2.1 Optimisation de géométrie périodique

Les modèles de solides décrits dans la section précédente permettent d'associer à un réseau ℓ une énergie $E^{\mathrm{TF(W)}}(\ell)$. Une question naturelle est l'existence d'un éventuel minimum à cette fonctionnelle d'énergie dans l'ensemble des réseaux. Cette étude fait l'objet du chapitre 3, dont le résultat principal est le suivant :

Résultat 1 (Optimisation de géométrie périodique, X. B. [P3]) *Notons $I^{\mathrm{TF(W)}}$ le problème de minimisation suivant :*

$$I^{\mathrm{TF(W)}}_{\mathrm{per}} = \inf\Big\{E^{\mathrm{TF(W)}}(\ell), \quad \ell \in \mathcal{L}_3(\mathbf{R}^3)\Big\}, \tag{22}$$

où $E^{\mathrm{TF(W)}}(\ell)$ est définie par (18), et $\mathcal{L}_3(\mathbf{R}^3)$ est l'ensemble des réseaux de $\mathbf{R}^3$.

Dans le cas TFW, ce problème a au moins une solution. Dans le cas TF, ce problème n'a pas de solutions, et le minimum n'est atteint que lorsque tous les noyaux se sont infiniment éloignés les uns des autres.

Remarquons que ce résultat est similaire au cas moléculaire : on peut l'interpréter comme un résultat de "binding" (dans le cas TFW) ou de "no-binding" (dans le cas TF) des cristaux : les cristaux périodiques sont stables pour le modèle TFW, instables pour le modèle TF.

La démonstration de ce résultat pour le cas TFW repose sur l'étude des suites minimisantes du problème (22). Nous montrons dans le chapitre 3 qu'elles sont bornées, donc compactes, car la variété des réseaux périodiques de $\mathbf{R}^3$ est de dimension finie. Supposons par exemple que l'on se restreigne au cas de réseaux rectangulaires (la généralisation aux réseaux quelconques n'étant en fait qu'un problème technique), c'est-à-dire aux réseaux du type $\ell = R_1\mathbf{Z}e_1 + R_2\mathbf{Z}e_2 + R_3\mathbf{Z}e_3$, où (e_1, e_2, e_3) est la base canonique de $\mathbf{R}^3$. On peut de plus supposer sans perte de généralité que $0 < R_1 \leq R_2 \leq R_3$. Une suite minimisante de cette forme peut alors avoir essentiellement quatre comportements :

(a) $R_1 \longrightarrow +\infty$;
(b) $R_2 \longrightarrow +\infty$ et R_1 converge (à extraction près) ;
(c) $R_3 \longrightarrow +\infty$ et R_1 et R_2 convergent (à extraction près) ;
(d) ℓ est compacte.

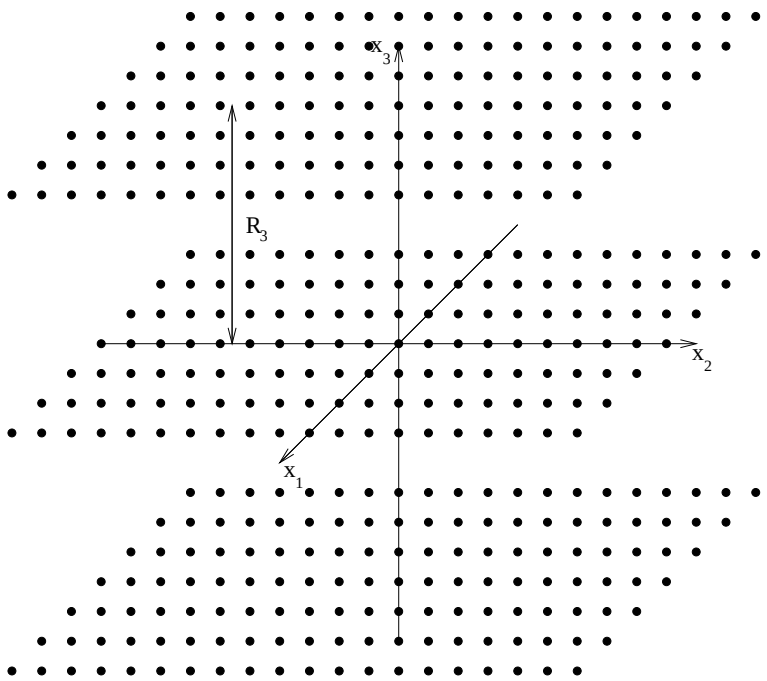

FIG. 1 – Le comportement (c) ($R_3 \longrightarrow \infty$) décrit ci-dessus.

Pour montrer que les trois premiers cas ne peuvent se produire, nous étudions la limite de l'énergie dans chacun des cas, et montrons que la convergence a lieu par valeurs inférieures. Par exemple dans le premier cas, on comprend aisément que l'énergie converge vers l'énergie atomique TFW, c'est-à-dire (17) avec $M = 1$, $X_1 = 0$, $N = Z_1 = 1$. Une étude très fine de la solution de ce problème, et en particulier de sa décroissance à l'infini, permet alors de conclure que la limite a lieu par valeurs inférieures, ce qui exclut ce premier

cas. Pour exclure de la même façon les autres cas, nous sommes donc amenés à étudier les problèmes limites correspondants, que nous appelons modèle de polymères dans le cas (b) puisque les atomes sont répartis périodiquement sur une droite, et modèle de film mince dans le cas (c) puisque les atomes sont répartis périodiquement dans un plan. C'est l'objet du chapitre 2, qui présente un processus de limite thermodynamique pour justifier puis étudier ces modèles. Ici encore, à des hypothèses techniques près (qui sont précisées au chapitre 2) sur la façon dont on fait tendre l'ensemble des positions des noyaux vers le réseau correspondant, nous avons :

Résultat 2 (Limite thermodynamique : polymères, X. B., C. Le Bris [P1])
Pour tout réseau périodique $\ell = a\mathbf{Z}$ de dimension 1, les questions (i), (ii), (iii) ci-dessus admettent des réponses positives, et la densité limite ρ_ℓ est solution du problème :

$$E^{\mathrm{TFW}}(\ell) = \inf\Big\{E^{\mathrm{TFW}}(\rho,\ell), \quad \rho \geq 0, \quad \sqrt{\rho} \in H^1_{\mathrm{per}}(Q(\ell)), \\ \log(2+|x|)\rho \in L^1(Q(\ell)), \quad \int_{Q(\ell)} \rho = 1\Big\}, \quad (23)$$

$$E^{\mathrm{TFW}}(\rho,\ell) = \int_{Q(\ell)} |\nabla\sqrt{\rho}|^2 + \int_{Q(\ell)} \rho^{5/3} - \int_{Q(\ell)} \rho G_\ell + \frac{1}{2}\int_{Q(\ell)}\int_{Q(\ell)} \rho(x) G_\ell(x-y)\rho(y)dxdy,$$

$$Q(\ell) = \Big\{ta + x, \quad -\frac{1}{2} \leq t < \frac{1}{2}, \quad x \in \{a\}^\perp\Big\}.$$

G_ℓ est ici le potentiel d'interaction coulombienne associé au réseau ℓ, i.e l'unique solution de :

$$\begin{cases} -\Delta G_\ell = \displaystyle\sum_{k\in\mathbf{Z}} \delta_{ka}, \\ \displaystyle\lim_{x\to 0}\Big(G_\ell(x) - \frac{1}{|x|}\Big) = 0, \\ G_\ell(x) \sim -\dfrac{2}{|a|}\log|x'| \quad \text{quand} \quad |x'| \to \infty, \end{cases} \quad (24)$$

où $x' = x \wedge \frac{a}{|a|}$.

Résultat 3 (Limite thermodynamique : films minces, X. B., C. Le Bris [P1])
Pour tout réseau périodique $\ell = a\mathbf{Z} + b\mathbf{Z}$ de dimension 2, les questions (i), (ii), (iii) ci-dessus admettent une réponse positive, et la densité limite ρ_ℓ est solution du problème :

$$\inf\Big\{E^{\mathrm{TFW}}(\rho,\ell), \quad \rho \geq 0, \quad \sqrt{\rho} \in H^1_{\mathrm{per}}(Q(\ell)), \quad |x|\rho \in L^1(Q(\ell))\Big\}, \quad (25)$$

$$E^{\mathrm{TFW}}(\rho,\ell) = \int_{Q(\ell)} |\nabla\sqrt{\rho}|^2 + \int_{Q(\ell)} \rho^{5/3} - \int_{Q(\ell)} \rho G_\ell + \frac{1}{2}\int_{Q(\ell)}\int_{Q(\ell)} \rho(x) G_\ell(x-y)\rho(y)dxdy,$$

$$Q(\ell) = \Big\{ta + sb + x, \quad t,s \in [-\frac{1}{2},\frac{1}{2}), \quad x \in \{a,b\}^\perp\Big\},$$

le potentiel G_ℓ étant l'unique solution de :

$$\begin{cases} -\Delta G_\ell = \sum_{k,j\in\mathbf{Z}} \delta_{ka+jb}, \\ \lim_{x\to 0}(G_\ell(x) - \frac{1}{|x|}) = 0, \\ G_\ell(x) \sim -\frac{2\pi}{|a\wedge b|}|x''| \quad \text{quand} |x''| \to \infty, \end{cases} \tag{26}$$

où x'' est défini par : $x'' = x \cdot \frac{a\wedge b}{|a\wedge b|}$.

Les résultats 2 et 3 sont également vrais pour le modèle TF.

Remarquons que la preuve du Résultat 2 utilise le résultat suivant, également démontré dans le chapitre 2 :

Résultat 4 (X. B., C. Le Bris, [P1]) *Soit μ une mesure positive sur $\mathbf{R}^3$, périodique en la troisième variable x_3, de période 1, et telle que :*

(a) $\mathrm{Supp}\,\mu$ *est compact en* (x_1, x_2),

(b) $0 < \mu(\{|x_3| < \frac{1}{2}\}) < \infty$.

Alors le système

$$\begin{cases} -\Delta u + \frac{5}{3}u^{7/3} - u\phi = 0, \\ -\Delta\phi = 4\pi(\mu - u^2), \\ u \geq 0 \end{cases} \tag{27}$$

admet une unique solution $(u,\phi) \in (L^2_{\mathrm{unif}} \cap L^{7/3}_{\mathrm{loc}})(\mathbf{R}^3) \times L^1_{\mathrm{unif}}(\mathbf{R}^3)$. De plus, cette solution est x_3-périodique de période 1, et vérifie :

$$u \in L^\infty(\mathbf{R}^3), \quad \phi \in L^p_{\mathrm{unif}}(\mathbf{R}^3), \quad \forall p < 3.$$

(On rappelle que $L^p_{\mathrm{unif}}(\Omega) = \{f \in L^p_{\mathrm{loc}}(\Omega), \quad \sup_{x\in\Omega} \|f\|_{L^p(\Omega\cap B_1(x))} < \infty\}$.)

En effet, ce système d'EDP est à la fois l'équation d'Euler-Lagrange du problème (23) et la limite des équations vérifiées par le couple $(u_\Lambda, \phi_\Lambda)$ solution du problème fini. Des bornes naturelles sur $(u_\Lambda, \phi_\Lambda)$ permettent d'obtenir la compacité de cette suite, puis de passer à la limite dans l'équation d'Euler-Lagrange dont elle est solution. Par unicité, on en déduit la convergence de toute la suite, et le fait que la limite est solution du problème convexe (23). Et bien qu'un tel théorème ne soit pas disponible dans le cas des films minces, des techniques similaires permettent de démontrer un résultat plus faible mais qui suffit à démontrer le résultat 3.

2.2 Le "Crystal problem"

Jusqu'à ce point, nous avons posé la périodicité comme une donnée exogène de notre problème. La question se pose également de savoir si cette périodicité est inscrite d'une façon ou d'une autre dans le modèle que nous étudions. Autrement dit, considérant la solution du problème d'optimisation de géométrie pour N atomes identiques, les positions des noyaux tendent-elles à remplir un réseau périodique quand N tend vers l'infini ?

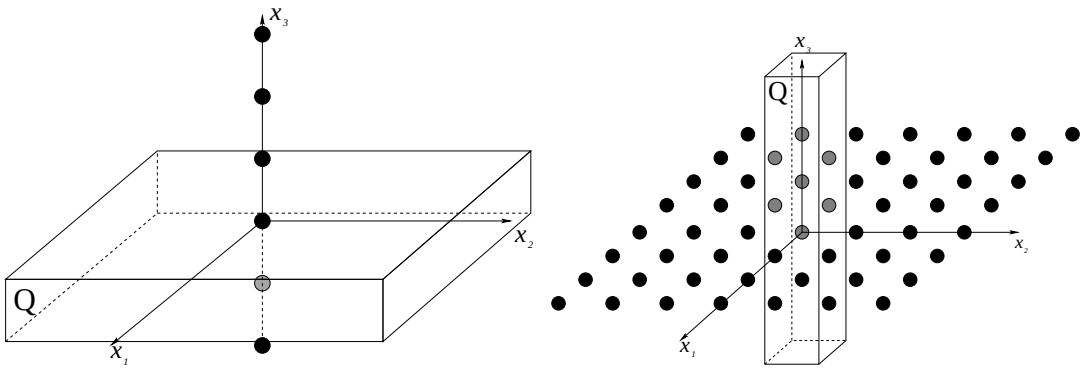

FIG. 2 – L'ensemble Λ et la cellule unité $Q = Q(\ell)$ dans le cas des polymères (à gauche) et des films minces (à droite).

Physiquement, cela correspond à se demander pourquoi la matière est cristalline à température nulle[2]. Ce problème est identifié par les anglophones par le terme "crystal problem". Même pour des modèles très simples comme des interactions à deux corps, ce problème n'est essentiellement résolu qu'en dimension 1 [15, 36, 26, 27, 30, 32], ou en dimension 2 pour des cas très particuliers [31].

Nous avons donc commencé par poser ce problème pour le modèle TFW en dimension 1. Le résultat suivant est démontré dans le chapitre 4 :

Résultat 5 ("Crystal problem" en dimension 1, X. B., C. Le Bris, [P4]) *Soit $(\rho_N, \{X_i^N\}_{1\le i\le N})$ une solution du problème $I_N^{\rm TFW}$ d'optimisation de géométrie TFW (17)* **en dimension 1**, *avec $Z_i = 1$ et $M = N$. Alors nous avons :*

- *la suite $\frac{I_N^{\rm TFW}}{N}$ converge vers la valeur du problème d'optimisation de géométrie périodique $I_{\rm per}^{\rm TFW}$;*
- *il existe une suite i_N d'indices telle que*
  - *(a) $\lim_{N\to+\infty} i_N = \lim_{N\to+\infty} (N - i_N) = +\infty$;*
  - *(b) Il existe un réseau $\ell = R\mathbf{Z}$ solution du problème d'optimisation de géométrie périodique (22) tel que, notant ρ_ℓ la densité électronique associée, on ait :*

$$\forall j \in \mathbf{Z}, \quad \lim_{N\to+\infty} X_{i_N+j}^N - X_{i_N}^N = jR,$$

$$\forall K \quad \text{compact}, \quad \lim_{N\to+\infty} \|\rho_N(\cdot - X_{i_N}^N) - \rho_\ell(\cdot - X_{i_N}^N)\|_{L^\infty(K)} = 0.$$

Notons que pour ce modèle mono-dimensionnel, il est nécessaire dans l'expression de l'énergie de remplacer le Coulombien de dimension 3 $\frac{1}{|x|}$ par celui de dimension 1, à savoir $-\frac{1}{2}|x|$, et d'adapter de façon similaire la définition de G_ℓ. Tout ceci est précisé dans le chapitre 4. La démonstration de ce résultat est essentiellement basée sur le théorème de Cauchy-Lipschitz (ce qui explique qu'elle n'est pas du tout adaptable telle quelle aux cas de

[2]Rappelons que dans tous les modèles évoqués ici la température est nulle.

dimension supérieure). En effet imaginons que nous soyons dans le cas TF[3]. La solution du problème d'optimisation de géométrie vérifie alors les équations d'Euler-Lagrange associées, qui s'écrivent, à des coefficients près que nous ne précisons pas ici,

$$\begin{cases} -\phi_N'' + \phi_N^\alpha = \sum_{i=1}^N \delta_{X_i^N} \\ \phi_N'(X_i^{N\,+}) = -\frac{1}{2}, \quad \phi_N'(X_i^{N\,-}) = \frac{1}{2}, \end{cases}$$

où $\phi_N = \rho_N^{1/\alpha}$ est le potentiel électrostatique total du système, et α un réel fixé. La première équation traduit l'optimalité de la densité ρ_N, la deuxième celle des X_i^N. Cette dernière peut être retrouvée en remarquant que les noyaux doivent être à l'équilibre, donc que le champ électrique subi par X_i^N, à savoir $\nabla(\phi_N + \frac{1}{2}|x - X_i^N|)$, doit être nul. Ainsi, $\phi_N(x + X_i^N)$ et $\phi_N(-x + X_i^N)$ sont toutes les deux solutions de $\phi'' = \phi^\alpha$ à droite de 0, avec la même donnée de Cauchy. Elles sont donc égales tant qu'elles vérifient cette équation. En d'autres termes, ϕ_N est symétrique par rapport à X_i^N. Comme X_{i+1}^N est le premier point à droite de X_i^N où la dérivée de ϕ_N atteint $\frac{1}{2}$ (car $\phi_N'' \geq 0$ sur $]X_j^N, X_{j+1}^N[$), ceci implique que $X_{i+1}^N - X_i^N = X_i^N - X_{i-1}^N$. Le cas TFW est plus technique, mais se traite avec les mêmes outils.

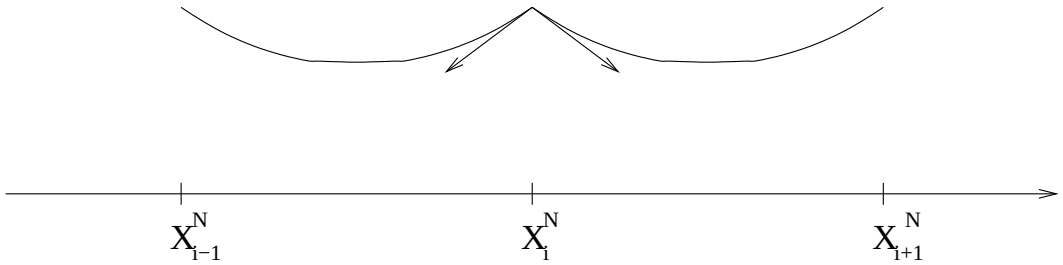

FIG. 3 – La fonction ϕ^N est symétrique par rapport à X_i^N, car de même valeur et de pentes opposées de part et d'autre de X_i^N

Le même problème en dimension 2 n'est pas résolu à ce jour, même pour des modèles d'interaction à deux corps. Cependant, des expériences numériques que nous avons menées (voir section 5) semblent indiquer que pour des potentiels confinants comme par exemple le potentiel de Lennard-Jones ($W(x) = \frac{1}{|x|^{12}} - \frac{1}{|x|^6}$) ou le potentiel de Morse ($W(x) = e^{-8(|x|-1)} - 2e^{-4(|x|-1)}$), la configuration minimisant l'énergie

$$E(\{X_i\}_{1 \leq i \leq N}) = \frac{1}{2} \sum_{i \neq j} W(X_i - X_j),$$

ressemble, pour N grand, à un sous-ensemble du réseau hexagonal (voir figure 4). Ce comportement n'est bien entendu que qualitatif, et peut évidemment être lié à des phénomènes purement numériques.

[3] Dans ce cas, il n'y a pas de solution à l'optimisation de géométrie, et il faut confiner artificiellement le système, par exemple en imposant $|X_i^N| \leq N$

De même, dans le cas d'un potentiel purement répulsif (qui correspond au modèle TF en dimension 2, comme indiqué dans la section 4 du chapitre 6), le même problème avec condition aux bords (hexagonales)-périodiques donne comme solution le réseau hexagonal.

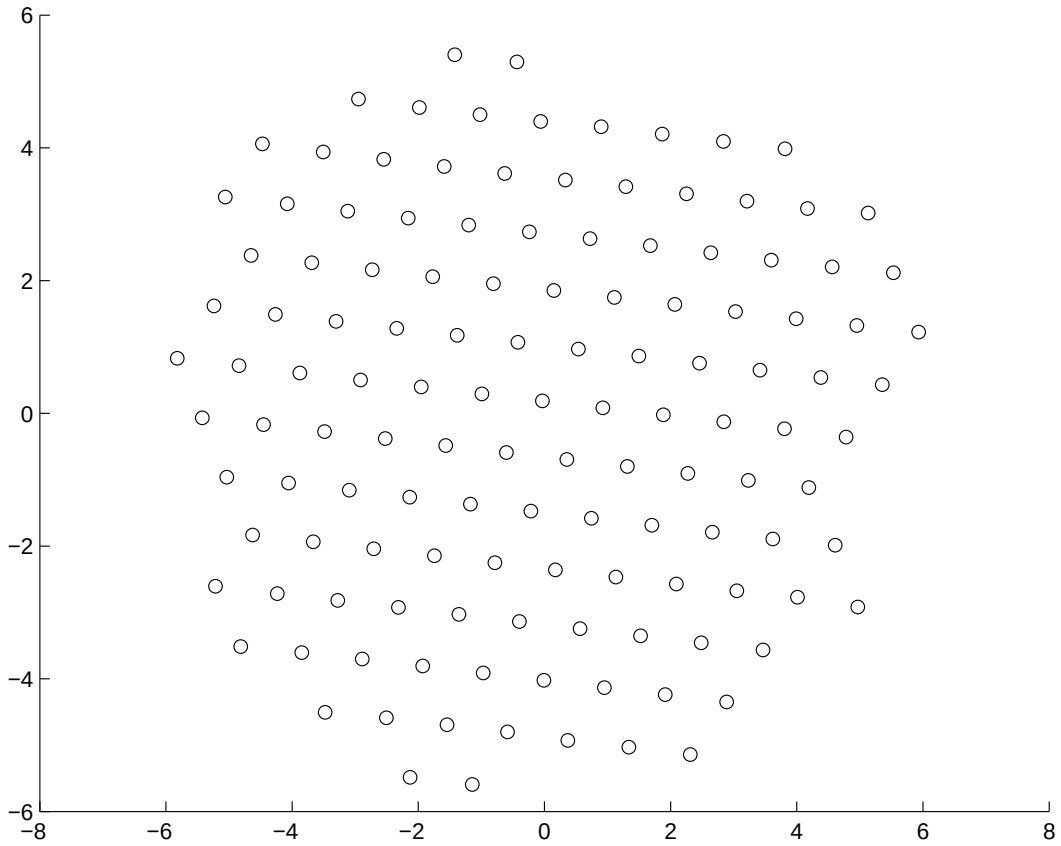

FIG. 4 – Le résultat d'un calcul de gradient conjugué sur le cas du potentiel de Morse (le point de départ est une configuration aléatoire).

3 Limite thermodynamique non périodique

Nous venons de voir que, bien que cela soit communément admis, le fait que la périodicité découle des modèles eux-mêmes n'est pas démontré pour l'instant, sauf dans certains cas très particuliers. Ceci nous amène à un autre problème : la définition de l'état fondamental électronique pour ces modèles de type Thomas-Fermi est possible dans le cas d'une infinité *périodique* de particules ; qu'en est-il dans le cas où cette hypothèse de périodicité est levée ? Comme remarqué dans [9], le cas presque périodique[4] est traitable avec les

[4]Une fonction presque périodique est par exemple la somme de deux fonctions périodiques de périodes incommensurables, comme $\cos(x) + \cos(\sqrt{2}x)$.

mêmes outils que le cas périodique. Mais dans un cas plus général, ceci est beaucoup moins clair.

Une autre motivation à cette question est le fait que, même si le cristal parfait est dans certains cas une bonne approximation de la géométrie réelle des noyaux, il arrive (souvent !) que ce ne soit pas le cas. Il est par exemple connu [1] qu'un cristal parfait est également un conducteur parfait, et que c'est la présence de défauts, comme par exemples des lacunes dans le réseau cristallin ou des impuretés, qui lui donne une conductivité finie.

Cette étude fait l'objet du chapitre 5, où nous démontrons en particulier les résultats suivants :

Résultat 6 (X. B., C. Le Bris, P.-L. Lions, [P5]) *Soit $\{X_i\}_{i\in\mathbf{N}}$ un ensemble de points deux à deux distincts de $\mathbf{R}^3$ satisfaisant les hypothèses suivantes :*

(H1) $\displaystyle\sup_{x\in\mathbf{R}^3} \#\big\{i\in\mathbf{N} \quad / \quad |x-X_i|<1\big\} < +\infty$

(H2) $\displaystyle\lim_{R\to\infty} \frac{1}{R} \inf_{x\in\mathbf{R}^3} \#\big\{i\in\mathbf{N} \quad / \quad |x-X_i|<R\big\} = +\infty$

(H3) pour tout $n\in\mathbf{N}$, la limite suivante, en tant que mesure en $h=(h_1,\dots h_n)\in(\mathbf{R}^3)^n$:

$$l^n(h_1,\dots h_n) = \lim_{R\to\infty} \frac{1}{|B_R|} \sum_{X_{i_0}\in B_R} \cdots \sum_{X_{i_n}\in B_R} \delta_{(X_{i_0}-X_{i_1},\dots X_{i_0}-X_{i_n})}(h_1,\dots,h_n),$$

existe et est une mesure localement bornée.

Notons alors $\mathcal{A}(\{X_i\}_{i\in\mathbf{N}})$ l'espace vectoriel engendré par les fonctions f de la forme

$$f(x) = \sum_{i_1\in\mathbf{N}} \sum_{i_2\in\mathbf{N}} \cdots \sum_{i_n\in\mathbf{N}} \varphi(x-X_{i_1}, x-X_{i_2},\dots,x-X_{i_n}),$$

avec $\varphi\in\mathcal{D}(\mathbf{R}^{3n})$, et notons $\mathcal{A}^{k,p}(\{X_i\}_{i\in\mathbf{N}})$ (respectivement $\mathcal{A}^p(\{X_i\}_{i\in\mathbf{N}})$) la fermeture de cet espace vectoriel pour la norme $W^{k,p}_{\rm unif}$ (respectivement $L^p_{\rm unif}$). Nous avons alors :

- *toute fonction f dans $\mathcal{A}^{k,p}$ admet une valeur moyenne $\langle f\rangle = \displaystyle\lim_{R\to\infty}\frac{1}{|B_R|}\int_{B_R} f$;*
- *toute solution (u,ϕ) dans $L^\infty\times L^1_{\rm unif}$ du système TFW (29) ci-dessous appartient à $\mathcal{A}^{2,p}\times\mathcal{A}^p$ pour tout $p<3$. De plus, $\rho=u^2$ est alors solution du problème variationel (28).*

Ce résultat nécessite quelques précisions. Tout d'abord, l'ensemble $\mathcal{A}^1$ est la plus petite algèbre fermée pour la norme $L^1_{\rm unif}$ engendrée par les fonctions du type

$$f(x) = \sum_{i\in\mathbf{N}} \varphi(x-X_i), \quad \varphi\in\mathcal{D}(\mathbf{R}^3).$$

Dans le cas particulier où $\{X_i\}_{i\in\mathbf{N}}$ est un réseau périodique, il s'agit en fait de l'espace $L^1_{\rm per}$ des fonctions $L^1_{\rm loc}$ périodiques. L'espace $\mathcal{A}^{k,p}$ joue donc le rôle des fonctions "$\{X_i\}$-périodiques" de régularité correspondante. L'hypothèse (H3) permet d'assurer que la construction de $\mathcal{A}^{k,p}$ est possible, ainsi que l'existence de la moyenne $\langle f\rangle$ de f pour

$f \in \mathcal{A}^{k,p}$. Toute la difficulté réside dans le fait que, contrairement au cas périodique, nous n'avons pas de caractérisation simple de l'appartenance d'une fonction à $\mathcal{A}^{k,p}$.

De plus, prolongeant le parallèle avec le cas périodique, puisque l'intégrale d'une fonction périodique sur la cellule de périodicité est égale à la valeur moyenne de cette fonction, on peut espérer que le problème variationnel limite sera :

$$E^{\mathrm{TFW}}(\{X_i\}) = \inf\Big\{ \langle |\nabla\sqrt{\rho}|^2 \rangle + \langle \rho^{5/3} \rangle - \langle W\rho \rangle + \frac{1}{2}\langle \phi(\mu-\rho)\rangle, \\ \rho \geq 0, \quad \rho \in \mathcal{A}^{1,2}(\{X_i\}_{i\in\mathbf{N}}) \Big\}, \quad (28)$$

où les deux derniers termes de l'énergie sont précisés au chapitre 5 et représentent une valeur moyenne de l'interaction électrostatique (formellement, il s'agit de la valeur moyenne de $|\nabla\phi|^2$, où ϕ est défini par la deuxième équation de (29)). On est alors tenté d'utiliser les mêmes techniques que pour le cas périodique, qui consistent essentiellement à passer à la limite dans le système d'équation d'Euler-Lagrange du problème fini, puis de montrer l'unicité des solutions du système limite, à savoir ($u = \sqrt{\rho}$) :

$$\begin{cases} -\Delta u + \frac{5}{3}u^{7/3} - u\phi = 0, \\ -\Delta\phi = 4\pi(\sum_{i\in\mathbf{N}} \delta_{X_i} - u^2), \\ u \geq 0 \end{cases} \quad (29)$$

Cette unicité est assurée par les hypothèses (H1) et (H2) (voir [9]). Cependant, le problème (28) est en fait mal posé en général, et une solution de (28) peut ne pas satisfaire (29). En revanche, la réciproque est vraie dans la mesure où l'appartenance à l'espace variationnel $\mathcal{A}^{1,2}$ est assurée. De plus, une version *locale* de cette minimisation d'énergie est possible, et en fait équivalente à (29). Ainsi, en passant à la limite thermodynamique, on obtient une solution de (29), qui donc appartient à l'espace $\mathcal{A}^{1,2}$ d'après le résultat 6, et est en fait solution de (28).

Le point essentiel de la démonstration consiste à démontrer que la solution de (29) appartient effectivement à l'espace $\mathcal{A}^{1,2}$. Donnons un aperçu de cette démonstration dans le cas TF, qui correspond à oublier le terme $-\Delta u$ dans la première équation de (29). Supposons de plus que la mesure qui définit les noyaux est régularisée, remplaçant $\sum \delta_{X_i}$ par $m = \sum m_0(\cdot - X_i)$, où m_0 est régulière à support compact. Il s'agit donc de montrer que

$$\text{Si} \quad m \in \mathcal{A}^{1,2}, \quad -\Delta\phi + \phi^{3/2} = m \Rightarrow \phi \in \mathcal{A}^{1,2}.$$

Pour cela, il suffit de contruire une suite de fonctions de $\mathcal{A}^{1,2}$ convergeant vers ϕ. Nous utilisons pour ce faire l'algorithme suivant :

$$\begin{cases} \phi_0 = 0, \\ -\Delta\phi_{n+1} + M\phi_{n+1} = M\phi_n - \phi_n^{3/2}. \end{cases}$$

Le paramètre de "shift" M est choisi pour que sur l'intervalle $[0, \|\phi\|_{L^\infty}]$, la fonction $t \mapsto Mt - t^{3/2}$ soit croissante. Il est alors facile de montrer par récurrence que la suite ϕ_n est

croissante et comprise entre 0 et ϕ; ce qui permet ensuite de conclure qu'elle converge *uniformément* vers ϕ. Le cas TFW est un peu plus difficile, mais repose sur des techniques similaires, associées au théorème des fonctions implicites.

Remarquons enfin que les hypothèses (H1)-(H2)-(H3) permettent effectivement de traiter des cas non périodiques, comme les exemples du chapitre 5 le montrent.

Il apparaît également dans la preuve du résultat précédent le résultat suivant :

Résultat 7 (X. B., C. Le Bris, P.-L. Lions, [P6]) *Soit* $f \in L^p_{\rm unif}(\mathbf{R}^3)$, $p > \dfrac{3}{2}$. *Alors les deux propriétés suivantes sont équivalentes :*

(i) il existe une fonction $\Phi \in L^\infty(\mathbf{R}^3)$ *telle que* $-\Delta\Phi = f$, *au sens des distributions (au moins)*

(ii) $$\sup_{x_0\in\mathbf{R}^3,\ 0<R<+\infty} \left| \int_{B_R(x_0)} \left(\frac{1}{4\pi|x-x_0|} - \frac{1}{4\pi R} \right) f(x)\,dx \right| < +\infty$$

Quand elle existe, la fonction Φ *est unique à constante additive près dans la classe des fonctions bornées, et appartient à* $W^{2,p}_{\rm unif}(\mathbf{R}^3)$.

Ce résultat permet de donner une condition nécessaire et suffisante sur ρ pour pouvoir définir ϕ solution de la deuxième équation de (29). Ici encore, cette condition est simple dans le cas périodique : pour que (i) soit vrai, il faut et il suffit dans ce cas que $\langle f \rangle = 0$. Cette condition n'est pas suffisante dans le cas général. Le résultat 7 est démontré dans l'annexe du chapitre 5, et est assorti de diverses extensions possibles. Le fait que (i) implique (ii) est une simple application de la formule de Green, tandis que la réciproque repose sur l'équivalence de semi-normes, qui permet d'obtenir la convergence d'approximations naturelles de la solution Φ.

4 Changements d'échelles

La dernière partie de la thèse concerne le lien possible entre les modèles microscopiques des sections 2 et 3 et certains modèles macroscopiques.

4.1 Modèles de mécanique des milieux continus

Le chapitre 6 présente un passage à la limite qui permet, moyennant une remise à l'échelle de la distance caractéristique du modèle moléculaire, d'obtenir des modèles de mécanique des milieux continus.

Pour cela, considérons d'abord une configuration de référence Ω (qui est un ouvert régulier de $\mathbf{R}^3$), dans laquelle les atomes sont répartis suivant un réseau $\varepsilon\ell$, où ε est la distance interatomique. Autrement dit, les positions $\{X_i\}$ des atomes satisfont $\{X_i\} = \varepsilon\ell \cap \Omega$. Si par exemple l'énergie du système est définie par une interaction à deux corps de potentiel W, l'énergie par particule vaut alors

$$\mathcal{E}(\{X_i\}) = \frac{1}{2N} \sum_{1\le i\neq j\le N} W(X_i - X_j) = \frac{1}{2N} \sum_{p\neq q\in\varepsilon\ell\cap\Omega} W(p-q).$$

L'entier N est ici égal au nombre de particules, à savoir $N = \#(\varepsilon\ell \cap \Omega)$. Si maintenant nous appelons δ la portée du potentiel, de sorte que $W(x) = W_0(\frac{x}{\delta})$, nous avons alors :

$$\mathcal{E}(\{X_i\}) = \frac{1}{2N} \sum_{p \neq q \in \ell \cap \frac{1}{\varepsilon}\Omega} W_0\Big(\frac{\varepsilon(p-q)}{\delta}\Big).$$

Enfin, si le solide est déformé par un difféomorphisme u et si l'on suppose que les particules sont déplacées de la même manière, l'énergie du système s'écrit alors :

$$\mathcal{E}_{\varepsilon,\delta}(u) = \frac{1}{2N} \sum_{p \neq q \in \ell \cap \frac{1}{\varepsilon}\Omega} W_0\Big(\frac{u(\varepsilon p) - u(\varepsilon q)}{\delta}\Big), \tag{30}$$

Le résultat suivant est démontré au chapitre 6 :

Résultat 8 (X. B., C. Le Bris, P.-L. Lions, [P8, P7]) *Soit W_0 un potentiel lipschitzien sur $\{x \in \mathbf{R}^3, \quad |x| > R\}$, pour tout $R > 0$, et tel qu'il existe $C \geq 0$ et $a > 0$ tels que $|W_0(x)| \leq \frac{C}{|x|^{3+a}}$. Soient Ω un ouvert régulier de $\mathbf{R}^3$ et u un C^∞-difféomorphisme de Ω dans $\mathbf{R}^3$. On considère $\mathcal{E}_{\varepsilon,\delta}(u)$ définie par (30). Alors*

(i) Si $\varepsilon = \delta$, alors

$$\lim_{\varepsilon \to 0} \mathcal{E}_{\varepsilon,\delta}(u) = \frac{1}{2|\Omega|} \int_\Omega \sum_{j \in \ell \setminus \{0\}} W_0(\nabla u(x) j) dx. \tag{31}$$

(ii) Si $\varepsilon \ll \delta$, et si $W_0 \in L^1(\mathbf{R}^3)$,

$$\lim_{\varepsilon \to 0} \Big(\frac{\varepsilon}{\delta}\Big)^d \mathcal{E}_{\varepsilon,\delta}(u) = \frac{1}{2|\Omega|} \Big(\int_{\mathbf{R}^3} W_0\Big) \int_\Omega \frac{dx}{|\det(\nabla u(x))|}. \tag{32}$$

(iii) Si $\delta \ll \varepsilon$ et si pour tout $p > 0$, $|x|^p W_0(x)$ est borné à l'infini, alors pour tout $p > 0$, $\lim_{\varepsilon \to 0} (\frac{\delta}{\varepsilon})^p \mathcal{E}_{\varepsilon,\delta}(u) = 0$. S'il existe $p > 0$ tel que $|x|^p W_0(x)$ ait une limite a quand $|x|$ tend vers l'infini, alors $\lim_{\varepsilon \to 0} (\frac{\delta}{\varepsilon})^p \mathcal{E}_{\varepsilon,\delta}(u) = \int_\Omega \sum_{j \in \ell \setminus \{0\}} \frac{a}{2|\nabla u(x) j|^p} dx$.

Remarquons que le cas physiquement le plus raisonnable est le cas (i), où la portée du potentiel est proportionnelle à la distance des particules dans leur état d'équilibre. Dans ce cas, on retrouve précisément une forme d'énergie hyperélastique utilisée dans des modèles de mécanique des milieux continus [12].

Ce résultat est également vrai dans le cas de modèles de type Thomas-Fermi, comme précisé dans le chapitre 6 (théorème 3.2). Dans ce cas, il est nécessaire de prendre en compte les constantes physiques présentes dans le modèle (et fixées égales à 1 jusqu'à présent par l'utilisation d'un système d'unités adéquat). L'analyse dimensionelle de ces constantes permet alors de déterminer la valeur de δ.

Il est également possible de considérer les limites ci-dessus comme les premiers termes d'un développement asymptotique en puissances de ε. En effet, le centre de la démonstration de ce résultat est une formule de Taylor : dans le cas $\varepsilon = \delta$ par exemple, il est clair

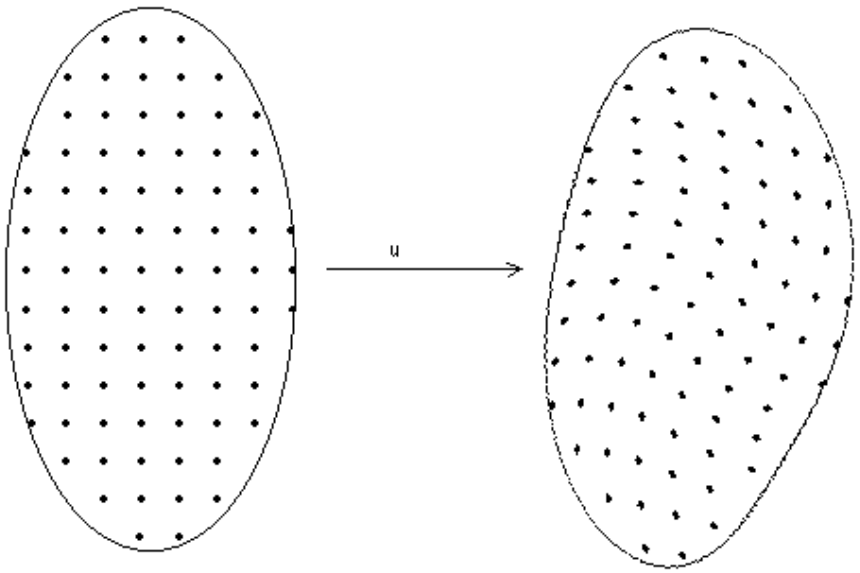

FIG. 5 – La configuration de référence et la configuration déformée.

que $\frac{u(\varepsilon p)-u(\varepsilon q)}{\varepsilon} = \nabla u(\varepsilon p)\cdot(q-p)+o(1)$. L'invariance par translation du réseau ℓ et les hypothèses de régularité sur W_0 permettent alors d'écrire

$$\mathcal{E}_{\varepsilon,\delta}(u) = \frac{1}{2N}\sum_{p\in\varepsilon\ell\cap\Omega}\sum_{j\in\ell\setminus\{0\}} W_0(\nabla u(\varepsilon p)\cdot j)+o(1),$$

dont le terme dominant peut être identifié comme une somme de Riemann approximant la limite (31). On peut donc pousser le développement aux ordres supérieurs, et on trouve alors à l'ordre 1 en ε un terme de surface, et à l'ordre deux un terme volumique faisant intervenir les dérivées secondes de u. Ceci est également précisé au chapitre 6 (théorème 2.3).

4.2 Champ électrique extérieur constant

Nous présentons dans le chapitre 7 l'étude du comportement de l'état fondamental électronique d'une plaque (autrement dit d'un cristal occupant le domaine de $\mathbf{R}^3$ défini par $\{|x_3|<1\}$) sous champ électrique constant. Ici encore, nous faisons tendre la distance interatomique ε vers 0. En supposant que le champ électrique est porté par le troisième

vecteur e_3 de la base canonique de $\mathbf{R}^3$ (donc perpendiculaire à la plaque), l'interaction des électrons avec ce champ est modélisée par l'ajout dans l'énergie TFW d'un terme qui vaut : $E^{\text{champ}}(\rho) = \int Ex_3\rho$, où E est l'intensité du champ. L'énergie correspondante *par unité de surface*, qui s'ajoute à l'énergie TFW de film mince apparaissant dans le résultat 3 est alors :

$$E^{\text{champ}}(\rho) = \int_{Q_\varepsilon} Ex_3\rho,$$

où $Q_\varepsilon = [-\frac{\varepsilon}{2}, \frac{\varepsilon}{2}) \times \mathbf{R}$ est la cellule unité associée à la géométrie des noyaux (nous supposons $\ell = \varepsilon\mathbf{Z}^3$ pour simplifier). Nous avons alors :

Résultat 9 (X. B., R. Monneau, [P9]) *Soit l'ensemble de noyaux $\varepsilon\mathbf{Z}^3 \cap \{|x_3| < 1\}$. Soit $0 \leq E < \frac{1}{\varepsilon}$, et soit ρ l'état fondamental électronique correspondant. Notons $\rho_{\mathbf{Z}^3}$ l'état fondamental TFW sans champ du réseau $\mathbf{Z}^3$, et $\phi_{\mathbf{Z}^3}$ le potentiel effectif associé ($\sqrt{\rho_{\mathbf{Z}^3}}$ et $\phi_{\mathbf{Z}^3}$ sont solutions de (21) avec $\ell = \mathbf{Z}^3$.) Il existe alors deux constantes C_1 et C_2 telles que*

$$|x_3| < 1 \Rightarrow |\rho(x) - \rho_{\mathbf{Z}^3}(\frac{x}{\varepsilon})| + |E_{\text{tot}} - \nabla\phi_{\mathbf{Z}^3}(\frac{x}{\varepsilon})| \leq C_1 e^{-C_2\frac{||x_3|-1|}{\varepsilon}},$$

où $E_{\text{tot}} = Ee_3 + \nabla\phi$ est le champ électrique total du système.

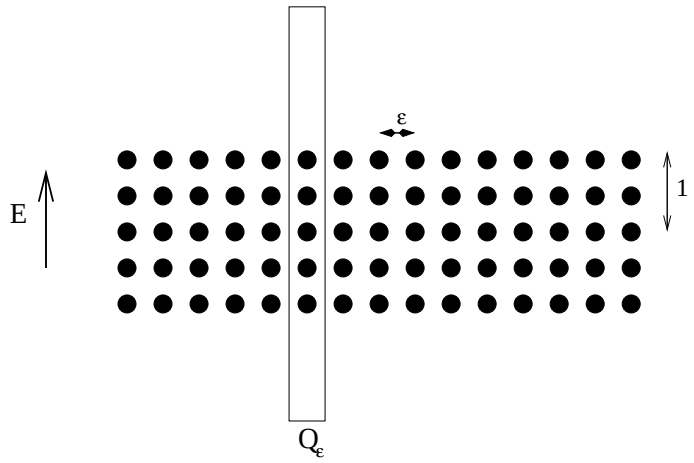

FIG. 6 – L'ensemble des noyaux et la cellule Q_ε (projetés dans le plan $\{x_2 = 0\}$).

Ce résultat implique donc en particulier que dans la limite $\varepsilon \to 0$, à l'intérieur du cristal, l'effet du champ électrique s'annule, et la densité ressemble de plus en plus à celle du cristal infini. D'autre part, la couche limite où l'effet du champ n'est pas négligeable est d'épaisseur comparable à ε.

Il est à noter cependant que l'état fondamental étudié ici est ionisé : la présence du champ expulse une partie des électrons. Cet aspect du modèle est discutable, puisqu'il est connu physiquement que cela ne se produit pas, sauf dans le cas de champs électriques intenses.

Remarquons également que même dans le cas $E = 0$, ce résultat comporte un intérêt : il montre que dans la limite $\varepsilon \to 0$, la densité à l'intérieur du cristal devient égale à la

densité du cristal périodique infini, donnant là aussi une estimation de l'épaisseur de la couche limite au-delà de laquelle cet effet de peau disparaît.

5 Perspectives

Bien entendu, ce bref exposé laisse un large éventail de problèmes non explorés. Nous en citons quelques-uns qui nous semblent intéressants.

Parmi les problèmes évoqués ci-dessus, le "crystal problem" en dimension 2 n'est pas résolu : même dans le cas d'une interaction à deux corps, les seuls résultats connus sont très particuliers [31]. L'approfondissement de l'étude numérique de ce problème est en cours avec A. Auger (CERMICS et CMAP), et A. Ben Haj Yedder (CERMICS). Les techniques classiques d'optimisation donnent des résultats relativement satisfaisants dans certains cas, mais il apparaît que pour un grand nombre de particules, la fonctionnelle d'énergie présente plusieurs minima locaux, et il est probable que l'utilisation d'algorithmes génétiques, éventuellement couplés avec des méthodes standards[5], améliore sensiblement ces résultats.

Également, un prolongement naturel du résultat 8 est l'étude des modèles de mécanique des milieux continus obtenus, et en particulier des termes correctifs (le cas du terme d'ordre zéro est étudié par exemple dans [11, 14]). Considérant par exemple le terme d'ordre 2, on peut se demander s'il exhibe les propriétés régularisantes des termes d'ordre 2 *postulés* dans la littérature [25], et qui permettent d'expliquer en partie la présence de microstructures dans les solides hyperélastiques. Même si, comme remarqué dans la section 5 du chapitre 6, cela peut être le cas en dimension 1, il n'est pas du tout clair que ce comportement persiste en dimension supérieure. Une collaboration sur ce sujet est en cours avec P.-L. Lions.

Il est également à noter que tous les résultats que nous avons évoqués ici sont des modèles *statiques*. Que deviennent ces questions dans un cadre dynamique ? Par exemple, le problème de limite thermodynamique a-t-il un équivalent dynamique ? Bien entendu, il est nécessaire pour cela d'utiliser un modèle dépendant du temps, par exemple "Time dependent Hartree-Fock" (TDHF), qui s'écrit :

$$i\partial_t \phi_k = F\phi_k, \quad \forall 1 \leq k \leq N,$$

où F désigne l'opérateur de Fock (9). Il s'agit donc de trouver un moyen de décrire ce système de N équations quand N devient infini. Ici encore, l'infinité de particules ne peut plus être "quotientée" par une quelconque périodicité (même si cette dernière est postulée à l'origine de temps, il n'est pas clair que la dynamique la conserve), comme c'était le cas pour des modèles statiques. L'enjeu est donc de trouver une alternative à ce type d'hypothèse. Nous avons sur ce sujet un projet de collaboration avec C. Bardos, F. Golse et N. Mauser.

Ce problème est à rapprocher du problème de modélisation sous champ électrique constant. En effet, comme évoqué à la section 4.2, un champ électrique constant, même

[5]Rappelons que dans le cas d'une interaction à deux corps, nous avons une expression analytique du gradient de la fonctionnelle d'énergie, ce qui permet un gain en temps de calcul appréciable.

faible, provoque l'ionisation en régime statique, ce qui n'est pas physiquement acceptable. Une parade possible serait d'étudier le même type de problème pour un modèle dynamique, puis d'utiliser des techniques similaires à celles du chapitre 7 pour passer à la limite $\varepsilon \to 0$, dont le préliminaire est bien entendu la limite thermodynamique correspondante.

Enfin, notons que le résultat 8 repose sur l'hypothèse simplificatrice que les atomes du cristal subissent la déformation macroscopique imposée, ce qui est *discutable*. Il serait bon de savoir étudier des cas plus généraux où l'on relaxe ce lien entre la déformation macroscopique et la déformation microscopique, par exemple par des techniques de type Γ-limites. Il s'agit dans ce cas de libérer la déformation microscopique, et de considérer que d'une certaine façon elle minimise *localement* l'énergie. Cette suite de minimiseurs devra ensuite converger (faiblement en général) vers la déformation macroscopique. Nous avons sur ce sujet un projet de collaboration avec S. Müller et A. Schlömerkemper (MPI Leipzig).

Liste de publications

[P1] X. Blanc, C. Le Bris, *Thomas-Fermi type theories for polymers and thin films*, Adv. Diff. Equ. 5 (7-9), pp 977-1032, 2000.

[P2] X. Blanc, C. Le Bris, *Optimisation de géométrie dans le cadre des théories de type Thomas-Fermi pour les cristaux périodiques*, C. R. Acad. Sci. Paris, Série I, 329, pp 551-556, 1999.

[P3] X. Blanc, *Geometry optimization for crystals in Thomas-Fermi type theories of solids*, Comm. PDE, 26 (3-4), pp 207-252, 2001.

[P4] X. Blanc, C. Le Bris, *Periodicity of the infinite volume of a one-dimensional quantum model*, Nonlinear Analysis T.M.A. 48 (6), pp 791-803, 2002

[P5] X. Blanc, C. Le Bris, P.-L. Lions, *Definition of the ground state energy of systems composed of infinitely many particles*, en préparation.

[P6] X. Blanc, C. Le Bris, P.-L. Lions, *Fonctions de $\mathbf{R}^3$ à potentiel newtonien borné*, C. R. Acad. Sci. Paris, à paraître.

[P7] X. Blanc, C. Le Bris, P.-L. Lions, *Convergence de modèles moléculaires vers des modèles de mécanique des milieux continus*, C. R. Acad. Sci. Paris, Série I, 332, pp 949-956, 2001.

[P8] X. Blanc, C. Le Bris, P.-L. Lions, *From molecular models to continuum mechanics*, en préparation.

[P9] X. Blanc, R. Monneau, *Screening of an applied electric field inside a metallic layer described with Thomas-Fermi-von Weizsäcker model*, à paraître dans Diff. Int. Equ.

[P10] X. Blanc, *A Mathematical insight into ab initio simulation of the solid phase*, dans "Mathematical methods and models for ab initio quantum chemistry", Lecture Notes in Chemistry 74, pp 133-158, M. Defranceschi et C. Le Bris (Ed.), Springer, 2000.

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Chapitre 2

Modèles de polymères et films minces

Ce chapitre reprend l'intégralité d'un article écrit en collaboration avec C. Le Bris et publié dans Advances in Differential Equations [P1]. Nous y présentons l'étude d'un processus de limite thermodynamique pour des polymères (où les atomes sont arrangés périodiquement le long d'une ligne plongée dans $\mathbf{R}^3$) et des films minces (où les atomes sont répartis périodiquement dans un plan plongé dans $\mathbf{R}^3$). Cette étude est un préliminaire au chapitre 3.

Thomas-Fermi type theories for polymers and thin films

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Abstract We define a Thomas-Fermi-von Weizsäcker model for polymers and thin films through a thermodynamic limit process. Our argument makes use of standard techniques for elliptic PDEs, such as maximum principles or supersolution methods. In the course of our work, we establish some existence and uniqueness results for a system of non-linear PDEs.

1 Introduction

In [6], I. Catto, P.L. Lions and one of us have studied the problem of thermodynamic limit for a three-dimensional crystal in the Thomas-Fermi-von Weizsäcker (TFW in short) setting. Given a finite set of nuclei represented by a set of points $\Lambda \subset \mathbf{R}^3$, each one of charge $+1$, the TFW model associates to this set an electronic density, denoted by ρ_Λ, which minimizes the so-called TFW energy, that is :

$$\begin{aligned} E_\Lambda(\rho) &= \int_{\mathbf{R}^3} |\nabla\sqrt{\rho}|^2 + \int_{\mathbf{R}^3} \rho^{5/3} - \sum_{k\in\Lambda} \int_{\mathbf{R}^3} \frac{\rho(x)}{|x-k|} dx \\ &\quad + \frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3} \frac{\rho(x)\rho(y)}{|x-y|} dxdy. \end{aligned} \tag{1}$$

In other words, the density ρ_Λ is a solution to the following minimization problem :

$$I_\Lambda = \inf\Big\{ E_\Lambda(\rho) + \frac{1}{2}\sum_{k\neq j\in\Lambda} \frac{1}{|k-j|}, \rho \geq 0,\ \sqrt{\rho} \in H^1(\mathbf{R}^3), \int_{\mathbf{R}^3} \rho = |\Lambda| \Big\}, \tag{2}$$

where $|\Lambda|$ denotes the cardinal of the set Λ. The case of smeared nuclei can be also considered ; that is when the measure defining the nuclei in (1) is replaced by a smooth measure m, having compact support and total mass one. In this latter case, (1) and (2) become :

$$\begin{aligned} E^m_\Lambda(\rho) &= \int_{\mathbf{R}^3} |\nabla\sqrt{\rho}|^2 + \int_{\mathbf{R}^3} \rho^{5/3} - \int_{\mathbf{R}^3} (m_\Lambda \star \frac{1}{|x|})\rho \\ &+ \frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3} \frac{\rho(x)\rho(y)}{|x-y|} dxdy, \end{aligned}$$

where $m_\Lambda = \sum_{k\in\Lambda} m(\cdot - k)$, and $\star$ is the convolution product over $\mathbf{R}^3$,

$$\begin{aligned} I^m_\Lambda &= \inf\Big\{ E^m_\Lambda(\rho) + \frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3} \frac{m_\Lambda(x) m_\Lambda(y)}{|x-y|} dxdy, \\ &\quad \rho \geq 0,\ \sqrt{\rho} \in H^1(\mathbf{R}^3), \int_{\mathbf{R}^3} \rho = |\Lambda| \Big\}. \end{aligned} \tag{3}$$

It is well-known that the problem (2) (respectively (3)) has a unique minimizer (see for instance [2], [10] or [12]), basically because the energy functional E_Λ is convex with respect to ρ.

The thermodynamic limit problem is the following : letting Λ be a subset of a periodic lattice, determine the behaviour of I_Λ and ρ_Λ as Λ progressively fills in the entire lattice.

In order to tackle this problem mathematically, we introduce the notion of Van Hove sequences :

Let $\Lambda = (\Lambda_h)_{h\in\mathbf{N}}$ be a sequence of subsets of $\mathbf{Z}^n$, having cardinal $|\Lambda|$. Λ is a Van Hove sequence of $\mathbf{Z}^n$ if it satisfies the following :

(An) For any finite subset A of $\mathbf{Z}^n$, there exists $h_0 \in \mathbf{N}$ such that for all $h \geq h_0$, $A \subset \Lambda_h$.

(Bn) Denoting by Γ the unit cube centered at the origin, by $\Gamma(\Lambda)$ the set $\cup_{k\in\Lambda}(\Gamma + k)$, by Λ^a the set $\{x \in \mathbf{R}^n \,/\, d(x, \partial\Gamma(\Lambda)) < a\}$, where d is the Euclidean distance in $\mathbf{R}^n$, and by $|\Lambda_h^a|$ the Lebesgue measure (in $\mathbf{R}^n$) of the set Λ_h^a, we have, for all $a > 0$, the Van Hove condition, that is :

$$\lim_{h\to\infty} \frac{|\Lambda_h^a|}{|\Lambda_h|} = 0 \tag{4}$$

The thermodynamic limit problem studied in [6] consists then in answering the following questions, for any Van Hove sequence Λ of $\mathbf{Z}^3$:

(L1) Does the energy per cell $\frac{I_\Lambda}{|\Lambda|}$ converge as $|\Lambda|$ goes to infinity ?

(L2) Does the density ρ_Λ converge to a limit ρ_∞ as $|\Lambda|$ goes to infinity ?

(L3) Does the limit ρ_∞ have the same periodicity as that of the lattice ?

In this article, we study questions (L1), (L2), (L3) in two cases that do not satisfy conditions (A3) and (B3) :

(a) The first case is the thermodynamic limit of a lineic molecule, that is $\Lambda = \{(0,0)\}\times\Lambda_3$ will be a subset of $\{(0,0)\} \times \mathbf{Z}$, such that Λ_3 is a Van Hove sequence of $\mathbf{Z}^1$,

(b) The second case is the same problem concerning a thin film : $\Lambda = \Lambda_2 \times \{0\}$ is a subset of $\mathbf{Z}^2 \times \{0\}$, and the sequence Λ_2 is a Van Hove sequence of $\mathbf{Z}^2$.

1.1 Lineic molecules

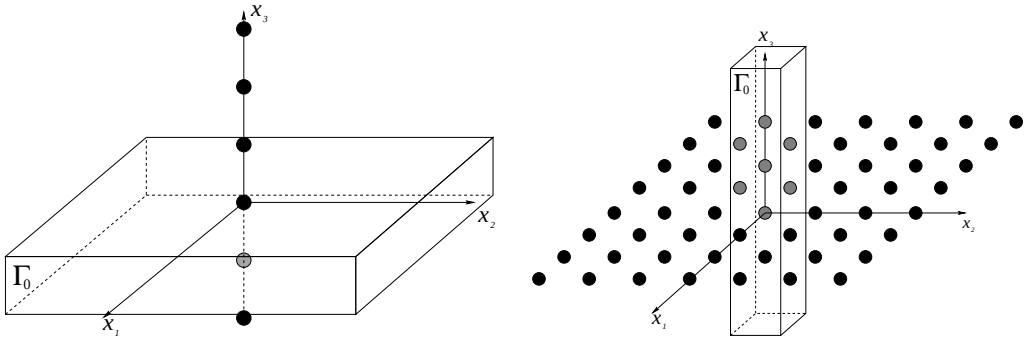

Figure 1: The set Λ in the case of polymers (on the left) and thin films (on the right)

In this case, to which Section 2 is devoted, we are going to answer affirmatively the questions (L1), (L2), and (L3). More precisely, we introduce the following notation :

(i) we denote by $\Gamma_0 = \mathbf{R}^2\times]-\frac{1}{2},\frac{1}{2}]$ the periodic cell of the problem, and by $\Gamma(\Lambda)$ the set $\cup_{k\in\Lambda}\Gamma_0 + k$.

(ii) For any functional space S, $S_{per}(\Gamma_0)$ denotes the set of elements of $S_{loc}(\mathbf{R}^3) \cap S(\Gamma_0)$ that are periodic with periodic cell Γ_0.

We introduce the following variational problem :

$$I_{per} = \inf\left\{ E_{per}(\rho), \rho \geq 0,\ \sqrt{\rho} \in X_{per},\ \int_{\Gamma_0} \rho = 1 \right\}, \tag{5}$$

where X_{per} is a subspace of $H^1_{per}(\Gamma_0)$ to be made precise later on (see formula 29), and E_{per} is defined by :

$$E_{per}(\rho) = \int_{\Gamma_0} |\nabla \sqrt{\rho}|^2 + \int_{\Gamma_0} \rho^{5/3} - \int_{\Gamma_0} G\rho + \frac{1}{2} \int_{\Gamma_0} \int_{\Gamma_0} \rho(x)\rho(y)G(x-y)dxdy. \tag{6}$$

The potential G, which is not to be confused with the potential G appearing in [6] (it is its 1-D analogue), is the periodic potential modeling the Coulombian interaction in the periodic lattice $\{(0,0)\} \times \mathbf{Z}$. (In the smeared nuclei case, the only necessary change is to take $G \star_{\Gamma_0} m$ instead of G in the third term of the energy (6).) From the conclusions of [11], it is natural to introduce :

$$G(x) = -2\log|x'| + \sum_{k \in \mathbf{Z}} \left(\frac{1}{|x - ke_3|} - \int_{-\frac{1}{2}}^{\frac{1}{2}} \frac{dy}{|x - (y+k)e_3|} \right), \tag{7}$$

where we denote by x' the vector (x_1, x_2), and by (e_1, e_2, e_3) the canonical basis of $\mathbf{R}^3$. It is easy to check that G is periodic, with periodic cell Γ_0, and that it satisfies :

$$-\Delta G = 4\pi \sum_{k \in \mathbf{Z}} \delta_{ke_3}.$$

The constant M is defined by follows :

- In the point nuclei case, $M = \lim_{x \to 0} \left(G(x) - \frac{1}{|x|} \right)$.
- In the smeared nuclei case, $M = \int_{\Gamma_0} \int_{\Gamma_0} m(x)m(y) \left(G(x-y) - \frac{1}{|x-y|} \right)$.

The main result of Section 2 is the following theorem :

Theorem 1.1 *Let Λ be a Van Hove sequence in the third dimension, in the sense made precise above, and ρ_Λ the minimizing density of the TFW energy. Then we have :*

(i) $\lim_{\Lambda \to \infty} \frac{I_\Lambda}{|\Lambda|} = I_{per} + \frac{M}{2}$.

(ii) The density ρ_Λ converges to ρ_{per} uniformly on any subset of the form $\mathbf{R}^2 \times K$, K being a compact subset of $\mathbf{R}$.

The strategy of the proof is as follows : we first write down I_Λ's Euler-Lagrange equation, that is : (setting $\rho_\Lambda = u_\Lambda^2$ and $m_\Lambda = \sum_{k\in\Lambda} m(\cdot - k)$, m being either δ_0 in the point nuclei case, or a smooth function in the smeared nuclei case)

$$-\Delta u_\Lambda + \frac{5}{3}u_\Lambda^{7/3} - \left((m_\Lambda - u_\Lambda^2) \star \frac{1}{|x|}\right)u_\Lambda = -\theta_\Lambda u_\Lambda,$$

where θ_Λ denotes the Lagrange multiplier associated to the mass constraint in I_Λ. Hence, denoting by ϕ_Λ the function $(m_\Lambda - u_\Lambda^2) \star \frac{1}{|x|} - \theta_\Lambda$, we get a solution of the system :

$$\left\{\begin{array}{l} -\Delta u_\Lambda + \frac{5}{3}u_\Lambda^{7/3} - u_\Lambda\phi_\Lambda = 0, \\ -\Delta\phi_\Lambda = 4\pi(m_\Lambda - u_\Lambda^2), \\ u_\Lambda \geq 0. \end{array}\right. \tag{8}$$

As in [6], we then establish bounds on u_Λ and ϕ_Λ, so that we can pass locally to the limit in the above system. Next, we show the following uniqueness result :

Theorem 1.2 *Let $\mu \not\equiv 0$ be a non-negative measure with compact support with respect to (x_1, x_2). Assume that μ is periodic with periodic cell Γ_0, and that $\mu(\Gamma_0) = 1$. Then the following system*

$$\left\{\begin{array}{l} -\Delta u + \frac{5}{3}u^{7/3} - u\phi = 0, \\ -\Delta\phi = 4\pi(\mu - u^2), \\ u \geq 0 \end{array}\right. \tag{9}$$

has a unique solution $(u, \phi) \in \left(L^2_{unif} \cap L^{7/3}_{loc}(\mathbf{R}^3)\right) \times L^1_{unif}(\mathbf{R}^3)$. In addition, this solution satisfies the following properties :

(i) $u \in L^\infty(\mathbf{R}^3)$, *and* $u(x) \leq \frac{C}{1+(x_1^2+x_2^2)^{3/4}}$, $C > 0$ *being a constant independent of* x.

(ii) $\phi \in L^p_{unif}(\mathbf{R}^3)$ *for all* $p < 3$, *and there exists a constant* θ_{per} *such that* $\phi = G \star_{\Gamma_0} (\mu - u^2) - \theta_{per}$.

(iii) $\int_{\Gamma_0} u^2 = 1$.

The space $L^p_{unif}(\mathbf{R}^3)$ is $\{f \in L^p_{loc}(\mathbf{R}^3) \ / \ \sup_{x\in\mathbf{R}^3} \|f\|_{L^p(B_1+x)} < \infty\}$.

Once this result is established, applying it to the case $\mu = \sum_{k\in\mathbf{Z}^3} m(\cdot + k)$, we may therefore identify the limit of u_Λ as the unique solution of this system.

Concerning the proof of Theorem 1.2, the strategy consists in showing that any solution of system (9) is periodic, with periodic cell Γ_0, hence that $\rho = u^2$ is a critical point of I_{per}, with nuclei defined by $m = \mu$ on Γ_0, and next showing that this problem is strictly convex, so that ρ is necessarily its unique minimizer. In order to show that I_{per} is convex, we introduce the bilinear form D_G defined by :

$$D_G(f, g) = \int_{\Gamma_0}\int_{\Gamma_0} f(x)g(y)G(x-y)dxdy = \int_{\Gamma_0} (f \star_{\Gamma_0} G)g,$$

and we rewrite E_{per} as :

$$E_{per}(\rho) = \int_{\Gamma_0} |\nabla\sqrt{\rho}|^2 + \int_{\Gamma_0} \rho^{5/3} + \frac{1}{2}D_G(m-\rho, m-\rho) - \frac{1}{2}D_G(m,m).$$

Of course, this is possible only in the smeared nuclei case, or equivalently if m is smooth. If it is not, we introduce the characteristic function of the unite cube, denoted by 1_Q, and write :

$$\begin{aligned} E_{per}(\rho) &= \int_{\Gamma_0} |\nabla\sqrt{\rho}|^2 + \int_{\Gamma_0} \rho^{5/3} + \frac{1}{2}D_G(1_Q-\rho, 1_Q-\rho) - \frac{1}{2}D_G(1_Q,1_Q) \\ &\quad + \int_{\Gamma_0} \big((1_Q - m) \star_{\Gamma_0} G\big)\rho. \end{aligned}$$

In both cases, the point is that, by studying closely the potential G, we find that D_G is positive on a set that includes $m-\rho$ and $1_Q-\rho$ as far as $\sqrt{\rho}$ lies in X_{per} and ρ has total mass one over Γ_0. So D_G is a convex functional on that set. Hence I_{per} becomes a convex problem.

Those results answer questions (L2) and (L3). Next, we use them as in [6] to show the convergence of the energy, answering question (L1).

All these results give a TFW model for any molecule which nuclei are periodically ditributed with respect to x_3, and contained in a cylinder having vertical axis. This is the case for many polymers, and for DNA molecules.

1.2 Thin films

The second part of our work concerns problem (b).

As above, we denote by Γ_0 the periodic cell of the problem, which is now $]-\frac{1}{2},\frac{1}{2}]^2\times\mathbf{R}$, and by $\Gamma(\Lambda)$ the set $\cup_{k\in\Lambda}\Gamma_0+k$. The notation $H^1_{per}(\Gamma_0)$ follows as in the one-dimensional case.

Here again, we introduce a periodic potential, that we still denote by G, though it is neither the same as in [6] nor as in (7) :

$$G(x) = -2\pi|x_3| + \sum_{k\in\mathbf{Z}^2\times\{0\}} \left(\frac{1}{|x-k|} - \int_{K\times\{0\}} \frac{dy}{|x-y-k|}\right), \tag{10}$$

where K is the unit square of $\mathbf{R}^2$, namely $]-\frac{1}{2},\frac{1}{2}[^2$. We notice that G satisfies the equation

$$-\Delta G = 4\pi \sum_{k\in\mathbf{Z}^2\times\{0\}} \delta_k.$$

The energy E_{per} is defined by (6), and the problem I_{per} by (5). We also define the constant M exactly in the same way as in the polymers case.

We do not have here a convergence result as general as that of the preceding section, although we suspect it to hold. In fact, in order to be able to show a convergence theorem as Theorem 1.1, we need the additional assumption that Λ is symmetric with respect to x_1 and x_2. However, it is only a technical hypothesis, and the convergence result that is stated in Theorem 1.3 below is likely to be true for any Van Hove sequence.

Theorem 1.3 *Let Λ be a Van Hove sequence in the first two directions. Assume that Λ is symmetric with respect to x_1 and x_2. (In the smeared nuclei case, m is also supposed to be symmetric.) Then, we have :*

(i) $\lim_{|\Lambda|\to\infty} \frac{I_\Lambda}{|\Lambda|} = I_{per} + \frac{M}{2}$.

(ii) ρ_Λ *uniformly converges to* ρ_{per} *on any set of the form* $K \times \mathbf{R}$, K *being a compact subset of* $\mathbf{R}^2$.

As in the preceding section, we start by proving the second assertion of Theorem 1.3, the first one being a consequence of it. For this purpose, we use exactly the same strategy as above, showing first that the Euler-Lagrange equation passes to the limit, and then that such a solution is a critical point of I_{per}. The same positiveness property holds concerning D_G, and so the proof carries through. The only difference is that, for technical reasons, we are not able to show a uniqueness result similar to that of Theorem 1.2 : such a result would hold only (so far as we know) to a solution coming from the thermodynamic limit process for a sequence of symmetric domains.

This model remains valid for any set of nuclei which is periodic and has compact support with respect to x_3. This is the case in practice for thin films, which contain a few layers of nuclei.

Remark 1.4 *The thermodynamic limit problem may also be investigated in the case of a semicrystal, that is when the set of nuclei fills in a half-space (in view of adsorption problems.) In this case, which we have studied, an analogous result as that of Theorem 1.2 holds, and it is possible to show that in the inner cells of the semicrystal, the density tends to be periodic and looks like that of a full crystal.*

Remark 1.5 *In all the results we have stated above, we have used the Coulombian interaction potential, that is* $V(x) = \frac{1}{|x|}$. *Another choice is possible, namely the Yukawa potential :*

$$V(x) = \frac{e^{-a|x|}}{|x|}, \tag{11}$$

where $a > 0$.

Then (1) and (8) become :

$$\begin{aligned} E_\Lambda(\rho) \;=\; & \int_{\mathbf{R}^3} |\nabla\sqrt{\rho}|^2 + \int_{\mathbf{R}^3} \rho^{5/3} - \sum_{k\in\Lambda} \int_{\mathbf{R}^3} \rho V(\cdot - k) \\ & + \frac{1}{2} \int_{\mathbf{R}^3} (\rho \star V)\rho. \end{aligned} \tag{12}$$

$$\left\{ \begin{array}{l} -\Delta u_\Lambda + \frac{5}{3} u_\Lambda^{7/3} - u_\Lambda \phi_\Lambda = 0, \\ -\Delta \phi_\Lambda + a^2 \phi_\Lambda = 4\pi(m_\Lambda - u_\Lambda^2), \\ u_\Lambda \geq 0. \end{array} \right. \tag{13}$$

In this case, we have stronger results that are briefly exposed (without proofs) in Section 4, together with uniqueness results for some related semi-linear PDEs.

2 Polymers

We study here the thermodynamic limit problem in one dimension, that is to say the limit of a line growing to infinity. More precisely, we consider a sequence $\Lambda = \{(0,0)\} \times \Lambda_3 \subset \{(0,0)\} \times \mathbf{Z}$, such that Λ_3 is a Van Hove sequence of $\mathbf{Z}$. We recall that Γ_0 is the periodic cell of the problem, i.e $\Gamma_0 = \mathbf{R}^2 \times]-\frac{1}{2}, \frac{1}{2}]$, and $\Gamma(\Lambda) = \bigcup_{k\in\Lambda} \Gamma_0 + k$. Putting $x = (x_1, x_2, x_3)$ a point in $\mathbf{R}^3$, we denote by $r = r(x)$ the quantity $\sqrt{x_1^2 + x_2^2}$. For all Λ, we denote by :

$$E_\Lambda(\rho) = \int_{\mathbf{R}^3} |\nabla\sqrt{\rho}|^2 + \int_{\mathbf{R}^3} \rho^{5/3} - \int_{\mathbf{R}^3} (m_\Lambda \star \frac{1}{|x|})\rho + \frac{1}{2}\int_{\mathbf{R}^3} (\rho \star \frac{1}{|x|})\rho \tag{14}$$

the Thomas-Fermi-von Weizsäcker energy. Here $m_\Lambda = \sum_{k\in\Lambda} \delta_k$. In the case of smeared nuclei, δ_k will be replaced by $m(\cdot - k)$, where m is the measure defining the shape of a nucleus. In this case, m will be considered to be in $\mathcal{D}(\mathbf{R}^3)$, such that its support lies in Γ_0. We will denote by I_Λ the minimization problem :

$$I_\Lambda = \inf\{E_\Lambda(\rho) + \sum_{k\neq j\in\Lambda} \frac{1}{|k-j|}, \rho \geq 0,\ \sqrt{\rho} \in H^1(\mathbf{R}^3), \int_{\mathbf{R}^3} \rho = |\Lambda|\}. \tag{15}$$

We will denote by ρ_Λ the solution of the problem I_Λ.
We also recall the Euler-Lagrange equation of problem (15) :

$$-\Delta u_\Lambda + \frac{5}{3} u_\Lambda^{7/3} - \phi_\Lambda u_\Lambda = 0, \tag{16}$$

where $u_\Lambda = \sqrt{\rho}_\Lambda$ and $\phi_\Lambda = (m_\Lambda - u_\Lambda^2) \star \frac{1}{|x|} - \theta_\Lambda$, $\theta_\Lambda \in \mathbf{R}$ being the Lagrange multiplier associated to the constraint in (15). Hence ϕ_Λ satisfies

$$-\Delta\phi_\Lambda = 4\pi(m_\Lambda - u_\Lambda^2). \tag{17}$$

Let us begin with some a priori estimates.

2.1 A priori estimates

2.1.1 Energy bounds

First of all, we establish some bounds on ρ_Λ and ϕ_Λ. For this purpose, we follow exactly the proof of [6], Chapter 3, Section 3.2, which carries through here since it does not depend on the sequence Λ, and we get :

Theorem 2.1 (Catto, Le Bris, Lions, [6]) *There exist various positive constants C such that, for any sequence $\Lambda \subset \mathbf{Z}^3$, we have :*

(i) $|I_\Lambda| \leq C|\Lambda|$,

(ii) $\int_{\mathbf{R}^3} |\nabla u_\Lambda|^2 \leq C|\Lambda|$,

(iii) $\|\rho_\Lambda\|_{L^p} \leq C|\Lambda|^{1/p}$ *for all* $p \leq \frac{5}{3}$,

(iv) $0 \leq \int_{\mathbf{R}^3} \phi_\Lambda \rho_\Lambda \leq C|\Lambda|$,

(v) $0 < \theta_\Lambda \leq C$,

(vi) $|\sum_{k \neq j \in \Lambda} \frac{1}{|k-j|} - \int_{\mathbf{R}^3} \rho_\Lambda (m_\Lambda \star \frac{1}{|x|})| \leq C|\Lambda|$.

In the case of smeared nuclei, we also have :

(vii) $D(m_\Lambda - \rho_\Lambda, m_\Lambda - \rho_\Lambda) \leq C|\Lambda|$, *i.e* $\int_{\mathbf{R}^3} |\nabla \phi_\Lambda|^2 \leq C|\Lambda|$.

2.1.2 L^∞ bounds

Next, we may obtain L^∞ bounds, still exactly as in [6], Section 3.2. Here again, the proof does not depend on the sequence Λ, so we have :

Theorem 2.2 (Catto, Le Bris, Lions, [6]) *There exist positive constants C independent of Λ such that, for all $\Lambda \subset \mathbf{Z}^3$, we have :*

(i) $\|\rho_\Lambda\|_{L^\infty(\mathbf{R}^3)} \leq C$.

(ii) *In the smeared nuclei case,* $\|\phi_\Lambda\|_{L^\infty(\mathbf{R}^3)} \leq C$.

In the point nuclei case, we have :

(ii') $\|\phi_\Lambda\|_{L^\infty(Q(\Lambda)^c)} \leq C$, *where* $Q(\Lambda) = \cup_{k \in \Lambda} Q + k$, Q *being the unit cube of* $\mathbf{R}^3$ *and :*

(iii') $\|\phi_\Lambda\|_{L^p_{unif}(\mathbf{R}^3)} \leq C$, *for all* $1 \leq p < 3$.

The norm $\|\cdot\|_{L^p_{unif}(\mathbf{R}^3)}$ *is defined by* $\sup_{x \in \mathbf{R}^3} \|\cdot\|_{L^p(x+B_1)}$.

Remark 2.3 *Let us point out that the proof of Theorem 2.2 is based only on the Euler Lagrange equations (16)-(17), and the fact that the measure m is positive, bounded, and has compact support. Hence it holds for any such solutions, and in particular if m_Λ is replaced by $m_\infty = \sum_{k \in \mathbf{Z}} m(\cdot - ke_3)$, or by any Γ_0-periodic measure with compact support in the direction (x_1, x_2). This will be useful in the proof of the uniqueness Theorem 2.16 below.*

2.1.3 Asymptotic estimates

As the set of nuclei remains confined in a subset of $\mathbf{R}^3$ which is bounded with respect to r, we expect the above uniform bounds not to be optimal. More precisely, we expect, at least concerning the density ρ_Λ, a decay as r goes to infinity. For this purpose, we use Solovej's method [14] (see also [1]).

Let e_R be the ground state of the Laplacian with homogeneous Dirichlet boundary conditions on the ball B_R of radius R centered at the origin, normalized by the condition $\|e_R\|_{L^2} = 1$, and prolonged by 0 outside B_R. That is, $e_R(x) = \frac{sin(\pi|x|/R)}{|x|\sqrt{2\pi R}}$ on B_R. Then we have $\|\nabla e_R\|_{L^2} = \pi/R$. We set $g_R = e_R^2$.

Lemma 2.4 (Benguria, Lieb, [1]) *Let Ω be any open subset of $\mathbf{R}^3$. If $u_\Lambda \in H_0^1(\Omega)$ is positive and satisfies (16) with $\phi_\Lambda \in L^2(\Omega) + L^\infty(\Omega)$ satisfying (17), then for all $x \in \Omega$ such that $d(x, \partial\Omega) > R$, we have :*

$$g_R \star \phi_\Lambda \leq g_R \star u_\Lambda^{4/3} + \pi^2 R^{-2}. \tag{18}$$

And if $B_R + x$ does not contain any nuclei, i.e $m_\Lambda = 0$ in $B_R + x$, we have :

$$\phi_\Lambda(x) \leq g_R \star \phi_\Lambda(x). \tag{19}$$

Proof : For the sake of consistency, we reproduce here the proof of this lemma. Since u_Λ is positive, and u_Λ satisfies (16), it is the ground state of the operator $H = -\Delta + u_\Lambda^{4/3} - \phi_\Lambda$ with Dirichlet condition on Ω. Hence, for all $w \in H_0^1(\Omega)$, we have :

$$\int_\Omega |\nabla w|^2 + \int_\Omega (u_\Lambda^{4/3} - \phi_\Lambda) w^2 \geq 0. \tag{20}$$

We now apply this inequality to $w = e_R(x - \cdot)$, and we get (18), provided $d(x, \partial\Omega) > R$. Let us now show (19) : if ϕ_Λ satisfies (17) and $B_R + x$ contains no nuclei, ϕ_Λ is subharmonic on $B_R + x$, hence applying the mean-value inequality (see for instance [9]), we get :

$$g_R \star \phi_\Lambda(x) = \int_0^R \left(\int_{S_r} \phi_\Lambda(x - y) dy \right) g_R(r) dr \geq \int_0^R 4\pi r^2 \phi_\Lambda(x) g_R(r) dr = \phi_\Lambda(x)$$

because g_R is of total mass one. $\Diamond$

Now we turn to the estimate at infinity :

Theorem 2.5 *For any solution $(u_\Lambda, \phi_\Lambda)$ of the system (16)-(17) satisfying $u_\Lambda \geq 0$, we have :*

$$\begin{aligned} \phi_\Lambda &\leq \frac{C}{1 + r^2}, \ \forall r \geq 1, \\ 0 \leq u_\Lambda &\leq \frac{C}{1 + r^{3/2}} \quad , \end{aligned}$$

where C denotes various positive constants independent of the measure m_Λ.

Furthermore, in the smeared nuclei case, i.e when m in (17) is supposed to be smooth, the first inequality holds everywhere in $\mathbf{R}^3$.

Remark 2.6 *The first estimate is not efficient for Λ fixed : $\phi_\Lambda = (m_\Lambda - u_\Lambda^2) \star \frac{1}{|x|} - \theta_\Lambda$ is negative at infinity, since θ_Λ is positive (see [14]). However, the point is that this estimate does not depend on the measure m_Λ, hence is independent of the sequence Λ, as far as it satisfies the hypotheses we have required at the beginning of this section.*

Proof :

We apply Lemma 2.4, with $\Omega = \mathbf{R}^3$, and get :

$$g_R \star \phi_\Lambda \leq g_R \star u_\Lambda^{4/3} + \frac{\pi^2}{R^2},$$

for all $R > 0$. We define $\tilde{\phi} = g_R \star \phi_\Lambda - \frac{\pi^2}{R^2}$, and get, using Jensen's inequality :

$$\tilde{\phi} \leq g_R \star u_\Lambda^{4/3} \leq (g_R \star u_\Lambda^2)^{2/3}.$$

Now, convoluting (17) on both sides, we get :

$$-\Delta(g_R \star \phi_\Lambda) = 4\pi(m_\Lambda \star g_R - u_\Lambda^2 \star g_R),$$

that is,

$$-\Delta\tilde{\phi} + (\tilde{\phi})_+^{3/2} \leq 4\pi(m_\Lambda \star g_R).$$

Now, we may assume, without loss of generality, that the support of m_Λ lies in $\{r \leq 1\}$. So we have $m_\Lambda \star g_R = 0$ on $C_{R+1} = \{r \geq R+1\}$, hence $-\Delta\tilde{\phi} + (\tilde{\phi})_+^{3/2} \leq 0$ on that set.

We are going now to use a comparison argument on $\tilde{\phi}$, in the spirit of [4]. For that purpose, we fix an $R' > R+1$ and introduce the function

$$U = \frac{a}{(r^2 - R^2)^2} + \frac{bR'^4}{(R'^2 - |x|^2)^4},$$

where a and b are positive constants to be determined later on. In particular, we need U to be a supersolution of the differential inequality satisfied by $\tilde{\phi}$, that is, $-\Delta U + U_+^{3/2} \geq 0$. One easily computes :

$$-\Delta U = -8a\frac{R^2 + 2r^2}{(r^2 - R^2)^4} - 8bR'^4\frac{3R'^2 + 7|x|^2}{(R'^2 - |x|^2)^6}. \tag{21}$$

Using the inequality $(\alpha + \beta)^{3/2} \geq \alpha^{3/2} + \beta^{3/2}$, which is valid for all $\alpha, \beta > 0$, one finds :

$$-\Delta U + U^{3/2} \geq \frac{a(\sqrt{a} - 8\frac{R^2+2r^2}{r^2-R^2})}{(r^2 - R^2)^3} + \frac{bR'^4(\sqrt{b}R'^2 - 24R'^2 - 56|x|^2)}{(R'^2 - |x|^2)^6}. \tag{22}$$

We want this quantity to be positive on $C_{R+1} \cap B_{R'}$, which is true as soon as $a \geq (16 + \frac{24R^2}{2R+1})^2$ and $b \geq 80^2$. We also need that $U \geq \tilde{\phi}$ on $\partial C_{R+1} \cap B_{R'}$, i.e $\frac{a}{(2R+1)^2} \geq \|\tilde{\phi}\|_{L^\infty}$. The latter quantity exists because $\phi_\Lambda \in L^1_{unif}$ and g_R is smooth with compact support. So we can choose a large enough to ensure all those properties, together with $a \leq cR^2$, c being a universal constant.

We then have :

$$-\Delta(\tilde{\phi} - U) + (\tilde{\phi})_+^{3/2} - U^{3/2} \leq 0.$$

Hence, using Kato's inequality :

$$-\Delta(\tilde{\phi} - U)_+ \leq -\mathrm{sgn}^+(\tilde{\phi} - U)((\tilde{\phi})_+^{3/2} - U^{3/2}) \leq 0.$$

We use now the maximum principle to conclude that on the set $C_{R+1} \cap B_{R'}$,

$$\tilde{\phi} \leq \frac{cR^2}{(r^2 - R^2)^2} + \frac{bR'^4}{(R'^2 - |x|^2)^4}.$$

This holds for any $R' > R+1$, with c and b being universal constants. So, by letting R' go to infinity, we find :

$$\tilde{\phi} \leq \frac{cR^2}{(r^2-R^2)^2}$$

on C_{R+1}.

Furthermore, from Lemma 2.4, we know that on this set, (19) holds. Therefore, we finally get :

$$\phi_\Lambda \leq \frac{cR^2}{(r^2-R^2)^2} + \frac{\pi^2}{R^2}.$$

This inequality holds whenever $R > 0$ and $r \geq R+1$. So if r is fixed and larger than 2, we may choose $R = r/2$, and we find

$$\forall r \geq 2,\ \phi_\Lambda \leq \frac{\frac{4c}{9} + 4\pi^2}{r^2}.$$

Pointing out that $\phi_\Lambda \in L^\infty(\{r > 1\})$, we infer that

$$\forall r \geq 1,\ \phi_\Lambda \leq \frac{d}{1+r^2}.$$

And in the smeared nuclei case, we know that $\phi_\Lambda \in L^\infty$, so this inequality holds on $\mathbf{R}^3$.

We now turn to the second assertion, namely the estimate on u_Λ. For this purpose, we use the above inequality and (16), and write :

$$-\Delta u_\Lambda + \frac{5}{3} u_\Lambda^{7/3} \leq \frac{d u_\Lambda}{r^2},\ \forall r \geq 1.$$

Now, there exists a constant c such that for all $a, b \geq 0$, $ab \leq \frac{1}{3}a^{7/3} + cb^{7/4}$. So we have, on the set $\{r \geq 1\}$:

$$-\Delta u_\Lambda + \frac{4}{3} u_\Lambda^{7/3} \leq \frac{cd}{r^{7/2}}.$$

We are now going to use the same comparison argument as above, introducing the function $V = \frac{a}{r^{3/2}} + \frac{bR'^{3/2}}{(R'^2-|x|^2)^{3/2}}$. Computing $-\Delta V$, and using (here again) that $(\alpha+\beta)^{7/3} \geq \alpha^{7/3} + \beta^{7/3}$, we find that

$$-\Delta V + \frac{4}{3}V^{7/3} \geq \frac{a}{r^{7/2}}\left(\frac{4a^{4/3}}{3} - \frac{9}{4}\right) + \frac{bR'^{3/2}}{(R'^2-|x|^2)^{7/2}}\left(\frac{4}{3}b^{4/3}R'^2 - 9R'^2 - 6|x|^2\right).$$

Thus, choosing $a \geq \|u_\Lambda\|_{L^\infty}$ so that $a(\frac{4a^{4/3}}{3} - \frac{9}{4}) \geq cd$ and $b^{4/3} > \frac{45}{4}$, we have :

$$-\Delta V + \frac{4}{3}V^{7/3} \geq -\Delta u_\Lambda + \frac{4}{3}u_\Lambda^{7/3}.$$

So by the same argument as above, we conclude that $u_\Lambda \leq V$ on the set $\{r \geq 1\}$. Since $u_\Lambda \in L^\infty(\mathbf{R}^3)$, this concludes the proof. $\Diamond$

2.1.4 Compactness

The next step consists in proving the compactness of the sequence ρ_Λ, i.e the fact that no electrons escape at infinity. Mathematically, this will be stated as :

$$\frac{1}{|\Lambda|}\int_{\Gamma(\Lambda)} \rho_\Lambda \longrightarrow 1 \quad \text{as} \quad \Lambda \to \infty. \tag{23}$$

We start with the smeared nuclei case, and next generalize the result to the point nuclei case :

Proposition 2.7 *In the smeared nuclei case, (23) holds.*

Proof : The key-point of the proof is, as in [6], that we have, for all $h \in H^1(\mathbf{R}^3)$,

$$|\int_{\mathbf{R}^3} (m_\Lambda - \rho_\Lambda)h| \leq \frac{1}{(2\pi)^3} D(m_\Lambda - \rho_\Lambda, m_\Lambda - \rho_\Lambda)^{1/2} \|\nabla h\|_{L^2(\mathbf{R}^3)}. \tag{24}$$

(We recall that $D(f,g) = \int_{\mathbf{R}^3}\int_{\mathbf{R}^3} \frac{f(x)g(y)}{|x-y|}dxdy$.) This inequality holds because $m_\Lambda - \rho_\Lambda \in L^{6/5}(\mathbf{R}^3) \subset H^{-1}(\mathbf{R}^3)$: it is exactly the Cauchy-Schwarz inequality in $H^{-1} \times H^1$, through the Fourier transform.

Now, we know from Theorem 2.5, that $D(m_\Lambda - \rho_\Lambda, m_\Lambda - \rho_\Lambda) \leq C|\Lambda|$.

Next, we choose $h = h_\Lambda$: we put $h_\Lambda(x) = f_\Lambda(r)g_\Lambda(x_3)$, where :

- $f_\Lambda(r) = 1 - (\frac{r}{R})^\alpha$ if $r \leq R$, 0 otherwise, with $1 > \alpha > 0$, and $R = R(\Lambda) > 0$ being chosen below.
- $g_\Lambda \in \mathcal{D}(\mathbf{R})$, $g_\Lambda = 1$ on the set $\{x \in \mathbf{R}/d(x,\Lambda_3) < \frac{1}{2}\}$, 0 on the set $\{x \in \mathbf{R}/d(x,\Lambda_3) > 1\}$, $0 \leq g_\Lambda \leq 1$ and $|g'_\Lambda| \leq 4$.

(We recall that $\Lambda = \{(0,0)\} \times \Lambda_3$, and that $|\Lambda_3^h| = \{t \in \mathbf{R},\, d(t, \partial(\cup_{k\in\Lambda_3}[k-1/2, k+1/2])) < h\}$.)

For such an h_Λ, we compute :

$$\begin{aligned}
\int_{\mathbf{R}^3} |\nabla h_\Lambda|^2 &= \int_{\mathbf{R}^2\times[0,\infty[} g'_\Lambda(x_3)^2 f_\Lambda(r)^2 2\pi r dr dx_3 + \int_{\mathbf{R}^2\times[0,\infty[} g_\Lambda(x_3)^2 f'_\Lambda(r)^2 2\pi r dr dx_3 \\
&\leq C|\Lambda_3^1| \int_0^R (1 - (\frac{r}{R})^\alpha)^2 r dr + C|\Lambda| \int_0^R \alpha^2 \frac{r^{2\alpha-1}}{R^{2\alpha}} dr \\
&\leq C(R^2|\Lambda_3^1| + \alpha|\Lambda|).
\end{aligned}$$

We now choose $R = \left(\frac{|\Lambda|}{|\Lambda_3^1|}\right)^{1/4}$, so that we have $R \longrightarrow \infty$ as $|\Lambda| \to \infty$, together with $R|\Lambda_3^1|^{1/2} \ll |\Lambda|^{1/2}$. Thus, we find that $\|\nabla h_\Lambda\|_{L^2(\mathbf{R}^3)} \leq C(\sqrt{\alpha|\Lambda|} + o(\sqrt{|\Lambda|}))$, hence

$$\frac{1}{|\Lambda|}|\int_{\mathbf{R}^3} (m_\Lambda - \rho_\Lambda)h_\Lambda| \leq C\sqrt{\alpha} + o(1).$$

Now, because $h_\Lambda \leq 1$, $\int_{\mathbf{R}^3} m_\Lambda h_\Lambda \leq |\Lambda|$. On the other hand,

$$\int_{\mathbf{R}^3} m_\Lambda h_\Lambda \geq |\Lambda| - \int_{\mathbf{R}^3} m_\Lambda (\frac{r}{R})^\alpha.$$

And $\int_{\mathbf{R}^3} m_\Lambda (\frac{r}{R})^\alpha \leq C|\Lambda|/R^\alpha$, so we have :

$$\frac{1}{|\Lambda|} \int_{\mathbf{R}^3} m_\Lambda h_\Lambda \longrightarrow 1.$$

Furthermore,

$$\begin{aligned} \int_{\mathbf{R}^3} \rho_\Lambda h_\Lambda &= \int_{\Gamma(\Lambda)\cap\{r<R\}} \rho_\Lambda - \int_{\Gamma(\Lambda)\cap\{r<R\}} \rho_\Lambda (\frac{r}{R})^\alpha + \int_{\Gamma(\Lambda)^c} \rho_\Lambda h_\Lambda \\ &= \int_{\Gamma(\Lambda)} \rho_\Lambda + O(|\Lambda_3^1|) - \int_{\Gamma(\Lambda)\cap\{r<R\}} \rho_\Lambda (\frac{r}{R})^\alpha - \int_{\Gamma(\Lambda)\cap\{r>R\}} \rho_\Lambda, \end{aligned}$$

because $\int_{\Gamma(\Lambda)^c} h_\Lambda \rho_\Lambda \leq C|\Lambda_3^1| \int_0^R \frac{r dr}{1+r^3} \leq C|\Lambda_3^1|$, according to Theorem 2.5.

Concerning the remaining terms of the right-hand side of the above equality, we have :

$$0 \leq \int_{\Gamma(\Lambda)\cap\{r>R\}} \rho_\Lambda \leq C|\Lambda| \int_{r>R} \frac{dr}{r^2} \leq C\frac{|\Lambda|}{R} \ll |\Lambda|,$$

and :

$$0 \leq \int_{\Gamma(\Lambda)\cap\{r<R\}} \rho_\Lambda (\frac{r}{R})^\alpha \leq C\frac{|\Lambda|}{R^\alpha} \int_0^\infty \frac{r^{\alpha+1}}{1+r^3} dr \leq C\frac{|\Lambda|}{R^\alpha} \ll |\Lambda|,$$

because $3 - \alpha - 1 > 1$.

Collecting all those convergence results, we get :

$$|1 - \frac{1}{|\Lambda|} \int_{\Gamma(\Lambda)} \rho_\Lambda| \leq C\sqrt{\alpha} + o(1).$$

Letting $|\Lambda| \longrightarrow \infty$, this implies that

$$\limsup_{\Lambda\to\infty} |1 - \frac{1}{|\Lambda|} \int_{\Gamma(\Lambda)} \rho_\Lambda| \leq C\sqrt{\alpha}.$$

Here C does not depend on $\alpha > 0$, so letting $\alpha \to 0$, we find (23). $\Diamond$

Let us now turn to the point nuclei case. The only difference between this case and the preceding one is that $D(m_\Lambda - \rho_\Lambda, m_\Lambda - \rho_\Lambda)$ does not exist. So we are going to replace m_Λ by $1_{Q(\Lambda)}$, $Q(\Lambda)$ denoting $\bigcup_{k\in\Lambda} Q+k$, where Q is the unit cube in $\mathbf{R}^3$. The function $1_{Q(\Lambda)}$ lies in $L^1 \cap L^\infty(\mathbf{R}^3)$ and have compact support, so that the existence of $\frac{1}{|\Lambda|} D(1_{Q(\Lambda)} - \rho_\Lambda, 1_{Q(\Lambda)} - \rho_\Lambda)$ is ensured. The point is then to prove that this quantity is bounded independently of Λ, so that the smeared nuclei case proof will apply. Since this is only a technical adaptation of [6], Section 3.3.4, we skip this proof.

Proposition 2.8 *In the point nuclei case, (23) holds.*

Proof: In order to prove that

$$D(1_{Q(\Lambda)} - \rho_\Lambda, 1_{Q(\Lambda)} - \rho_\Lambda) \leq C|\Lambda| \tag{25}$$

where C does not depend on Λ, we write again it as :

$$\begin{aligned} D(1_{Q(\Lambda)} - \rho_\Lambda, 1_{Q(\Lambda)} - \rho_\Lambda) &= D(1_{Q(\Lambda)}, 1_{Q(\Lambda)}) - U_\Lambda \\ &+ 2(\frac{1}{2}U_\Lambda - \int V_\Lambda \rho_\Lambda + \frac{1}{2}D(\rho_\Lambda, \rho_\Lambda)) \\ &+ 2[\int V_\Lambda \rho_\Lambda - D(\rho_\Lambda, 1_{Q(\Lambda)})] \end{aligned}$$

(where we have set $V_\Lambda = m_\Lambda \star \frac{1}{|x|}$, and $U_\Lambda = \sum_{k \neq j \in \Lambda} \frac{1}{|k-j|}$). We already know, from Theorem 2.1, (iv) and (vi), that the second term is of order $|\Lambda|$. Concerning the other terms, we are going to use the following result shown in [11] (see also [6]) : denoting by $f(x) = \frac{1}{|x|} - \int_Q \frac{dy}{|x-y|}$, where Q is the unit cube in $\mathbf{R}^3$, we have :

$$f(x) = O(\frac{1}{|x|^4}) \text{ as } |x| \to \infty \tag{26}$$

We first consider the first term :

$$\begin{aligned} |D(1_{Q(\Lambda)}, 1_{Q(\Lambda)}) - U_\Lambda| &= \left| \int_{Q(\Lambda)} \int_{Q(\Lambda)} \frac{dxdy}{|x-y|} - \sum_{k \neq j \in \Lambda} \frac{1}{|k-j|} \right| \\ &= \left| \sum_{k,j \in \Lambda} \int_Q \int_Q \frac{dxdy}{|x-y+k-j|} - \sum_{k \neq j \in \Lambda} \frac{1}{|k-j|} \right| \\ &= \left| \sum_{k \in \Lambda} \int_Q \int_Q \frac{dxdy}{|x-y|} \right. \\ &\quad \left. + \sum_{k \in \Lambda} \int_Q \sum_{j \neq k, j \in \Lambda} (\int_Q \frac{dx}{|x+k-y-j|} - \frac{1}{|k-j|}) dy \right| \\ &\leq C|\Lambda| \\ &\quad + \sum_{k \in \Lambda} \int_Q \sum_{j \in \Lambda, j \neq k} \left| \int_Q \frac{dx}{|x+k-y-j|} - \frac{1}{|k-y-j|} \right| dy \\ &\quad + \sum_{k \in \Lambda} \sum_{j \in \Lambda, j \neq k} \left| \int_Q \frac{dy}{|k-y-j|} - \frac{1}{|k-j|} \right| \\ &\leq C|\Lambda| + C \sum_{k \in \Lambda} \sum_{j \in \Lambda, j \neq k} \frac{1}{|k-j|^4} \\ &\leq C|\Lambda| + C|\Lambda| \sum_{j \in \mathbf{Z}, j \neq 0} \frac{1}{|k|^4} \\ &\leq C|\Lambda| \end{aligned}$$

Next, we consider the last term, and write it as :

$$\begin{aligned}\left|\int_{\mathbf{R}^3} V_\Lambda \rho_\Lambda - D(\rho_\Lambda, 1_{Q(\Lambda)})\right| &= \left|\sum_{k\in\Lambda}\int_{\mathbf{R}^3}\frac{\rho_\Lambda}{|x-k|} - \int_{\mathbf{R}^3}\int_{Q(\Lambda)}\frac{\rho_\Lambda(x)dxdy}{|x-y|}\right| \\ &\leq \int_{\mathbf{R}^3}\sum_{k\in\Lambda}\left|\frac{1}{|x-k|} - \int_Q \frac{dy}{|x-y-k|}\right|\rho_\Lambda(x)dx \\ &\leq \int_{\mathbf{R}^3} F(x)\rho_\Lambda(x)dx,\end{aligned}$$

where F is the function defined by $F(x) = \sum_{k\in\mathbf{Z}} f(x-ke_3)$, which belongs to $L^1_{unif}(\mathbf{R}^3)\cap L^\infty(\{r>1\})$ because of (26). Thus, we have :

$$\left|\int_{\mathbf{R}^3} V_\Lambda\rho_\Lambda - D(\rho_\Lambda, 1_{Q(\Lambda)})\right| \leq C|\Lambda|$$

because ρ_Λ is of total mass $|\Lambda|$ and $\rho_\Lambda \in L^\infty$. This implies (25), and concludes our proof. $\Diamond$

2.2 Uniqueness for the system of PDE-Identification of the limit

Now that we have bounds on the sequence ρ_Λ, we may pass locally to the limit (up to a subsequence) in the system (16)-(17). Denoting by $\rho_\infty = u_\infty^2$ and ϕ_∞ the corresponding limits, we get a solution to the system :

$$\begin{cases} -\Delta u_\infty + \frac{5}{3}u_\infty^{7/3} - u_\infty\phi_\infty = 0, \\ -\Delta\phi_\infty = 4\pi(m_\infty - u_\infty^2), \end{cases} \tag{27}$$

where the measure m_∞ is equal to $\sum_{k\in\mathbf{Z}}\delta_{ke_3}$ in the point nuclei case and to $\sum_{k\in\mathbf{Z}} m(\cdot - ke_3)$ in the smeared nuclei case. In both cases, m_∞ is periodic and its periodic cell is Γ_0.

The aim of this section is to show a uniqueness result on the system, so as to identify the limit (u_∞, ϕ_∞) as the solution of the system (27). The first step will be the periodicity of the solution. Next, when the solution is shown to be periodic, we will compare it with the solution of the periodic variational problem :

$$I_{per} = \inf\{E_{per}(\rho), \rho \geq 0, \sqrt{\rho}\in X_{per}, \int_{\Gamma_0}\rho = 1\}, \tag{28}$$

X_{per} being defined by :

$$X_{per} = \{u \in H^1_{per}(\Gamma_0),\ \left(\log(2+|x|)\right)^{1/2}u \in L^2(\Gamma_0)\}, \tag{29}$$

The energy E_{per} is defined by :

$$E_{per}(\rho) = \int_{\Gamma_0} |\nabla\sqrt{\rho}|^2 + \int_{\Gamma_0} \rho^{5/3} - \int_{\Gamma_0} (G \star_{\Gamma_0} m)\rho + \int_{\Gamma_0}\int_{\Gamma_0} G(x-y)\rho(x)\rho(y)dxdy. \quad (30)$$

(We denote by $f \star_{\Gamma_0} g$ the convolution product over Γ_0 for periodic functions, that is, $f \star_{\Gamma_0} g(x) = \int_{\Gamma_0} f(x-y)g(y)dy$.)

The potential G is the periodic potential defined by (7).

We first study this periodic potential.

2.2.1 The potential G

We recall that in this section,

$$G(x) = -2\log(r) + \sum_{k\in\mathbf{Z}} \left(\frac{1}{|x-ke_3|} - \int_{-\frac{1}{2}}^{\frac{1}{2}} \frac{dy}{|x-(y+k)e_3|} \right).$$

Lemma 2.9 *We have :*

(o) G *is smooth on* $\mathbf{R}^3 \setminus \mathbf{Z}e_3$.

(i) $G(x) = \frac{1}{|x|} + C + O(|x|)$ as $x \to 0$.

(ii) $G(x) = -2\log(r) + O(\frac{1}{r})$ as $r \to \infty$, *uniformly with respect to* x_3.

Proof :

First of all, we prove that the sum defining G does exist on $\mathbf{R}^3 \setminus \{r = 0\}$: indeed, denoting by $f(x)$ the quantity $\frac{1}{|x|} - \int_{-\frac{1}{2}}^{\frac{1}{2}} \frac{dt}{|x-te_3|}$, we have, for $|x| \longrightarrow \infty$, and $r \neq 0$:

$$\begin{aligned} f(x) &= \frac{1}{|x|} - \int_{-\frac{1}{2}}^{\frac{1}{2}} \frac{dt}{\sqrt{|x|^2 - 2tx_3 + t^2}} \\ &= \frac{1}{|x|} - \frac{1}{|x|}\int_{-\frac{1}{2}}^{\frac{1}{2}} \frac{dt}{\sqrt{1 - \frac{2tx_3}{|x|^2} + \frac{t^2}{|x|^2}}} \\ &= \frac{1}{|x|} - \frac{1}{|x|}\int_{-\frac{1}{2}}^{\frac{1}{2}} (1 + \frac{tx_3}{|x|^2} + O(\frac{1}{|x|^2}))dt \\ &= O(\frac{1}{|x|^3}), \end{aligned} \quad (31)$$

so this shows that $\sum_{k\in\mathbf{Z}} f(x+ke_3)$ is normally convergent on any compact subset of $\mathbf{R}^3 \setminus \{r=0\}$. This proves our claim, and that G is smooth on this set, and periodic with periodic cell Γ_0.

We now turn to the proof of (i) : we isolate the interesting terms, and write G as :

$$G(x) = -2\log(r) + \frac{1}{|x|} - \int_{-\frac{1}{2}}^{\frac{1}{2}} \frac{dt}{|x - te_3|} + \sum_{k\in\mathbf{Z}^*} \left(\frac{1}{|x-ke_3|} - \int_{-\frac{1}{2}}^{\frac{1}{2}} \frac{dt}{|x-(t+k)e_3|} \right). \tag{32}$$

Now, we compute, with $x \longrightarrow 0$, $x \neq 0$:

$$\begin{aligned} \int_{-\frac{1}{2}}^{\frac{1}{2}} \frac{dt}{|x-te_3|} &= \mathrm{Argsh}(\frac{\frac{1}{2}-x_3}{r}) + \mathrm{Argsh}(\frac{\frac{1}{2}+x_3}{r}) \\ &= \log\left(\frac{x_3 + \frac{1}{2} + \sqrt{r^2 + (x_3+\frac{1}{2})^2}}{x_3 - \frac{1}{2} + \sqrt{r^2 + (x_3-\frac{1}{2})^2}} \right) \\ &= \log\left(\frac{x_3 + \frac{1}{2} + \sqrt{r^2 + (x_3+\frac{1}{2})^2}}{x_3 - \frac{1}{2} + \frac{1}{2}(1 - 2x_3 + 2|x|^2 - 2x_3^2 + O(|x|^3))} \right), \end{aligned}$$

because

$$\begin{aligned} \sqrt{r^2 + (x_3 - \frac{1}{2})^2} &= \frac{1}{2}\sqrt{1 - 4x_3 + 4|x|^2} \\ &= \frac{1}{2}(1 - 2x_3 + 2|x|^2 - \frac{1}{8}(4x_3)^2) + O(|x|^3). \end{aligned}$$

Hence

$$\begin{aligned} \int_{-\frac{1}{2}}^{\frac{1}{2}} \frac{dt}{|x-te_3|} &= \log\left(\frac{1 + O(|x|)}{r^2 + O(|x|^3)} \right) \\ &= -2\log(r) + O(|x|). \end{aligned}$$

So we may write

$$G(x) = \frac{1}{|x|} + \sum_{k\in\mathbf{Z}^*} \left(\frac{1}{|x-ke_3|} - \int_{-\frac{1}{2}}^{\frac{1}{2}} \frac{dt}{|x-(t+k)e_3|} \right) + O(|x|)$$

as $|x| \longrightarrow 0$.

Now, all the terms of the remaining sum are clearly defined on Γ_0, so using the estimate (31) on f, we conclude that this series defines a smooth function on Γ_0. With the periodicity of G, this shows (o) and (i), with $C = \sum_{k\in\mathbf{Z}^*} \left(\frac{1}{|k|} - \int_{-\frac{1}{2}}^{\frac{1}{2}} \frac{dt}{|k+t|} \right)$.

We now turn to the proof of (ii), which results only in showing that :

$$\sum_{k\in\mathbf{Z}}\left|\frac{1}{|x-ke_3|}-\int_{-\frac{1}{2}}^{\frac{1}{2}}\frac{dt}{|x-(k+t)e_3|}\right|\leq\frac{C}{r} \tag{33}$$

as $r\longrightarrow\infty$, uniformly with respect to x_3.

Using the function f defined above, this expression may be written as : $\sum_{k\in\mathbf{Z}}f(x-ke_3)$. So, as we know that

$$|f(x)|\leq\frac{C}{|x|^3},$$

we have :

$$|\sum_{k\in\mathbf{Z}}f(x-ke_3)|\leq\sum_{k\in\mathbf{Z}}\frac{1}{r^3+|k|^3},$$

for r sufficiently large. Now, we have

$$\sum_{k\in\mathbf{Z}}\frac{1}{r^3+|k|^3}\leq\frac{1}{r^3}+\sum_{k\in\mathbf{Z}^*}\frac{1}{r^{3/2}|k|^{3/2}}\leq\frac{C}{r^{3/2}}.$$

This proves (33). $\Diamond$

Now that we know the behaviour of G, we turn to a positiveness property for D_G. We recall that :

$$D_G(f,g)=\int_{\Gamma_0}\int_{\Gamma_0}f(x)g(y)G(x-y)dxdy. \tag{34}$$

Since D_G appears in the expression of the energy and is a bilinear form, its positiveness (in the sense of bilinear forms) will ensure its convexity, hence the convexity of the energy.

In the following Proposition, we assume that $\mathrm{Supp}(m)\subset\{r<1\}$, since this may be done without loss of generality

Proposition 2.10 *The bilinear form D_G is positive on the set $Y_{per}=\{f\in L^1_{per}(\Gamma_0)/$ $\sqrt{|f|}\in H^1_{per}(\Gamma_0\cap\{r>1\})$, $\int_{\Gamma_0}f=0$ and $\log(2+|x|)f\in L^1(\Gamma_0)\}$.*

Where the space $H^1_{per}(\Gamma_0\cap\{r>1\})$ is defined as the set of functions lying in $H^1_{loc}(\{r>1\})\cap H^1(\Gamma_0\cap\{r>1\})$ that are periodic with respect to x_3, of period 1.

Proof :

We define on $\mathcal{S}_{per}(\Gamma_0)$, that is, the set of functions that are C^∞ on $\mathbf{R}^3$, periodic with periodic cell Γ_0, and decaying faster than any power of r as $r\to\infty$, the Fourier transform $f\longmapsto\widehat{f}$ as :

$$\widehat{f}(\xi,n)=\int_{\Gamma_0}f(x)e^{-i2\pi(x'\cdot\xi+x_3n)}dx, \tag{35}$$

where $x = (x', x_3)$, $x', \xi \in \mathbf{R}^2$, and $n \in \mathbf{Z}$. It is easy to check out that this Fourier transform has the isometry-property of the classical Fourier transform, that is :

$$\int_{\Gamma_0} f(x)\overline{g(x)}dx = \sum_{n\in\mathbf{Z}} \int_{\mathbf{R}^2} \widehat{f}(\xi, n)\overline{\widehat{g}(\xi, n)}d\xi. \tag{36}$$

Hence it may be prolonged to $\mathcal{S}'_{per}(\Gamma_0)$. We also have :

$$\forall f \in \mathcal{S}'_{per}(\Gamma_0),\ \widehat{\partial_j f}(\xi, n) = i2\pi\xi_j \widehat{f}(\xi, n), \quad j = 1, 2.$$

And

$$\forall f \in \mathcal{S}'_{per}(\Gamma_0) \text{ and } g \in \mathcal{S}_{per}(\Gamma_0),\ \widehat{f \star_{\Gamma_0} g} = \widehat{f}\widehat{g}.$$

So, since we know that $-\Delta G = 4\pi\delta_0$ on Γ_0, we deduce :

$$4\pi^2(|\xi|^2 + n^2)\widehat{G}(\xi, n) = 4\pi.$$

Hence when $n \neq 0$, $\widehat{G}(\xi, n) = \frac{1}{\pi(|\xi|^2+n^2)}$. Now for $n = 0$, $\widehat{G}$ becomes the classical Fourier transform of $\log|x'|$ on $\mathbf{R}^2$. Indeed, we have, putting $G_0(x) = G(x) + 2\log(r)$,

$$\int_{-\frac{1}{2}}^{\frac{1}{2}} G_0(x)dx_3 = 0. \tag{37}$$

Because computing $-\Delta\int_{-\frac{1}{2}}^{\frac{1}{2}} G_0(x)dx_3$, with $x \in \Gamma_0$, one finds :

$$\begin{aligned} -\Delta\int_{-\frac{1}{2}}^{\frac{1}{2}} G_0(x)dx_3 &= \int_{-\frac{1}{2}}^{\frac{1}{2}} -\Delta(G_0(x))dx_3 \\ &= 4\pi\int_{-\frac{1}{2}}^{\frac{1}{2}} \big(\delta_0 - \delta_{r=0}\big)dx_3 \\ &= 4\pi(\delta_{r=0} - \delta_{r=0}) = 0. \end{aligned}$$

So the left-hand side of (37) is the expression of a harmonic function, which lies in L^∞ because of Lemma 2.9, hence is a constant. But, still because of Lemma 2.9, G_0 goes to 0 as r goes to infinity, so (37) holds.

The classical Fourier transform of $\log|x|$ on $\mathbf{R}^2$ is equal to $\mathrm{vp}(\frac{1}{|x|^2}) + a\delta_0$, with $a > 0$, and where $\mathrm{vp}(\frac{1}{|x|^2})$ is defined as follows (see [13]) :

$$< \mathrm{vp}(\frac{1}{|x|^2}), \varphi >= \lim_{\varepsilon\to 0^+}\left(\int_{|x|>\varepsilon} \frac{\varphi(x)}{|x|^2}dx + \frac{\log\varepsilon}{\varepsilon}\int_{|x|=\varepsilon}\varphi\right). \tag{38}$$

(In fact, $\mathrm{vp}(\frac{1}{|x|^2}) = \mathrm{div}(\frac{\log|x|}{|x|^2}x)$ in $\mathcal{D}'(\mathbf{R}^2)$.)

So we have :

$$\widehat{G}(\xi, 0) = \mathrm{vp}(\frac{1}{|\xi|^2}) + a\delta_0.$$

Now, we compute, for all $f \in Y_{per}$:

$$\begin{aligned} D_G(f,f) &= \int_{\Gamma_0} (G \star_{\Gamma_0} f) f \\ &= \sum_{n\in\mathbf{Z}} \int_{\mathbf{R}^2} \widehat{G \star_{\Gamma_0} f}(\xi,n)\widehat{f}(\xi,n)d\xi \\ &= \sum_{n\in\mathbf{Z}^*} \int_{\mathbf{R}^2} \frac{(\widehat{f}(\xi,n))^2}{4\pi^2(|\xi|^2+n^2)}d\xi + < \mathrm{vp}(\frac{1}{|\xi|^2}), (\widehat{f}(\xi,0))^2 >, \end{aligned}$$

since $\widehat{f}(0) = \int_{\Gamma_0} f = 0$. So we only need to show that $\forall f \in Y_{per}$, $< \mathrm{vp}(\frac{1}{|\xi|^2}), (\widehat{f}(\xi,0))^2 > \geq 0$.

From the fact that $f \in Y_{per}$, we have :

$$\begin{aligned} |\widehat{f}(\xi,0)| &= \left| \int_{\Gamma_0} (e^{-2i\pi x'\xi} - 1) f(x) dx \right| \\ &\leq \int_{\Gamma_0 \cap \{r > \frac{1}{\sqrt{|\xi|}}\}} |e^{-2i\pi x'\xi} - 1||f(x)|dx + \int_{\Gamma_0 \cap \{r < \frac{1}{\sqrt{|\xi|}}\}} |e^{-2i\pi x'\xi} - 1||f(x)|dx \\ &\leq \frac{2}{\log(2 + \frac{1}{\sqrt{|\xi|}})} \int_{\Gamma_0 \cap \{r > \frac{1}{\sqrt{|\xi|}}\}} \log(2+r)|f(x)|dx \\ &\quad + \int_{\Gamma_0 \cap \{r < \frac{1}{\sqrt{|\xi|}}\}} |x'||\xi||f(x)|dx. \end{aligned}$$

Hence :

$$\begin{aligned} |\widehat{f}(\xi,0)| &\leq \frac{4}{|\log|\xi||} \int_{\Gamma_0} \log(2+|x|)|f(x)|dx + \sqrt{|\xi|} \int_{\Gamma_0} |f(x)|dx \\ &\leq \frac{C}{|\log|\xi||} \end{aligned} \tag{39}$$

as $|\xi| \longrightarrow 0$.

Hence, (39) implies that $\frac{\widehat{f}(\xi,0)}{|\xi|} \in L^2_{loc}(\Gamma_0)$, and that $\frac{\log\varepsilon}{\varepsilon} \int_{|\xi|=\varepsilon} \widehat{f}(\xi,0)^2$ vanishes as $\varepsilon \to 0$. Since $\widehat{f}(\cdot,0) \in L^2(\mathbf{R}^2)$, we conclude from (38) that we have :

$$< \mathrm{vp}(\frac{1}{|\xi|^2}), (\widehat{f}(\xi,0))^2 > = \int_{\Gamma_0} \frac{\widehat{f}(\xi,0)^2}{|\xi|^2} d\xi \geq 0.$$

This concludes the proof. $\Diamond$

Remark 2.11 *Let us point out that the important property of f is that its integral vanishes. For example, if $f = \delta_{ke_1} + \delta_{-ke_1}$ on Γ_0, f being periodic with periodic cell Γ_0, one may compute that, for $k > 0$ large enough, we have $D_G(f,f) \sim -\log k < 0$. And we may even convolute f with a regularizing kernel, so as to get a C^∞ function g, having compact support, and such that $D_G(g,g) < 0$.*

We now turn to our main result : the uniqueness of the solution of the system (27), which will be stated more precisely in Theorem 2.16 below. We consider a positive measure μ with compact support, periodic with periodic cell Γ_0, such that $\mu \not\equiv 0$, and the system :

$$\begin{cases} -\Delta u + \frac{5}{3}u^{7/3} - u\phi = 0, \\ -\Delta \phi = 4\pi(\mu - u^2), \\ u \geq 0, \end{cases} \tag{40}$$

and intend to prove a uniqueness result for this system.

We write

$$\mu = \sum_{k \in \mathbf{Z}} m(\cdot - ke_3),$$

with m having its support in Γ_0. With no loss of generality, we may assume that $\mathrm{Supp} m \subset \{r < 1\}$, and that $m(\Gamma_0) = 1$. We first need some a priori estimates on the solution of the system. It is the aim of the following section.

2.2.2 A priori bounds

Proposition 2.12 *Let (u, ϕ) be a solution of (40), with $u \in L^\infty(\mathbf{R}^3)$ and $\phi \in L^1_{unif}(\mathbf{R}^3)$. Then for any $R > 0$, there exists a constant $\nu > 0$ such that $\inf_{r<R} u \geq \nu$.*

Proof : First of all, we remark that, by elliptic regularity, the fact that $\phi \in L^1_{unif}$ implies that $u \in W^{2,1}_{unif}$, hence belongs to $H^1_{unif}(\mathbf{R}^3)$. So $\phi \in H^3_{unif}(\{r > 1\}) \subset L^\infty(\{r > 1\})$, and u lies in $L^\infty \cap C^{0,\alpha}(\{r > 1\})$ for some $\alpha > 0$. Moreover, the fact that $\phi \in L^1_{unif}(\mathbf{R}^3)$ and $\Delta\phi$ is a uniformly locally bounded measure, we deduce that $\phi \in L^p(\mathbf{R}^3)$, for all $p < 3$.

We argue by contradiction, and suppose that the above property is false, i.e that there exists $R > 0$ such that :

$$\inf_{r<R} u = 0. \tag{41}$$

This means in particular that there exists a sequence $(x_n)_{n\geq 0}$ such that $r(x_n) \leq R$ and $u(x_n) \longrightarrow 0$ as $n \to \infty$. So, denoting by u_n and ϕ_n the functions $u(\cdot + x_n)$ and $\phi(\cdot + x_n)$ respectively, we have that

$$u_n(0) \longrightarrow 0 \text{ as } n \to \infty. \tag{42}$$

Now, we may write $x_n = k_n + x_n^0$, with $k_n \in \mathbf{Z}e_3$ and $x_n^0 \in \Gamma_0$. Since $r(x_n) = r(x_n^0) \leq R$, we may extract a subsequence so as to have $x_n^0 \longrightarrow x^0$, for some $x^0 \in \overline{\Gamma}_0$, satisfying $r(x^0) \leq R$.

But from (40), (42) and Harnack's inequality (see for instance [9]), we deduce that $u_n \longrightarrow 0$ uniformly on any compact subset of $\mathbf{R}^3$. Considering the bounds on u and ϕ,

we may pass locally to the limit, up to a subsequence, in (40). We then get $\overline{\phi} \in L^1_{unif}$ a solution to :

$$-\Delta\overline{\phi} = 4\pi\mu(\cdot + x^0). \tag{43}$$

Hence, denoting by ψ the function $\overline{\phi}(\cdot - x^0)$, we have $\psi \in L^1_{unif}$, satisfying :

$$-\Delta\psi = 4\pi\mu. \tag{44}$$

With no loss of generality, we may assume that $r(x^0) = 0$, so that $-\Delta\psi$ has its support in $\{r < 1\}$.

We are now going to use a scaling argument to show that the fact that ψ is a solution to (44) is in contradiction with its belonging to L^1_{unif}. The first thing is that ψ is harmonic on the set $\{r > 1\}$, hence continuous on this set, and thus belongs to $L^\infty(\{r > 1\})$.

Let $\xi_0 \in C^\infty(\mathbf{R})$, such that $\xi_0 = 1$ on $[-1, 1]$, $\xi_0 = 0$ on $[-2, 2]^c$, and $|\xi_0''| \leq 4$. Let $\alpha \in]0, 1[$ and $\eta_R : \mathbf{R}^2 \longrightarrow \mathbf{R}$ be the solution of $-\Delta\eta = 0$ on $\{1 < |x| < R^\alpha\}$ with boundary conditions $\eta = 1$ on $\{1 = |x|\}$, $\eta = 0$ on $\{|x| = R^\alpha\}$. Namely, we have

$$\eta_R(x) = 1 - \frac{\log|x|}{\alpha \log R}$$

on the set $\{1 < |x| < R^\alpha\}$. We prolong it by 1 on $\{1 > |x|\}$, 0 on $\{|x| > R^\alpha\}$. We set $\xi_R(x) = \eta_R(x')\xi_0(\frac{x_3}{R})$, for all $x \in \mathbf{R}^3$.

And we compute :

$$\begin{aligned}
< -\Delta\psi, \xi_R > &= 4\pi < \mu, \xi_R > \\
&= \sum_{k\in\mathbf{Z}} < m(\cdot + ke_3), \xi_R > \\
&= \sum_{k\in\mathbf{Z}, |k|\leq 2R} \int_{\Gamma_0} \xi_0(\frac{x_3 - k}{R}) m(x) dx \\
&\geq \sum_{k\in\mathbf{Z}, |k|\leq R} \int_{\Gamma_0} m.
\end{aligned}$$

So we conclude that :

$$< -\Delta\psi, \xi_R > \geq 2R. \tag{45}$$

On the other hand, we have, denoting by Ω_R the set $\{r < R^\alpha, |x_3| < 2R\}$ and by ω_R the set $\{r < 1, |x_3| < R\}$,

$$\begin{aligned}
\int_{\mathbf{R}^3} -\Delta\psi\xi_R &= \int_{\Omega_R} -\Delta\psi\xi_R \\
&= \int_{\Omega_R\setminus\omega_R} \nabla\psi\nabla\xi_R \\
&= -\int_{\Omega_R\setminus\omega_R} \psi\Delta\xi_R - \int_{r=R^\alpha, |x_3|<2R} \psi\frac{\partial\xi_R}{\partial r} + \int_{r=1, |x_3|<2R} \psi\frac{\partial\xi_R}{\partial r}.
\end{aligned}$$

We know that $\Delta\xi_R = \frac{1}{R^2}\eta_R(r)\xi_0''(\frac{x_3}{R})$ on the set $\Omega_R \setminus \omega_R$, so we have :

$$\begin{aligned}\left|\int_{\Omega_R\setminus\omega_R}\psi\Delta\xi_R\right| &= \frac{1}{R^2}\left|\int_{\Omega_R\setminus\omega_R}\psi\eta_R(r)\xi_0''(\frac{x_3}{R})\right| \\ &\leq \frac{4}{R^2}\left|\int_{\Omega_R}\psi\right| \\ &\leq \frac{C}{R^2}|\Omega_R| = CR^{2\alpha-1} \ll R,\end{aligned}$$

because $\psi \in L^1_{unif}$ and $\alpha < 1$.

Next, we compute that

$$\frac{\partial\xi_R}{\partial r} = -\frac{\xi_0(\frac{x_3}{R})}{\alpha r \log R},$$

so we also have, using the fact that ψ belongs to $L^\infty(\{r > 1\})$ and is smooth on this set :

$$\left|\int_{r=R^\alpha,|x_3|<2R}\psi\frac{\partial\xi_R}{\partial r}\right| \leq \frac{CR^{\alpha+1}}{\alpha R^\alpha \log R} = \frac{CR}{\log R} \ll R. \tag{46}$$

And :

$$\left|\int_{r=1,|x_3|<2R}\psi\frac{\partial\xi_R}{\partial r}\right| \leq \frac{CR}{\log R} \ll R. \tag{47}$$

So we conclude that

$$\left|< -\Delta\psi, \xi_R >\right| \ll R,$$

reaching a contradiction with (45). This concludes the proof. ◊

We now have a lower bound on u, and intend to get upper bounds :

Proposition 2.13 *Let (u, ϕ) be a solution of (40), satisfying $u \in L^\infty$ and $\phi \in L^1_{unif}$. Then we have :*

(i) $\phi \leq \frac{C}{1+r^2}$ $\forall r > 1$; *and*

(ii) $u \leq \frac{C}{1+r^{3/2}}$.

Proof : The proof follows exactly the same pattern as that of Theorem 2.5. Indeed, this proof only uses the fact that the measure m_Λ has its support in $\{r < 1\}$ and that the functions u_Λ, ϕ_Λ are solutions of the system (16)-(17). So the whole proof carries through to this case. ◊

2.2.3 Periodicity of the solutions

We are now going to show that the solutions of the system (40) are necessarily periodic.
For this purpose, we denote, for any function f defined on $\mathbf{R}^3$,

$$\tau f(x) = f(x + e_3). \tag{48}$$

We then have, if (u, ϕ) is a solution to (40),

$$-\Delta(\tau\phi - \phi) = 4\pi(u^2 - \tau u^2). \tag{49}$$

Hence, from elliptic regularity, $(\tau\phi - \phi) \in C^0 \cap L^\infty(\mathbf{R}^3)$.

Proposition 2.14 *Let $(u, \phi) \in L^\infty(\mathbf{R}^3) \times L^1_{unif}(\mathbf{R}^3)$ be a solution of (40). Then*

$$\tau\phi - \phi = u^2 \star (\frac{1}{|x|} - \tau\frac{1}{|x|}).$$

And

$$|\tau\phi - \phi| \leq \frac{C}{1+r} \ ,$$

for some constant C independent of x_3.

Proof : The first thing is to check out if this convolution product exists : Since we have

$$u^2 \leq \frac{C}{1+r^3}$$

and

$$\begin{aligned} |\frac{1}{|x|} - \tau\frac{1}{|x|}| &\leq \frac{|2x_3+1|}{|x||x+e_3|(|x|+|x+e_3|)} \\ &\leq \frac{1}{|x|(|x|+|x+e_3|)} + \frac{1}{|x+e_3|(|x|+|x+e_3|)}, \end{aligned}$$

this is easy to check. Moreover, we have :

$$\begin{aligned} \left|u^2 \star (\tau\frac{1}{|x|} - \frac{1}{|x|})\right| &\leq \int_{\mathbf{R}^3} \frac{1}{1+r(y)^3} \frac{dy}{|x-y+e_3|(|x-y|+|x-y+e_3|)} \\ &\quad + \int_{\mathbf{R}^3} \frac{1}{1+r(y)^3} \frac{dy}{|x-y|(|x-y|+|x-y+e_3|)} \\ &\leq 2\int_{\mathbf{R}^3} \frac{1}{1+r(y)^3} \frac{dy}{|x-y|(|x-y|+|x-y+e_3|)}. \end{aligned}$$

We split this integral into two others, and write, with $r(x) > 2$:

$$\begin{aligned} &\int_{\mathbf{R}^3} \frac{1}{1+r(y)^3} \frac{dy}{|x-y|(|x-y|+|x-y+e_3|)} \\ &\quad = \int_{|x-y|<2} \frac{1}{1+r(y)^3} \frac{dy}{|x-y|(|x-y|+|x-y+e_3|)} \\ &\qquad + \int_{|x-y|>2} \frac{1}{1+r(y)^3} \frac{dy}{|x-y|(|x-y|+|x-y+e_3|)}. \end{aligned}$$

So that we have, denoting by $A(x)$ and $B(x)$ respectively the terms of this sum,

$$A(x) \leq \frac{C}{1+r(x)^3}, \tag{50}$$

because

$$\int_{|x-y|<2} \frac{dy}{|x-y||x-y+e_3|} = \int_{|y|<2} \frac{dy}{|y||y+e_3|} \leq C,$$

and because the fact that $|x-y|<2$ together with $r(x)>2$ imply that $\frac{1}{1+r(y)^3} \leq \frac{C}{1+r(x)^3}$, where C does not depend on x.

Concerning B, we have, for an $R < r(x) = |x'|$ that will be chosen later on :

$$\begin{aligned}
B(x) &\leq \int_{\mathbf{R}^3} \frac{C}{1+r(y)^3} \frac{dy}{1+|x-y|^2} \\
&\leq \int_{\mathbf{R}^2} \frac{C}{1+|y'|^3} \left(\int_{\mathbf{R}} \frac{dy_3}{1+|x'-y'|^2+|x_3-y_3|^2} \right) dy' \\
&\leq \int_{\mathbf{R}^2} \frac{1}{1+|y'|^3} \frac{C}{|x'-y'|} dy' = \int_{\mathbf{R}^2} \frac{C}{(1+|x'-y'|^3)} \frac{dy'}{|y'|} \\
&\leq \int_{|y'|<R} \frac{C}{(1+|x'-y'|^3)} \frac{dy'}{|y'|} + \int_{|y'|>R} \frac{C}{(1+|x'-y'|^3)} \frac{dy'}{|y'|} \\
&\leq \int_{|y'|<R} \frac{dy'}{|y'|} \frac{1}{1+(|x'|-R)^3} + \frac{1}{R} \int_{|y'|>R} \frac{dy'}{1+|x'-y'|^3} \\
&\leq \frac{CR}{1+(|x'|-R)^3} + \frac{C}{R},
\end{aligned}$$

where C is a constant independent of x. Finally, we choose $R = \frac{|x'|}{2}$, so as to have :

$$B(x) \leq \frac{C}{r(x)}. \tag{51}$$

Now, collecting (50) and (51), we get :

$$\left| u^2 \star (\tau \frac{1}{|x|} - \frac{1}{|x|}) \right| \leq \frac{C}{r}. \tag{52}$$

Finally, since $u^2 \star (\tau \frac{1}{|x|} - \frac{1}{|x|})$ is continuous, (52) implies :

$$\left| u^2 \star (\tau \frac{1}{|x|} - \frac{1}{|x|}) \right| \leq \frac{C}{1+r}. \tag{53}$$

So there only remains to prove that this expression is indeed equal to $\tau\phi - \phi$. In order to do so, we compute its Laplacian, and find :

$$-\Delta(u^2 \star (\tau \frac{1}{|x|} - \frac{1}{|x|})) = u^2 \star (-\Delta(\tau \frac{1}{|x|} - \frac{1}{|x|})) = u^2 \star (\delta_{e_3} - \delta_0) = \tau u^2 - u^2.$$

So the function $\tau\phi - \phi - u^2 \star (\tau\frac{1}{|x|} - \frac{1}{|x|})$ is harmonic. But since, from (53), it lies in $L^\infty(\mathbf{R}^3)$, it must be a constant. Hence

$$\tau\phi - \phi = u^2 \star (\tau\frac{1}{|x|} - \frac{1}{|x|}) + a. \tag{54}$$

Now, considering (53), we know that for some R large enough,

$$|u^2 \star (\tau\frac{1}{|x|} - \frac{1}{|x|})| < \frac{|a|}{2}$$

on the set $\{r > R\}$. So we have

$$a - \frac{|a|}{2} \leq \tau\phi - \phi \leq a + \frac{|a|}{2}$$

on this set, which implies that, for all $n \in \mathbf{N}$, we have :

$$|\tau^n\phi - \phi| \geq n\frac{|a|}{2}$$

on $\{r > R\}$. So

$$2\|\phi\|_{L^1_{unif}} \geq \int_{B_1+2Re_1} |\tau^n\phi - \phi| \geq n\frac{|a|}{2}|B_1|.$$

This is valid for all $n \in \mathbf{N}$, so we reach a contradiction with the fact that $\phi \in L^1_{unif}$, unless $a = 0$. This concludes the proof. $\Diamond$

Next we turn to a uniqueness result that will ensure the periodicity of u, hence of ϕ.

Lemma 2.15 *Let (u, ϕ) and (v, ψ) be two solutions of system (40), both lying in $L^\infty \times L^1_{unif}$, such that $|\phi - \psi| \leq \frac{C}{1+r}$ for some constant C. Then $u = v$ and $\phi = \psi$.*

Proof : The proof follows exactly the same pattern as the uniqueness Theorem of [6], Section 5.3 : we are going to collect all the former results, and then use a scaling argument on u and ϕ.

First of all, we know from Proposition 2.12 that there exists a positive function η, independent of x_3, such that :

$$u, v \geq \eta. \tag{55}$$

Next, denoting by w the function $u - v$, we get, substracting the two systems :

$$-\Delta w + u^{7/3} - v^{7/3} - (\phi u - \psi v) = 0. \tag{56}$$

and :

$$-\Delta(\phi - \psi) = v^2 - u^2. \tag{57}$$

Hence, for any $\xi \in \mathcal{D}(\mathbf{R}^3)$, we have :

$$\int_{\mathbf{R}^3} \nabla w \nabla(w\xi^2) + \int_{\mathbf{R}^3} (u^{7/3} - v^{7/3}) w\xi^2 - \int_{\mathbf{R}^3} (\phi u - \psi v) w\xi^2 = 0. \tag{58}$$

The first term of this sum may be rewritten as :

$$\int_{\mathbf{R}^3} \nabla w \nabla(w\xi^2) = \int_{\mathbf{R}^3} |\nabla(w\xi)|^2 - \int_{\mathbf{R}^3} w^2 |\nabla \xi|^2. \tag{59}$$

Now, from (55), we deduce that there exists a positive function $\nu(r)$ such that :

$$(u^{7/3} - v^{7/3})(u - v) \geq \frac{1}{2}(u^{4/3} + v^{4/3})(u - v)^2 + \nu(u - v)^2.$$

That is,

$$(u^{7/3} - v^{7/3}) w \geq \frac{1}{2}(u^{4/3} + v^{4/3}) w^2 + \nu w^2. \tag{60}$$

On the other hand, we write :

$$\phi u - \psi v = \frac{1}{2}(\phi + \psi) w + \frac{1}{2}(\phi - \psi)(u + v). \tag{61}$$

We denote by L the operator $-\Delta + \frac{1}{2}(u^{4/3} + v^{4/3}) - \frac{1}{2}(\phi + \psi)$, and deduce from (58), (60) and (61) that :

$$< L(w\xi), w\xi > + \int_{\mathbf{R}^3} \nu w^2 \xi^2 \leq \frac{1}{2} \int_{\mathbf{R}^3} (\phi - \psi)(u^2 - v^2)\xi^2 + \int_{\mathbf{R}^3} w^2 |\nabla \xi|^2. \tag{62}$$

We claim that the operator L (with homogeneous Dirichlet boundary conditions on a bounded set) is positive. Indeed, we may write it as

$$L = \frac{1}{2}\big((-\Delta + u^{4/3} - \phi) + (-\Delta + v^{7/3} - \psi)\big) = \frac{1}{2}(L_1 + L_2),$$

and the only thing to prove is that L_1 and L_2 are positive. This comes from the first equation of (40) : denoting by λ_1 the first eigenvalue of L_1 on Ω, and by f_1 the associated eigenvector, satisfying $f_1 > 0$ on Ω, we have :

$$\int_\Omega -\Delta f_1 u + \int_\Omega u^{4/3} f_1 u - \int_\Omega \phi f_1 u = \int_\Omega \lambda_1 f_1 u.$$

Integrating by parts and using the first equation of (40), we find :

$$-\int_{\partial\Omega} u \frac{\partial f_1}{\partial n} + \int_{\partial\Omega} f_1 \frac{\partial u}{\partial n} = \lambda_1 \int_\Omega f_1 u.$$

Since the second term of the left-hand side is 0, and because of Hopf's Lemma, which shows that $\frac{\partial f_1}{\partial n} < 0$ on $\partial\Omega$, we infer that $\lambda_1 > 0$, hence that L_1 is positive. L_2 may be dealt with exactly in the same way, so our claim is proved.

So the equation (62) implies :

$$\int_{\mathbf{R}^3} \nu w^2 \xi^2 \leq \frac{1}{2} \int_{\mathbf{R}^3} (\phi - \psi)(u^2 - v^2)\xi^2 + \int_{\mathbf{R}^3} w^2 |\nabla \xi|^2. \tag{63}$$

We now go back to (57), and use it to rewrite the first term of (63)'s right-hand side as :

$$\frac{1}{2} \int_{\mathbf{R}^3} (\phi - \psi)\Delta(\phi - \psi)\xi^2 = -\frac{1}{2} \int_{\mathbf{R}^3} |\nabla(\phi - \psi)\xi|^2 + \frac{1}{2} \int_{\mathbf{R}^3} (\phi - \psi)^2 |\nabla \xi|^2.$$

So the inequality (63) becomes :

$$\int_{\mathbf{R}^3} \nu w^2 \xi^2 + \int_{\mathbf{R}^3} |\nabla((\phi - \psi)\xi)|^2 \leq \int_{\mathbf{R}^3} w^2 |\nabla \xi|^2 + \frac{1}{2} \int_{\mathbf{R}^3} (\phi - \psi)^2 |\nabla \xi|^2. \tag{64}$$

Since this holds for any $\xi \in \mathcal{D}(\mathbf{R}^3)$, we may apply it to a sequence ξ_n converging to

$$\xi(x) = \frac{1}{(1 + x_3^2)^{\alpha/2}(1 + r^2)^{\beta/2}}.$$

With $\alpha > \frac{1}{2}$, $\beta > 0$ and $\alpha + \beta < 1$. We then get (64) for this choice of ξ. Now, for this function ξ, it is clear, from the hypotheses on α and β, and from Proposition 2.13, (ii) that we have $\int_{\mathbf{R}^3} w^2 \xi^2 < \infty$ and $\int_{\mathbf{R}^3} (\phi - \psi)^2 \xi^2 < \infty$.

We are now going to use a scaling argument on the inequality (64). We define ξ_ε as :

$$\xi_\varepsilon(x) = \xi(\varepsilon x). \tag{65}$$

We then compute :

$$\begin{aligned}
|\nabla \xi_\varepsilon|^2 &= \left| \beta \frac{\varepsilon^2 x'}{(1 + \varepsilon^2 r^2)^{(\frac{\beta}{2}+1)}(1 + x_3^2)^{\frac{\alpha}{2}}} \right|^2 + \left| \alpha \frac{\varepsilon^2 x_3}{(1 + \varepsilon^2 r^2)^{\frac{\beta}{2}}(1 + \varepsilon^2 x_3^2)^{(\frac{\alpha}{2}+1)}} \right|^2 \\
&= \beta^2 \frac{\varepsilon^4 r^2}{(1 + \varepsilon^2 r^2)^{(\beta+2)}(1 + x_3^2)^{\alpha}} + \alpha^2 \frac{\varepsilon^4 x_3^2}{(1 + \varepsilon^2 r^2)^{\beta}(1 + \varepsilon^2 x_3^2)^{(\alpha+2)}} \\
&\leq \beta^2 \frac{\varepsilon^2}{(1 + \varepsilon^2 r^2)^{\beta}(1 + \varepsilon^2 x_3^2)^{\alpha}} + \alpha^2 \frac{\varepsilon^2}{(1 + \varepsilon^2 r^2)^{\beta}(1 + \varepsilon^2 x_3^2)^{\alpha}} \\
&\leq \frac{C\varepsilon^{2-2\alpha-2\beta}}{(1 + x_3^2)^{\alpha}(1 + r^2)^{\beta}} = C\varepsilon^{2-2\alpha-2\beta} \xi^2.
\end{aligned} \tag{66}$$

Now we consider inequality (64) together with (66), and find :

$$\int_{\mathbf{R}^3} \nu w^2 \xi_\varepsilon^2 \leq C\varepsilon^{2-2\alpha-2\beta}.$$

Fixing $R > 0$, we also have :

$$\int_{\mathbf{R}^3} \nu w^2 \xi_\varepsilon^2 \geq \frac{\inf_{B_R} \nu}{1 + \varepsilon^2 R^2} \int_{B_R} w^2 \geq \inf_{B_R} \nu \int_{B_R} w^2.$$

Letting ε go to 0, and using the fact that $\alpha + \beta < 1$, we deduce that

$$\int_{B_R} w^2 = 0,$$

hence $w = 0$. Now, since $u, v > 0$, we also conclude, from the first equation of (40), that $\phi = \psi$. $\Diamond$

This Lemma, together with Proposition 2.12, Proposition 2.13 and proposition 2.14, allows us to assert that any solution of (40) is periodic, with periodic cell Γ_0. Now, we are going to complete the proof of our uniqueness theorem.

2.2.4 Uniqueness for the system

We intend to prove the following theorem :

Theorem 2.16 *Let μ be a periodic positive measure, with periodic cell $\Gamma_0 = \mathbf{R}^2 \times]-\frac{1}{2}, \frac{1}{2}]$ such that :*

(a) $\operatorname{Supp} \mu \subset \{r < 1\}$.

(b) $\mu(\Gamma_0) = 1$.

Then the system (40), that is :

$$\begin{cases} -\Delta u + \frac{5}{3} u^{7/3} - u\phi = 0, \\ -\Delta \phi = 4\pi(\mu - u^2), \\ u \geq 0. \end{cases} \tag{67}$$

has a unique solution (u, ϕ) in $\left(L^2_{unif} \cap L^{7/3}_{loc}(\mathbf{R}^3)\right) \times L^1_{unif}(\mathbf{R}^3)$. Moreover, this solution is periodic with respect to x_3, of period 1, and we have :

(i) *$u \in L^\infty(\mathbf{R}^3)$, and there exists a constant $C > 0$ and a positive function ν depending only on r, such that $0 < \nu \leq u \leq \frac{C}{1+r^{3/2}}$; and*

(ii) *there exists a constant θ such that $\phi = G \star_{\Gamma_0} (\mu - u^2) + \theta$; and*

(iii) $\int_{\Gamma_0} u^2 = 1$.

Remark 2.17 *Of course, in properties (a)-(b), the number 1 may be replaced by any positive real. That is, those assumptions could be replaced by :*

(a') *μ has compact support with respect to (x_1, x_2).*

(b') $\mu \neq 0$.

And in this case, the conclusion (iii) would become :

(iii') $\int_{\Gamma_0} u^2 = \mu(\Gamma_0)$.

Remark 2.18 *In the three-dimensional case, that is if Λ is a Van Hove sequence of $\mathbf{Z}^3$, this uniqueness result holds provided μ satisfies weaker condition of the kind $(H_1)-(H_2)$ of Theorem 4.1. Here we are not able to adapt our proof to those kind of μ's. The periodicity is a necessary condition of our proof. However, in the Yukawa case, such a result holds (see Section 4).*

Proof : We give here two technical results that we will need in the course of the proof, their proof being postponed until the end of the present one :

Lemma 2.19 *Let $\psi \in L^2_{unif}(\mathbf{R}^2) \cap H^{3/2}_{loc}(B^c_{R_0})$ for some $R_0 > 0$, and denote by ψ_R the function $\psi - \frac{1}{2\pi R}\int_{|x|=R}\psi$. Assume that $(-\Delta\psi)\psi_R$ is bounded in $L^1(B^c_{R_0})$ independently of R. Then $\nabla\psi \in L^2(B^c_{R_0})$.*

Lemma 2.20 *Let $v \in Z_{per} = \{g \in \mathcal{S}'(\Gamma_0),\ \int_{\Gamma_0}\log(2+|x|)|g| < \infty,\ \int_{\Gamma_0} g = 0\}$, such that $v \in L^1_{loc}(\Gamma_0 \cap \{r > 1\})$ and $|v| \leq \frac{C}{1+r^3}$ on $\{r > 1\}$. Then $G \star_{\Gamma_0} v \in L^1_{unif}(\Gamma_0)$.*

The proof of the existence is a straight-forward adaptation of the thermodynamic limit process, using the measure m instead of a smooth function or δ_0. One checks easily that the point nuclei case proofs generalizes to any bounded measure with compact support. And the associated variational problem I_Λ has been studied in [10].

We refer the reader to [6], Section 5.3.2 for the belonging of u to L^∞. The proof also gives the information that $\phi \in L^p_{unif}(\mathbf{R}^3) \cap L^\infty(\{r > 1\})$, for all $1 \leq p < 3$. This comes from elliptic regularity results.

Now, we know that whenever $u \in L^\infty(\mathbf{R}^3)$ and $\phi \in L^1_{unif}(\mathbf{R}^3)$ satisfy (40), Lemma 2.15 and Propositions 2.12, 2.13 and 2.14 show that u and ϕ are periodic, with periodic cell Γ_0, and that (i) holds.

Now that the periodicity of u and ϕ is ensured, we introduce the variational problem (28), that is :

$$I_{per} = \inf\{E_{per}(\rho),\ \sqrt{\rho} \in X_{per},\ \int_{\Gamma_0}\rho = 1\}.$$

Where E_{per} is defined by (30), i.e

$$\begin{aligned} E_{per}(\rho) = \ & \int_{\Gamma_0}|\nabla\sqrt{\rho}|^2 \ + \int_{\Gamma_0}\rho^{5/3} - \int_{\Gamma_0}(G\star_{\Gamma_0}\mu)\rho \\ & + \qquad \frac{1}{2}\int_{\Gamma_0}\int_{\Gamma_0}\rho(x)\rho(y)G(x-y)dxdy. \end{aligned}$$

Here G is the periodic potential defined in (7), and X_{per} is the functional space :

$$X_{per} = \{v \in H^1_{per}(\Gamma_0),\ \big(\log(2+|x|)\big)^{1/2}v \in L^2(\Gamma_0)\}.$$

The first observation is that $u \in X_{per}$. Indeed, we already know from (i),the second equation of (40) and the fact that $\phi \in L^1_{unif}$, that :

$$\|-\Delta u\|_{L^p(B_1+x)} = \|-u^{7/3}+\phi u\|_{L^p(B_1+x)} \leq \frac{C}{1+r(x)^{3/2}}.$$

(We recall that $r(x) = |x'| = \sqrt{x_1^2 + x_2^2}$.) The same inequality holds for u instead of Δu, so by standard elliptic regularity results, and taking p large enough, we deduce that

$$|\nabla u| \leq \frac{C}{1 + r^{3/2}}. \tag{68}$$

Hence $u \in H^1(\Gamma_0)$. Since u is periodic, this shows that

$$u \in X_{per}.$$

The next step is to show that u is a critical point of the problem I_{per}. So we write the Euler-Lagrange equation of this problem :

$$-\Delta u + \frac{5}{3}u^{7/3} - (G \star_{\Gamma_0} (\mu - u^2))u = \theta u, \tag{69}$$

for some $\theta \in \mathbf{R}$. The point is then to show that

$$\phi = G \star_{\Gamma_0} (\mu - u^2) + d, \tag{70}$$

with $d \in \mathbf{R}$. We set :

$$\psi = \int_{-1/2}^{1/2} \phi(x) dx_3,$$

and

$$f = \int_{-1/2}^{1/2} (\mu - u^2) dx_3.$$

Those functions are defined on $\mathbf{R}^2$, and since we have $-\Delta\psi = \int_{-1/2}^{1/2} -\Delta\phi = \int_{-1/2}^{1/2} \mu - u^2$, from the periodicity of ϕ, the first Laplacian being a two-dimensional one, and the second one a three-dimensional one, we have :

$$-\Delta\psi = f$$

on $\mathbf{R}^2$.

We want here to apply Lemma 2.19 with $R_0 = 1$. For that purpose, we only need to show that $\|(-\Delta\psi)\psi_R\|_{L^1(B_1^c)}$ is bounded independently of R. So, denoting by Q the unit cube of $\mathbf{R}^3$, we write :

$$\begin{aligned}
\int_{B_1^c} |f\psi_R| &= \sum_{k \in (\mathbf{Z}^2)^*} \int_{(Q+k)\cap B_1^c} |f\psi_R| \\
&\leq \sum_{k \in (\mathbf{Z}^2)^*} \|f\|_{L^\infty(Q+k)} \|\psi_R\|_{L^1_{unif}(B_1^c)} \\
&\leq C \sum_{k \in (\mathbf{Z}^2)^*} \frac{\|\psi_R\|_{L^1_{unif}(B_1^c)}}{1 + |k|^3} \\
&\leq C\|\psi\|_{L^1_{unif}(B_1^c)} + C \sup_{R>1} \left| \frac{\int_{|x|=R} \psi}{2\pi R} \right| \\
&\leq C\|\phi\|_{L^1_{unif}(\{r>1\})} + C\|\phi\|_{L^\infty(\{r>1\})}.
\end{aligned}$$

So we may apply Lemma 2.19 to ψ, deducing that $\nabla\psi \in L^2(\mathbf{R}^2)$. Knowing this, we are going now to prove that :

$$\int_{\Gamma_0} u^2 = 1. \tag{71}$$

This will follow from :

$$\int_{\Gamma_0} -\Delta\phi = 0.$$

And, since this last property may be written as :

$$\int_{\mathbf{R}^2} -\Delta\psi = 0, \tag{72}$$

we focus on this last equation. Let ζ_R be a cut-off function, in the following sense :

$$\zeta_R(x) = \zeta(\frac{|x|}{R}), \text{ with :}$$

- $\zeta \in \mathcal{D}(\mathbf{R})$, $0 \leq \zeta \leq 1$, $|\zeta'| \leq 2$.
- $\zeta(t) = 1 \, \forall t \in [-1, 1]$.
- $\zeta(t) = 0 \, \forall t \in [-2, 2]^c$.

We have, for all $R > 1$:

$$\begin{aligned} \int_{\mathbf{R}^2} -\Delta\psi\zeta_R &= \int_{\mathbf{R}^2} \nabla\psi\nabla\zeta_R. \\ \left|\int_{\mathbf{R}^2} -\Delta\psi\zeta_R\right| &\leq \left(\int_{R<r<2R} |\nabla\psi|^2\right)^{1/2} \left(\int_{R<r<2R} |\nabla\zeta_R|^2\right)^{1/2}. \end{aligned}$$

And, since

$$|\nabla\zeta_R|^2 = \frac{1}{R^2}\left|\zeta'\left(\frac{|x|}{R}\right)\right|^2 \leq \frac{C}{R^2},$$

we conclude that

$$\left|\int_{\mathbf{R}^2} -\Delta\psi\zeta_R\right| \leq C\left(\int_{r>R} |\nabla\psi|^2\right)^{1/2}.$$

The right-hand side of this inequality vanishes as R goes to infinity, since $\nabla\psi \in L^2(B_1^c)$. Hence we get (72), that is (71), or (iii).

Now, we are going to prove (70). In order to do so, we compute the Laplacian of $\phi - G \star_{\Gamma_0} (\mu - u^2)$, and find, from the equality

$$-\Delta G = \sum_{k\in\mathbf{Z}} \delta_{ke_3}$$

that $\phi - G \star_{\Gamma_0} (\mu - u^2)$ is harmonic. On the other hand, we set $v = \mu - u^2$, hence we have $\int_{\Gamma_0} v = 0$, $v \in \mathcal{S}'_{per}(\Gamma_0)$ and v is smooth on $\{r > 1\}$, satisfying $|v| \leq \frac{C}{1+r^3}$. Hence, applying Lemma 2.20, we deduce that

$$G \star_{\Gamma_0} (\mu - u^2) \in L^1_{unif}. \tag{73}$$

Now, since a harmonic function belonging to L^1_{unif} is necessarily a constant, we conclude that (70) holds.

Thus, we know that $u \in X_{per}$, that u^2 has total mass one on Γ_0, and that it satisfies the Euler-Lagrange equation of I_{per}. Since this problem is convex, because the quadratic form D_G is positive, hence convex with respect to ρ, we conclude that u must be a solution of I_{per}. Hence u is unique, and so is ϕ. $\Diamond$

We now give proofs of the two lemmas that we have stated at the beginning of our proof :

Proof of Lemma 2.19 : This result seems to be a standard one, but since we have found no proof in the literature, we provide one for the convenience of the reader.

We first notice that $\psi_R \in L^2_{unif}(\mathbf{R}^2)$, since $\psi \in L^2_{unif}(\mathbf{R}^2)$.

We fix an $R > R_0$. Let ξ_R be a cut-off function, that is, $\xi_R \in \mathcal{D}(\mathbf{R}^2)$, such that $\xi_R(x) = 1$ on $B_R \setminus B_{2R_0}$ and 0 on $B^c_{R+1} \cup B_{R_0}$, $0 \leq \xi_R \leq 1$, and $\|\nabla \xi_R\|_{L^\infty} \leq 1 + \frac{2}{R_0}$.

We have :

$$\begin{aligned} \left| \int_{\mathbf{R}^2} -\Delta \psi_R \psi_R \xi_R^2 \right| &\leq C \\ \left| \int_{\mathbf{R}^2} \nabla \psi_R \nabla (\xi_R^2 \psi_R) \right| &\leq C. \end{aligned} \tag{74}$$

This implies :

$$\begin{aligned} \int_{\mathbf{R}^2} |\nabla(\psi_R \xi_R)|^2 &\leq C + \int_{\mathbf{R}^2} \psi_R^2 |\nabla \xi_R|^2 \\ &\leq C + CR, \end{aligned} \tag{75}$$

from the fact that $\psi_R \in L^2_{unif}(B^c_{R_0}$. We also have :

$$\begin{aligned} \int_{\mathbf{R}^2} |\nabla(\psi_R \xi_R)|^2 &\geq \int_{\mathbf{R}^2} |\nabla \psi_R|^2 \xi_R^2 + 2 \int_{\mathbf{R}^2} \psi_R \nabla \psi_R \xi_R \nabla \xi_R \\ &\geq \int_{\mathbf{R}^2} |\nabla \psi_R|^2 \xi_R^2 \\ &\quad -2 \left(\int_{\mathbf{R}^2} |\nabla \psi_R|^2 \xi_R^2 \right)^{1/2} \left(\int_{\mathbf{R}^2} |\nabla \xi_R|^2 \psi_R^2 \right)^{1/2} \\ &\geq \int_{\mathbf{R}^2} |\nabla \psi_R|^2 \xi_R^2 - 2C\sqrt{R} \left(\int_{\mathbf{R}^2} |\nabla \psi_R|^2 \xi_R^2 \right)^{1/2} \\ &\geq \frac{1}{2} \int_{\mathbf{R}^2} |\nabla \psi_R|^2 \xi_R^2 - CR. \end{aligned}$$

This, together with (75), shows that

$$\int_{B_R\setminus B_{2R_0}} |\nabla\psi|^2 = \int_{B_R\setminus B_{2R_0}} |\nabla\psi_R|^2 \leq \int_{\mathbf{R}^2} |\nabla\psi_R|^2\xi_R^2 \leq CR, \tag{76}$$

for some constant C independent of R. We also have, integrating by parts over $B_R\setminus B_{2R_0}$,

$$\int_{B_R\setminus B_{2R_0}} (-\Delta\psi_R)\psi_R = \int_{B_R\setminus B_{2R_0}} |\nabla\psi_R|^2 - \int_{|x|=R} \psi_R\frac{\partial\psi_R}{\partial r} + \int_{|x|=2R_0} \psi_R\frac{\partial\psi_R}{\partial r}. \tag{77}$$

And from Poincaré inequality, we know that :

$$\left(\int_{|x|=R} {\psi_R}^2\right)^{1/2} \leq \frac{1}{R}\left(\int_{|x|=R}\left|\frac{\partial\psi_R}{\partial\theta}\right|^2\right)^{1/2}. \tag{78}$$

This, together with (77) and (74), gives :

$$\begin{aligned}\int_{B_R\setminus B_{2R_0}} |\nabla\psi|^2 - C_0 &\leq R\left(\int_{|x|=R}\left|\frac{\partial\psi_R}{\partial r}\right|^2\right)^{1/2}\frac{1}{R}\left(\int_{|x|=R}\left|\frac{\partial\psi_R}{\partial\theta}\right|^2\right)^{1/2}\\ &\leq \frac{R}{2}\int_{|x|=R}|\nabla\psi_R|^2 = \frac{R}{2}\int_{|x|=R}|\nabla\psi|^2,\end{aligned}$$

C_0 being a constant bounding $\left|\int_{|x|=2R_0}\psi_R\frac{\partial\psi}{\partial r} + \int_{B_R\setminus B_{2R_0}}(-\Delta\psi_R)\psi_R\right|$.

So, letting g be the function

$$g(R) = \int_{B_R\setminus B_{2R_0}} |\nabla\psi|^2 - C_0,$$

we get the differential inequality :

$$g(R) \leq \frac{R}{2}g'(R).$$

Hence

$$\frac{d}{dR}\big(\frac{1}{R^2}g(R)\big) = \frac{1}{R^3}(Rg'(R) - 2g(R)) \geq 0.$$

So, integrating from $R_1 > R_0$ to R, we get, for all $R > R_1$,

$$g(R) \geq \frac{g(R_1)}{R_1^2}R^2.$$

If there exists at least one R_1 such that $g(R_1) > 0$, we reach a contradiction with (76). Hence $g \leq 0$, that is

$$\int_{B_R\setminus B_{2R_0}} |\nabla\psi|^2 \leq C_0.$$

Which implies that $\nabla\psi \in L^2(B_{R_0}^c)$. $\Diamond$

Proof of Lemma 2.20 : We already know that $G \star_{\Gamma_0} v$ lies in $L^1_{loc}(\Gamma_0)$, so the only thing to check out is that it is bounded as $r \to \infty$.

We now write :

$$\begin{aligned} G \star_{\Gamma_0} v &= \int_{\Gamma_0} v(y)(G(x-y) + 2\log(r(x-y)))dy \\ &\quad - \int_{\Gamma_0} 2v(y)(\log(r(x-y)) - \log(r(x)))dy. \end{aligned}$$

We first consider the first term of this expression : from Lemma 2.9, we know that

$$|G(x) + 2\log(r)| \leq \frac{C}{r},$$

for $x \in 2\Gamma_0$. Hence :

$$\begin{aligned} \left| \int_{\Gamma_0} v(y)(G(x-y) + 2\log(r(x-y)))dy \right| &\leq C \int_{\Gamma_0} \frac{|v(y)|}{r(x-y)} dy \\ &\leq C \int_{\Gamma_0 \cap \{r(x-y)>1\}} |v(y)| dy \\ &\quad + C \int_{\Gamma_0 \cap \{r(x-y)<1\}} \frac{|v(y)|}{r(x-y)} dy \\ &\leq C + C \int_{|y_3|<\frac{1}{2}, r(y)<1} \frac{dy}{r(y)} \\ &\leq C. \end{aligned} \tag{79}$$

Now we rewrite the second term as :

$$\int_{\Gamma_0} 2|v(y)||\log(r(x-y)) - \log(r(x))|dy \leq C \int_{\Gamma_0} |v(y)| \left| \log \left| \frac{x'}{|x'|} - \frac{y'}{|x'|} \right| \right| dy \tag{80}$$

$$\leq C \int_{\Gamma_0 \cap \{|y'|<R\}} |v(y)| \left| \log \left| \frac{x'}{|x'|} - \frac{y'}{|x'|} \right| \right| dy + C \int_{\Gamma_0 \cap \{|y'|>R\}} |v(y)| \left| \log \left| \frac{x'}{|x'|} - \frac{y'}{|x'|} \right| \right| dy. \tag{81}$$

Where $R = R(x)$ satisfies $R \ll |x'|$. So we may write, for $|y'| < R$:

$$\left| \log \left| \frac{x'}{|x'|} - \frac{y'}{|x'|} \right| \right| = \frac{1}{2} \left| \log \left(1 - \frac{2x'y'}{|x'|^2} + \frac{|y'|^2}{|x'|^2} \right) \right| = O(\frac{R}{|x'|}).$$

Which implies :

$$\begin{aligned} \int_{\Gamma_0 \cap \{|y'|<R\}} |v(y)| \left| \log \left| \frac{x'}{|x'|} - \frac{y'}{|x'|} \right| \right| dy &\leq \frac{CR}{|x'|} \int_{\Gamma_0 \cap \{|y'|<R\}} |v(y)| dy \\ &\leq \frac{CR}{|x'|} \int_R^\infty \frac{r dr}{r^3} \leq \frac{C}{|x'|}. \end{aligned}$$

Concerning the remaining term of (81), we integrate first over the set

$$\Gamma_0 \cap \{|y'| > R\} \cap \{|x' - y'| > 1\} = D_R,$$

then over the set

$$\Gamma_0 \cap \{|y'| > R\} \cap \{|x' - y'| < 1\} = E_R.$$

On the first one, we have :

$$|\log\left|\frac{x'}{|x'|} - \frac{y'}{|x'|}\right|| \leq C \log\left(1 + \frac{|y'|}{|x'|}\right). \tag{82}$$

The second one is a compact subset of $\mathbf{R}^3$, so, as $\log|x'| \in L^1_{loc}(\mathbf{R}^3)$, we may bound the integral of $|v(y)|\left|\log\left|\frac{x'}{|x'|} - \frac{y'}{|x'|}\right|\right|$ over E_R by $\frac{C}{R^3}$.

And coming back to (82), we write :

$$\begin{aligned}
\int_{\Gamma_0 \cap \{|y'|>R\}} |v(y)|\left|\log\left|\frac{x'}{|x'|} - \frac{y'}{|x'|}\right|\right| dy &\leq \int_{D_R} |v(y)|\left|\log\left(1 + \frac{|y'|}{|x'|}\right)\right| dy + \frac{C}{R^3} \\
&\leq C\int_R^\infty \frac{|\log(1 + \frac{r}{|x'|})|}{r^2} dr + \frac{C}{R^3} \\
&\leq \frac{C}{|x'|}\int_{R/|x'|}^\infty \frac{|\log(1+t)|}{t^2} dt + \frac{C}{R^3} \\
&\leq \frac{C}{|x'|}\left(\frac{|x'|\log(1 + \frac{R}{|x'|})}{R}\right) \\
&\quad + \frac{C}{|x'|}\int_{R/|x'|}^\infty \frac{dt}{t(1+t)} + \frac{C}{R^3} \\
&\leq \frac{C}{|x'|} + \frac{C}{R} + \frac{C}{R^3}.
\end{aligned} \tag{83}$$

All this is bounded as $|x'| \longrightarrow \infty$, so this ends the proof. $\Diamond$

Remark 2.21 *Looking closely at inequality (83), we notice that the bound may be $\frac{C}{|x'|^\alpha}$, for any $\alpha < 1$. (Just take $R = |x'|^\alpha$.) On the other hand, the same kind of computation could be done in (79), by developing $\frac{1}{|x'-y'|}$ as $|x'| \longrightarrow \infty$. One would find the same kind of inequality, namely C in (79) would be replaced by $\frac{C}{|x'|^\alpha}$. So we may in fact assert that $\phi = \phi_0 + d$, with $d \in \mathbf{R}$ and $\phi_0 \in L^1_{unif}$, satisfying*

$$|\phi_0| \leq \frac{C}{|x'|^\alpha}, \ \forall \alpha < 1.$$

We may also notice that, in the course of our proof, we have found a solution to the problem I_{per}, and hence ensured that this problem is well-posed :

Remark 2.22 *As a corollary of Theorem 2.16, one may state the result that the periodic problem I_{per} is well-posed. Of course, this result could be proved without using the above theorem, by using standard variational methods, but it is not our point here.*

2.2.5 Convergence and identification of the limit

Now that we have a uniqueness result for the system (40), we are able to show the convergence of the sequence ρ_Λ :

Proposition 2.23 *The sequence u_Λ converges to u_{per} in $H^1(\Gamma_0)$.*

Proof : The proof only consists in collecting the preceding results, as pointed out above. $\Diamond$

Actually, as in [6], we establish in Theorem 2.25 below a much stronger convergence result. In order to do so, we introduce what we will in this context call interior domains :

Definition 2.24 *Let $\Lambda \subset \{(0,0)\} \times \mathbf{Z}$ be a Van Hove sequence in the third direction. Λ' will be said to be a sequence of interior domains, denoted by $\Lambda' \subset\subset \Lambda$, if it satisfies the following properties :*

(i) $\Lambda' \subset \Lambda$.

(ii) *For any finite subset A of $\mathbf{Z}e_3$, there exists an $h_0 \in \mathbf{N}$ such that $\forall h \geq h_0$, $A \subset \Lambda'_h$.*

(iii) $\frac{|\Lambda'|}{|\Lambda|} \longrightarrow 1$ *as* $\Lambda \to \infty$.

(iv) $d(\Lambda', \partial\Gamma(\Lambda)) \longrightarrow \infty$ *as* $\Lambda \to \infty$.

Theorem 2.25 *For any sequence $\Lambda' \subset\subset \Lambda$ and any $R > 0$, we have :*

$$\|u_\Lambda - u_{per}\|_{L^\infty(\Gamma(\Lambda')),} \longrightarrow 0 \tag{84}$$

$$\|\phi_\Lambda - \phi_{per}\|_{L^\infty(\Gamma(\Lambda') \cap \{r<R\})} \longrightarrow 0, \tag{85}$$

as $\Lambda \longrightarrow \infty$. (We recall that $\phi_{per} = G \star_{\Gamma_0} (m - u_{per}^2) - \theta_{per}$)

Proof : We follow step by step, here again, the proof of [6]. We only provide a proof of (84), the proof of (85) following exactly the same pattern. We argue by contradiction, and suppose that (84) does not hold. This implies that there exists, extracting a subsequence if necessary, a sequence x_Λ in $\Gamma(\Lambda')$, such that :

$$|u_\Lambda(x_\Lambda) - u_{per}(x_\Lambda)| > \frac{\varepsilon}{2}, \tag{86}$$

for some $\varepsilon > 0$. On the other hand, we have :

$$|u_\Lambda(x_\Lambda) - u_{per}(x_\Lambda)| \leq \frac{C}{1 + r(x_\Lambda)^{3/2}}.$$

Hence $r(x_\Lambda)$ is necessarily bounded. Now we write $x_\Lambda = y_\Lambda + k_\Lambda e_3$, with $y_\Lambda \in \Gamma_0$ and $k_\Lambda \in \mathbf{Z}$. Since the sequence $r(x_\Lambda)$ is bounded, so is y_Λ. We then may assume that this

sequence is convergent, and that the limit $\overline{y}$ lies in $\overline{\Gamma}_0$. We then have, using (86), and taking $|\Lambda|$ large enough,

$$|u_\Lambda(x_\Lambda) - u_{per}(\overline{y})| > \frac{\varepsilon}{4}. \tag{87}$$

We denote by $\overline{u}_\Lambda$ the function $u_\Lambda(\cdot + x_\Lambda)$, and by $\overline{\phi}_\Lambda$ the function $\phi_\Lambda(\cdot + x_\Lambda)$. One may then rewrite (16)-(17) as :

$$\left\{ \begin{array}{l} -\Delta\overline{u}_\Lambda + \frac{5}{3}\overline{u}_\Lambda^{7/3} - \overline{u}_\Lambda\overline{\phi}_\Lambda = 0, \\ -\Delta\overline{\phi}_\Lambda = 4\pi(m_\Lambda(\cdot + x_\Lambda) - \overline{u}_\Lambda^2). \end{array} \right. \tag{88}$$

The bounds on u_Λ and ϕ_Λ hold for $\overline{u}_\Lambda$ and $\overline{\phi}_\Lambda$, so we may pass locally to the limit in the system (88) above, and denoting by $\overline{u}$ and $\overline{\phi}$ the corresponding limits, we have :

$$\left\{ \begin{array}{l} -\Delta\overline{u} + \frac{5}{3}\overline{u}^{7/3} - \overline{\phi}\overline{u} = 0, \\ -\Delta\overline{\phi} = 4\pi(m_\infty(\cdot + \overline{y}) - \overline{u}^2), \end{array} \right. \tag{89}$$

because $m_\Lambda(\cdot + x_\Lambda) \longrightarrow m_\infty(\cdot + \overline{y})$ in $\mathcal{D}'(\mathbf{R}^3)$ as $\Lambda \to \infty$. Indeed, we have, for any $\varphi \in \mathcal{D}(\mathbf{R}^3)$, K being its support :

$$\begin{aligned} < m_\Lambda(\cdot + x_\Lambda), \varphi > &= \sum_{k\in\Lambda} < m(\cdot + x_\Lambda + k), \varphi > \\ &= \sum_{k\in\Lambda\cap(\Gamma_0 - K - x_\Lambda)} < m, \varphi(\cdot - x_\Lambda - k) > . \end{aligned}$$

Using Definition 2.24-(iv), we have that the set $\Lambda\cap(\Gamma_0 - K - x_\Lambda)$ becomes $\mathbf{Z}e_3\cap(\Gamma_0 - K - x_\Lambda)$ when Λ is large enough, because in this case, $\Gamma_0 - K - x_\Lambda$ comes to be included in Λ. Hence,

$$\begin{aligned} < m_\Lambda(\cdot + x_\Lambda), \varphi > &= \sum_{k\in\mathbf{Z}e_3} < m, \varphi(\cdot - x_\Lambda - k) > \\ &= < m_\infty, \varphi(\cdot - y_\Lambda) > \longrightarrow < m_\infty(\cdot + \overline{y}), \varphi > . \end{aligned}$$

Now, from Theorem 2.16, we know that (89) implies that

$$\overline{u} = u_{per}(\cdot + \overline{y}).$$

Hence

$$\overline{u}_\Lambda \longrightarrow u_{per}(\cdot + \overline{y})$$

in $L^2_{loc}(\mathbf{R}^3)$. On the other hand, from the bounds we have on ∇u_Λ (see formula (68)), we deduce that the above convergence is point-wise, reaching a contradiction with (87).

Now, concerning (85), the only change is the fact that we do not need to show that y_Λ is bounded, all the other steps of the proof carrying through. $\Diamond$

2.2.6 Convergence of the energy

We are now going to answer the only question of the problem of thermodynamic limit that we have left aside so far, namely the convergence of the energy per unit volume.

Theorem 2.26 *For any Van Hove sequence, we have :*

$$\frac{I_\Lambda}{|\Lambda|} \longrightarrow I_{per} + \frac{M}{2}$$

as $\Lambda \to \infty$.

Proof : Here again, our proof is an adaptation of [6]'s, using the compactness result (23), and the decay we have obtained on ∇u in (68), that is :

$$|\nabla u_\Lambda| \leq \frac{C}{1 + r^{3/2}}.$$

The strategy of proof is to study one by one the terms of the energy, and to split the integrals over $\mathbf{R}^3$ into integrals over $\Gamma(\Lambda')$, $\Gamma(\Lambda) \setminus \Gamma(\Lambda')$ and $\Gamma(\Lambda)^c$, for some $\Lambda' \subset\subset \Lambda$, the first being dealt with using the convergence result of Theorem 2.25, the second using the bounds we have on u_{per} and u_Λ, and the third one using the compactness result (23). We refer the reader to [6] for more details. $\Diamond$

3 Thin films

This section is devoted to the thermodynamic limit problem in two dimension, that is to say, the problem of the thermodynamic limit concerning thin films. Throughout this section, $\Lambda = \Lambda_2 \times \{0\} \subset \mathbf{Z}^2 \times \{0\}$ will denote a Van Hove sequence in the first two dimensions, i.e such that Λ_2 is a Van Hove sequence of $\mathbf{Z}^2$. Γ_0 will denote the periodic cell of the problem, that is, $]-\frac{1}{2}, \frac{1}{2}]^2 \times \mathbf{R}$, and $\Gamma(\Lambda) = \bigcup_{k \in \Lambda} \Gamma_0 + k$. For such a Λ, we define as in the preceding section the energy $E_\Lambda(\rho)$ and the minimizing problem I_Λ by formulas (14) and (15).

The unique minimizer $\rho_\Lambda = u_\Lambda^2$ satisfies here again :

$$-\Delta u_\Lambda + \frac{5}{3} u_\Lambda^{7/3} - \phi_\Lambda u_\Lambda = 0, \tag{90}$$

where $\phi_\Lambda = (m_\Lambda - u_\Lambda^2) \star \frac{1}{|x|} - \theta_\Lambda$ satisfies :

$$-\Delta \phi_\Lambda = 4\pi (m_\Lambda - u_\Lambda^2). \tag{91}$$

Following exactly the steps of Section 2, we start with some a priori estimates.

3.1 A priori estimates

3.1.1 Energy bounds and L^∞ bounds

We have exactly the same results as in Section 2, namely Theorems 2.1 and 2.2. Here again, as in Section 2, we notice that the proof of theorem 2.2 is only based on equations (90)-(91), and on the fact that the measure m_Λ is non-negative, bounded and has compact support with respect to x_3. Hence it will hold for any such solutions, and in particular if we replace m_Λ by $m_\infty = \sum_{k\in\mathbf{Z}} m(\cdot - ke_3)$, or by any Γ_0-periodic measure having compact support with respect to x_3.

3.1.2 Asymptotic estimates

As in Section 2, we now derive bounds at infinity, that is estimates of the decay of u_Λ as $|x_3| \longrightarrow \infty$, which are uniform with respect to Λ. As in Section 2, we use Lemma 2.4 to prove the following estimates :

Theorem 3.1 *For any solution $(u_\Lambda, \phi_\Lambda)$ of the system (90)-(91) satisfying $u_\Lambda \geq 0$, we have :*

$$\begin{aligned} \phi_\Lambda &\leq \frac{C}{1+|x_3|^2}, \quad \forall\, |x_3| \geq 1, \\ 0 \leq u_\Lambda &\leq \frac{C}{1+|x_3|^{3/2}}, \end{aligned}$$

where C denotes various positive constants independent of the measure m_Λ.

Furthermore, in the smeared nuclei case, i.e when m in (91) is supposed to be smooth, the first inequality holds everywhere.

Proof : The proof is only a copy of that of Theorem 2.5. We only point out the necessary changes in that proof : the function g_R is unchanged, and so is $\tilde{\phi}$. In all the inequalities and definition of sets, r becomes $|x_3|$. Hence C_{R+1} is now the set $\{|x_3| > R+1\}$, and U is the function :

$$U = \frac{a}{(|x_3|^2 - R^2)^2} + \frac{bR'^4}{(R'^2 - |x_3|^2)^4}.$$

Computations follow exactly the same pattern, and we find in U the desired supersolution, the only change being the constants $\frac{a}{(2R+1)^2}$ and b. The whole proof carries through, and we finally get the desired conclusion. $\Diamond$

3.1.3 Compactness

We now study the compactness of the sequence ρ_Λ, namely we are going to show that :

Proposition 3.2 *For any sequence $\Lambda \subset \mathbf{Z}^2 \times 0$, being a Van Hove sequence in the first two dimensions, we have :*

$$\frac{1}{|\Lambda|} \int_{\Gamma(\Lambda)} \rho_\Lambda \longrightarrow 1 \quad \text{as} \quad \Lambda \to \infty. \tag{92}$$

Proof : Here again, we provide only a smeared nuclei case proof, referring to [6] for the generalization to the point nuclei case. We start exactly as in Proposition 2.7, writing that for all $h \in H^1(\mathbf{R}^2)$, we have :

$$|\int_{\mathbf{R}^3}(m_\Lambda - \rho_\Lambda)h| \leq \frac{1}{(2\pi)^3} D(m_\Lambda - \rho_\Lambda, m_\Lambda - \rho_\Lambda)^{1/2} \|\nabla h\|_{L^2(\mathbf{R}^3)}. \tag{93}$$

We then choose $h = h_\Lambda$: we set $h_\Lambda(x) = f_\Lambda(x_3)g_\Lambda(x_1, x_2)$, with :

- $f_\Lambda(t) = 1 - \frac{|t|}{R}$ if $|t| < R$, 0 otherwise, where $R = R(\Lambda)$ will be chosen later on.
- $g_\Lambda \in \mathcal{D}(\mathbf{R}^2)$, $0 \leq g_\Lambda \leq 1$, $g_\Lambda = 1$ on the set $\{x \in \mathbf{R}^2 / d(x, \Lambda_2) < \frac{1}{\sqrt{2}}\}$, 0 on the set $\{x \in \mathbf{R}^2 / d(x, \Lambda_2) > 1\}$, and satisfying $|\nabla g_\Lambda| \leq 4$.

(We recall that $\Lambda = \Lambda_2 \times \{0\}$, that $\Lambda_2^1 = \{t \in \mathbf{R}^2,\ d(t, \cup_{k\in\Lambda_2}(k+]-\frac{1}{2}, \frac{1}{2}]^2)) < 1\}$, and that the Van-Hove hypotheses imply $|\Lambda_2^1| \ll |\Lambda|$.)

We have, for such an h_Λ :

$$\begin{aligned}
\int_{\mathbf{R}^3} |\nabla h_\Lambda|^2 &= \int_{\mathbf{R}^3} f'_\Lambda(x_3)^2 g_\Lambda(x')^2 dx' dx_3 + \int_{\mathbf{R}^3} f_\Lambda(x_3)^2 |\nabla g_\Lambda|^2(x') dx' dx_3 \\
&\leq C|\Lambda| \int_0^R \frac{dt}{R^2} + C|\Lambda_2^1| \int_0^R (1 - \frac{t}{R})^2 dt \\
&\leq C\frac{|\Lambda|}{R} + CR|\Lambda_2^1|.
\end{aligned}$$

We now choose $R = \left(\frac{|\Lambda|}{|\Lambda_2^1|}\right)^{1/2}$, so that we have $\frac{|\Lambda|}{R} \ll |\Lambda|$, and $R|\Lambda_2^1| \ll |\Lambda|$. Hence, we have :

$$\|\nabla h_\Lambda\|_{L^2(\mathbf{R}^3)} = o(|\Lambda|). \tag{94}$$

Thus, since we already know from Theorem 2.1 (vii) that $D(m_\Lambda - \rho_\Lambda, m_\Lambda - \rho_\Lambda) \leq C|\Lambda|$, (94) implies :

$$\frac{1}{|\Lambda|} \int_{\mathbf{R}^3} (m_\Lambda - \rho_\Lambda) h_\Lambda \longrightarrow 0 \tag{95}$$

as $\Lambda \to \infty$.

On the other hand, since $h_\Lambda \leq 1$, we have $\int_{\mathbf{R}^3} m_\Lambda h_\Lambda \leq |\Lambda|$. We also have :

$$\int_{\mathbf{R}^3} m_\Lambda h_\Lambda \geq |\Lambda| - \int_{\mathbf{R}^3} m_\Lambda \frac{|x_3|}{R},$$

and $0 \leq \int_{\mathbf{R}^3} m_\Lambda \frac{|x_3|}{R} \leq \frac{|\Lambda|}{R}$, hence we infer that :

$$\frac{1}{|\Lambda|}\int_{\mathbf{R}^3} m_\Lambda h_\Lambda \longrightarrow 1. \tag{96}$$

Next, we compute :

$$\begin{aligned}\int_{\mathbf{R}^3}\rho_\Lambda h_\Lambda &= \int_{\Gamma(\Lambda)}\rho_\Lambda - \int_{\Gamma(\Lambda)\cap\{|x_3|<R\}}\rho_\Lambda\frac{|x_3|}{R} + \int_{\Gamma(\Lambda)^c}\rho_\Lambda h_\Lambda \\ &\quad - \int_{\Gamma(\Lambda)\cap\{|x_3|>R\}}\rho_\Lambda.\end{aligned} \tag{97}$$

Concerning the second term of the right-hand side, we write :

$$\left|\int_{\Gamma(\Lambda)\cap\{|x_3|<R\}}\rho_\Lambda\frac{|x_3|}{R}\right| \le C\frac{|\Lambda|}{R}\int_0^R\frac{tdt}{1+t^3} \le C\frac{|\Lambda|}{R} \ll |\Lambda|.$$

We then deal with the third term as follows :

$$\left|\int_{\Gamma(\Lambda)^c}\rho_\Lambda h_\Lambda\right| \le C\frac{|\Lambda_2^1|}{R}\int_0^R\frac{tdt}{1+t^3} \le C\frac{|\Lambda_2^1|}{R} \ll |\Lambda|.$$

Turning to the fourth one, we have :

$$\int_{\Gamma(\Lambda)\cap\{|x_3|>R\}}\rho_\Lambda \le C|\Lambda|\int_R^\infty\frac{tdt}{1+t^3} \le C\frac{|\Lambda|}{R} \ll |\Lambda|.$$

Hence (97) implies :

$$\frac{1}{|\Lambda|}\int_{\mathbf{R}^3}\rho_\Lambda h_\Lambda = \frac{1}{|\Lambda|}\int_{\Gamma(\Lambda)}\rho_\Lambda + o(1). \tag{98}$$

Thus, collecting (95), (96) and (98), we conclude that (92) holds. $\Diamond$

3.2 Identification of the limit

Following the steps of Section 2, and we are now able to pass locally to the limit in the system (90)-(91), getting solutions u_∞ and ϕ_∞ of the system :

$$\begin{cases} -\Delta u_\infty + \frac{5}{3}u_\infty^{7/3} - u_\infty\phi_\infty = 0, \\ -\Delta\phi_\infty = 4\pi(m_\infty - u_\infty^2). \end{cases} \tag{99}$$

m_∞ being the measure $\sum_{k\in\mathbf{Z}^2} m(\cdot - k)$, and in particular a periodic measure. We suspect a uniqueness result similar to that of Section 2 to be true in this case, but we did not manage to prove it. However, we are going to prove a convergence result for the sequence ρ_Λ.

We first need some preliminary results on the periodic potential G.

3.2.1 The potential G

In this section, we denote by G the function

$$G(x) = -2\pi|x_3| + \sum_{k\in\mathbf{Z}^2}\left(\frac{1}{|x-k|} - \int_K \frac{dy}{|x-y-k|}\right).$$

Where K denotes the unit square of $\mathbf{R}^2$, that is, $K =]-\frac{1}{2},\frac{1}{2}[^2$.
First of all, we check out that this sum clearly defines G :

Proposition 3.3 *The sum defining G is convergent over the set $\mathbf{R}^3 \setminus (\mathbf{Z}^2 \times \{0\})$, and normally convergent on any compact subset of this set.*

Proof : Here again, we develop the integrand as $|x| \longrightarrow \infty$:

$$\begin{aligned} f(x) &= \frac{1}{|x|} - \int_K \frac{dy}{|x-y|} \\ &= \frac{1}{|x|} - \int_K \frac{dy}{\sqrt{|x|^2 - 2xy + |y|^2}} \\ &= \frac{1}{|x|} - \frac{1}{|x|}\int_K \frac{dy}{\sqrt{1 - 2\frac{xy}{|x|^2} + \frac{|y|^2}{|x|^2}}} \\ &= \frac{1}{|x|} - \frac{1}{|x|}\int_K \big(1 + \frac{xy}{|x|^2} + O(\frac{1}{|x|^2})\big)dy \\ &= \frac{1}{|x|} - \frac{1}{|x|} + O(\frac{1}{|x|^3}). \end{aligned}$$

And this concludes our proof, since $\sum_{k\in\mathbf{Z}^2}\frac{1}{1+|k|^3}$ does converge. $\Diamond$

We now prove the analogue of Lemma 2.9 :

Lemma 3.4 *We have :*

(i) $G(x) = \frac{1}{|x|} + C + o(1)$ *as* $|x| \longrightarrow 0$.

(ii) $G(x) = -2\pi|x_3| + O(\frac{1}{|x_3|^\alpha})$ *as* $|x_3| \longrightarrow \infty$, *for any* $\alpha < 1$, *uniformly with respect to* $x' = (x_1, x_2)$.

Proof : We rewrite G as :

$$G(x) = -2\pi|x_3| + \frac{1}{|x|} - \int_K \frac{dy}{|x-y|} + \sum_{k\in(\mathbf{Z}^2)^*}\left(\frac{1}{|x-k|} - \int_K \frac{dy}{|x-y-k|}\right). \qquad (100)$$

From the computation of the preceding proposition's proof, we know that the remaining sum converges normally on a neighborhood of 0. Hence it is continuous on that neighborhood. On the other hand, $x \mapsto \int_K \frac{dy}{|x-y|}$ is continuous on $\mathbf{R}^3$, and this concludes the proof of (i).

We now turn to (ii). We intend to show that :

$$\sum_{k\in(\mathbf{Z}^2)^*}\left|\frac{1}{|x-k|}-\int_K\frac{dy}{|x-k-y|}\right|\leq\frac{C}{|x_3|^\alpha}. \tag{101}$$

Considering the function f defined above, we know that $|f(x)|\leq\frac{C}{|x|^3}$. So we may write :

$$\sum_{k\in(\mathbf{Z}^2)^*}|f(x-k)|\leq\sum_{k\in(\mathbf{Z}^2)^*}\frac{C}{|x-k|^3}\leq\sum_{k\in(\mathbf{Z}^2)^*}\frac{C}{|k|^3+|x_3|^3}.$$

We now use Young's inequality, finding that for all $\alpha<1$, we have :

$$|k|^3+|t|^3\geq C|k|^{3-\alpha}|t|^\alpha.$$

So we infer that :

$$\sum_{k\in(\mathbf{Z}^2)^*}|f(x-k)|\leq\frac{C}{|x_3|^\alpha}\sum_{k\in(\mathbf{Z}^2)^*}\frac{C}{|k|^{3-\alpha}}.$$

Since $\alpha<1$ implies $3-\alpha>2$, we conclude that (101) holds. $\Diamond$

Let us now establish a positiveness property on the operator D_G (We recall that it is defined by $D_G(f,g)=\int_{\Gamma_0}\int_{\Gamma_0}f(x)g(y)G(x-y)dxdy=\int_{\Gamma_0}(G\star_{\Gamma_0}f)g)$. We assume here that the support of m is contained in $\{r<1\}$. (This implies no loss of generality).

Proposition 3.5 *The bilinear form D_G is positive on the set $Y_{per}=\{f\in L^1_{per}(\Gamma_0)/\sqrt{|f|}\in H^1_{per}(\Gamma_0\cap\{|x_3|>1\}),\ \int_{\Gamma_0}f=0,\ and\quad(1+|x|)f\in L^1(\Gamma_0)\}$.*

Where the space $H^1_{per}(\Gamma_0\cap\{|x_3|>1\})$ is defined by the set of all functions belonging to $H^1_{loc}(\{|x_3|>1\})\cap H^1(\Gamma_0\cap\{|x_3|>1\})$ that are periodic of periodic cell Γ_0.
Proof : We introduce, as in Section 2, the Fourier transform on Γ_0, defined by :

$$\widehat{f}(n,\xi)=\int_{\Gamma_0}f(x)e^{-i2\pi(x_3\xi+nx')}dx, \tag{102}$$

where $\xi\in\mathbf{R}$, $n\in\mathbf{Z}^2$ and $x=(x',x_3)$. By a straightforward computation, one finds that for this Fourier transform, Parceval's and Plancherel's formulas hold, so that we may prolong it to $\mathcal{S}'_{per}(\Gamma_0)$. We also have :

$$\forall f\in\mathcal{S}'_{per}(\Gamma_0),\ \widehat{\partial_3 f}(n,\xi)=i2\pi\xi\widehat{f}(n,\xi). \tag{103}$$

And

$$\forall f\in\mathcal{S}'_{per}(\Gamma_0),\ \forall g\in\mathcal{S}_{per}(\Gamma_0),\ \widehat{f\star_{\Gamma_0}g}=\widehat{f}\widehat{g}.$$

So, since $-\Delta G=4\pi\delta_0$ on Γ_0, we deduce :

$$4\pi^2(\xi^2+|n|^2)\widehat{G}(n,\xi)=4\pi.$$

Thus, when $n \neq 0$, we have $\widehat{G}(n,\xi) = \frac{1}{\pi(|n|^2+\xi^2)}$. Concerning the case $n = 0$, we notice that $\widehat{G}(0,\xi)$ is exactly equal to the classical Fourier transform of $-2\pi|x_3|$ over $\mathbf{R}$. Indeed, putting $G_0(x) = G(x) + 2\pi|x_3|$, we notice that $\int_K G_0(x)dx'$ is a harmonic function, which goes to zero as $|x_3| \longrightarrow \infty$, from Lemma 3.4. So it is necessarily 0.

Furthermore, the Fourier transform of $-2\pi|x_3|$ is shown to be $4\pi \mathrm{vp}(\frac{1}{\xi^2}) + a\delta_0$ in [13], where $\mathrm{vp}(\frac{1}{\xi^2})$ is defined by :

$$\begin{aligned} < \mathrm{vp}(\frac{1}{\xi^2}), \varphi > &= \lim_{\varepsilon \to 0^+} \Big(\int_{|\xi|>\varepsilon} \frac{\varphi(\xi)}{\xi^2} d\xi - \frac{1}{\varepsilon}\big(\varphi(\varepsilon) + \varphi(-\varepsilon)\big) \\ &\quad + (\log \varepsilon)\big(\varphi'(\varepsilon) - \varphi'(-\varepsilon)\big) \Big). \end{aligned} \tag{104}$$

In fact, $\mathrm{vp}(\frac{1}{x^2}) = -(\log|x|)''$ in $\mathcal{D}'(\mathbf{R})$. Now let $f \in Y_{per}$. We have :

$$\begin{aligned} D_G(f,f) &= \int_{\Gamma_0} (G \star_{\Gamma_0} f) f \\ &= \sum_{k \in \mathbf{Z}^2} \int_{\mathbf{R}} \widehat{G \star_{\Gamma_0} f}(k,\xi) \widehat{f}(k,\xi) d\xi \\ &= \sum_{k \in (\mathbf{Z}^2)^*} \int_{\mathbf{R}} \frac{(\widehat{f}(k,\xi))^2}{4\pi^2(|k|^2+\xi^2)} d\xi + 4\pi < \mathrm{vp}(\frac{1}{\xi^2}), (\widehat{f}(0,\xi))^2 > . \end{aligned}$$

So the only thing to show is that $< \mathrm{vp}(\frac{1}{\xi^2}), (\widehat{f}(0,\xi))^2 > \geq 0$. We notice that the belonging of f to Y_{per} implies that $|\widehat{f}(0,\xi)| \leq C|\xi|$ as $\xi \to 0$, so that $\frac{(\widehat{f}(0,\xi))^2}{\xi^2} \in L^1(\mathbf{R})$, and (104) implies that

$$< \mathrm{vp}(\frac{1}{\xi^2}), (\widehat{f}(0,\xi))^2 > = \int_{\mathbf{R}} \frac{(\widehat{f}(0,\xi))^2}{\xi^2} d\xi \geq 0.$$

This concludes the proof. $\Diamond$

3.2.2 Periodicity of the limit

We will say from now on that a function u is symmetric with respect to x_1 if it satisfies the equality :

$$u(x_1,x_2,x_3) = u(-x_1,x_2,x_3). \tag{105}$$

And the sequence Λ will be said to be symmetric if $1_{\Gamma(\Lambda)}$ is.

For all function f, we denote by $\tau_1 f$ the function :

$$\tau_1 f(x) = f(x + e_1). \tag{106}$$

Proposition 3.6 *Assume that Λ is symmetric with respect to x_1, in addition to the hypotheses we have required so far. In the smeared nuclei case, m is also required to be symmetric. Let (u,ϕ) be the limit of (u_Λ,ϕ_Λ). Then $u \in L^\infty(\mathbf{R}^3)$, $\phi \in L^1_{unif}(\mathbf{R}^3)$, and we have :*

$$|\tau_1\phi - \phi| \leq \frac{C}{1+|x_3|}. \tag{107}$$

Proof : The belonging of (u,ϕ) to $L^\infty(\mathbf{R}^3) \times L^1_{unif}(\mathbf{R}^3)$ comes directly from the bounds of Theorem 2.2. Moreover, we have :

$$-\Delta(\tau_1\phi - \phi) = 4\pi(u^2 - \tau_1 u^2).$$

Hence $(\tau_1\phi - \phi) \in W^{2,p}_{unif}(\mathbf{R}^3)$ for all $p > 1$, and in particular it lies in $L^\infty(\mathbf{R}^3)$, so the bound (107) need only to be shown on the set $\{|x_3| > 2\}$. Hereafter, we assume that $|x_3| > 2$.

Now we are going to show this estimate for (u_Λ,ϕ_Λ), uniformly with respect to Λ, and hence deduce it for (u,ϕ).

From the uniqueness of u_Λ, we know that $v_\Lambda = m_\Lambda - u_\Lambda^2$ is symmetric with respect to x_1. Hence we have :

$$\int_{B_R} v_\Lambda(y)\frac{y_1}{|y|^k}dy = 0, \tag{108}$$

for all $k < 4$ and $R > 0$.

We split the expression of $\psi_\Lambda = \tau_1\phi_\Lambda - \phi_\Lambda$ into two terms :

$$\begin{aligned}\psi_\Lambda(x) &= \int_{|x-y|<R} v_\Lambda(y)\left(\frac{1}{|x-y+e_1|} - \frac{1}{|x-y|} - \frac{y_1}{|y|^3}\right)dy \\ &\quad + \int_{|x-y|>R} v_\Lambda(y)\left(\frac{1}{|x-y+e_1|} - \frac{1}{|x-y|} - \frac{y_1}{|y|^3}\right)dy,\end{aligned}$$

where $R = \frac{|x_3|}{2}$. We call $a(x)$ the first term, $b(x)$ the second one. We notice that

$$\int_{|x-y|<2} |v_\Lambda(y)|\left|\frac{1}{|x-y+e_1|} - \frac{1}{|x-y|} - \frac{y_1}{|y|^3}\right|dy \leq \frac{C}{|x_3|^3},$$

because $\frac{1}{|x-y+e_1|} - \frac{1}{|x-y|} + \frac{y_1}{|y|^3}$ lies in $L^1(B_2+x)$ and is bounded independently of x in this space. So we may as well restrict ourselves to integrals over $|x-y| > 2$, which is equivalent to replacing $|x-y|$ by $1+|x-y|$ in the integrals. The same remark holds concerning terms of the form $\frac{1}{|y|}$, which will be replaced by $\frac{1}{1+|y|}$.

On the other hand, we may bound $|\frac{1}{|x+e_1|} - \frac{1}{|x|}|$ by $\frac{C|x_1|}{|x|^3}$ on $\{|x| > 2\}$, for a universal constant C. Hence we have, x' and y' denoting the variables (x_1,x_2) and (y_1,y_2)

respectively :

$$\begin{aligned} |a(x)| &\leq \int_{|x-y|<R} \frac{C}{1+|y_3|^3}\left|\frac{1}{|x-y+e_1|}-\frac{1}{|x-y|}-\frac{y_1}{|y|^3}\right|dy \\ &\leq \int_{|x-y|<R} \frac{C}{1+|y_3|^3}\frac{|x_1-y_1|}{1+|x-y|^3}dy \\ &\quad + \int_{|x-y|<R} \frac{C}{1+|y_3|^3}\frac{|y_1|}{1+|y|^3}dy. \end{aligned}$$

$$\begin{aligned} |a(x)| &\leq \frac{C}{(|x_3|-R)^3}R\int_{|y'|<R}\frac{dy'}{1+|y'|^2} \\ &\quad + \frac{CR}{(|x_3|-R)^3}\int_{|x'-y'|<R}\frac{dy'}{1+|y'|^2} \\ &\leq \frac{CR\log R}{(|x_3|-R)^3}+\frac{CR^3}{(|x_3|-R)^3}\frac{1}{(|x|-R)^2} \\ &\leq \frac{C}{|x_3|}. \end{aligned} \tag{109}$$

Concerning $b(x)$, we split it again into two terms, writing :

$$\begin{aligned} b(x) &= \int_{|x-y|>R,|y|<R'} v_\Lambda(y)\left(\frac{1}{|x-y+e_1|}-\frac{1}{|x-y|}-\frac{y_1}{|y|^3}\right)dy \\ &\quad + \int_{|x-y|>R,|y|>R'} v_\Lambda(y)\left(\frac{1}{|x-y+e_1|}-\frac{1}{|x-y|}-\frac{y_1}{|y|^3}\right)dy, \end{aligned}$$

where $R' = |x|^\alpha$, for some $\alpha < 1$.

We call respectively $c(x)$ and $d(x)$ those two terms. In order to bound $c(x)$, we write, for $|y| < R' \ll |x|$:

$$\frac{1}{|x-y+e_1|}-\frac{1}{|x-y|} = \frac{-x_1}{|x|^3}+\frac{3}{2}\left(\frac{1-2x_1}{|x|^4}\right)+\frac{2y_1-1}{|x|^2}+O(\frac{R'^3}{|x|^3}). \tag{110}$$

This implies :

$$\left|\frac{1}{|x-y+e_1|}-\frac{1}{|x-y|}\right| \leq \frac{CR'}{|x|^2}+\frac{CR'^3}{|x|^3}.$$

On the other hand, we notice that (108) allows us to convert the term containing $\frac{y_1}{|y|^3}$ into

$$-\int_{|x-y|<R,|y|<R'} v_\Lambda(y)\frac{y_1}{|y|^3}dy,$$

and we have already bounded such a term when dealing with $a(x)$. So we have :

$$\begin{aligned} |c(x)| &\leq \int_{|y|<R'} \frac{1}{1+|y_3|^3}\frac{CR'}{|x|^2}dy + \int_{|y|<R'} \frac{1}{1+|y_3|^3}\frac{CR'^3}{|x|^3}dy \\ &\leq \frac{CR'}{|x|^2}\int_{|y'|<R'} dy' + \frac{CR'^3}{|x|^3}\int_{|y'|<R'} dy' \\ &\leq C(\frac{R'^3}{|x|^2} + \frac{R'^5}{|x|^3}) \\ &\leq \frac{C}{|x|^{2-3\alpha}} + \frac{C}{|x|^{3-5\alpha}}. \end{aligned} \tag{111}$$

We now turn to $d(x)$. Knowing that we have

$$\left|\frac{1}{|x-y+e_1|} - \frac{1}{|x-y|} + \frac{x_1-y_1}{|x-y|^3}\right| \leq \frac{C}{2+|x-y|^3}$$

on the set $\{|x-y|>R, |y|>R'\}$, we infer that :

$$\begin{aligned} |d(x)| &\leq \int_{|x-y|>R,|y|>R'} \frac{C}{(1+|y_3|^3)(2+|x-y|^3)}dy \\ &+ \int_{|x-y|>R,|y|>R'} \frac{C}{1+|y_3|^3}\frac{|x_1|}{|x-y|^3}dy \\ &+ \int_{|x-y|>R,|y|>R'} \frac{C}{1+|y_3|^3}\left|\frac{y_1}{|x-y|^3} - \frac{y_1}{|y|^3}\right|dy. \end{aligned} \tag{112}$$

Here we point out that bounding the second term, which we denote by $d_1(x)$, will be sufficient to bound the first one. In order to bound $d_1(x)$, we use the inequality $|x-y| \geq \big||x|-|y|\big|$, and write :

$$\begin{aligned} |d_1(x)| &\leq |x_1| \int_{|x-y|>R,|y|>R'} \frac{Cdy}{(1+|y_3|^3)(1+\big||x|-|y|\big|^3)} \\ &\leq \frac{|x|}{|x|^3}\int_{|\frac{x}{|x|}-z|>\frac{R}{|x|},|z|>\frac{R'}{|x|}} \frac{Cdz}{(1+|z_3|^3)(1+\big|1-|z|\big|^3)} \\ &\leq \frac{C}{|x|^2}, \end{aligned} \tag{113}$$

where we have set $y = |x|z$.

We now bound the third term of (112), which we call $d_2(x)$. In order to do so, we write :

$$\begin{aligned}
\left|\frac{y_1}{|x-y|^3}-\frac{y_1}{|y|^3}\right| &\leq |y_1|\left|\frac{|x-y|^4-|y|^4}{|x-y|^3|y|^3(|x-y|+|y|)}\right| \\
&\leq \frac{\big||x-y|^2-|y|^2\big|(|x-y|^2+|y|^2)}{|y|^2|x-y|^3(|x-y|+|y|)} \\
&\leq C\frac{|2xy-|x|^2|(|x-y|+|y|)}{|y|^2|x-y|^3} \\
&\leq C\frac{|x|(|y|+|x-y|)^2}{|y|^2|x-y|^3} \\
&\leq C|x|\left(\frac{1}{|x-y|^3}+\frac{1}{|y|^2|x-y|}\right).
\end{aligned}$$

Hence we see that $d_2(x)$ may be bounded by the sum of two terms, the first one being equivalent to $d_1(x)$, and the second one, which we call $d_3(x)$, being dealt with as follows :

$$\begin{aligned}
|d_3(x)| &\leq \int_{|x-y|>R,|y|>R'} \frac{C}{1+|y_3|^3}\frac{|x|}{1+|y|^2|x-y|}dy \\
&\leq \frac{|x|}{|x|^3}\int_{|\frac{x}{|x|}-z|>\frac{R}{|x|},|z|>\frac{R'}{|x|}} \frac{C}{1+|z_3|^3}\frac{dz}{1+|z|^2\big|1-|z|\big|} \\
&\leq \frac{C}{|x|^2}. \qquad (114)
\end{aligned}$$

Hence, collecting (112), (113) and (114), we find that

$$|d(x)| \leq \frac{C}{|x|^2}. \qquad (115)$$

Thus, gathering (115) and (111), we find that

$$|b(x)| \leq \frac{C}{|x|^{2-3\alpha}}+\frac{C}{|x|^{3-5\alpha}}+\frac{C}{|x|^2}.$$

Choosing now an α such that $\alpha \leq \frac{1}{3}$ and $\alpha \leq \frac{2}{5}$, we find that

$$|b(x)| \leq \frac{C}{|x|}. \qquad (116)$$

There only remains to collect (109) and (116) to conclude that (107) holds for ϕ_Λ. Now, since this bound is uniform with respect to Λ, ϕ inherits it. $\Diamond$

We now need a lower bound on u, which is the aim of the following proposition :

Proposition 3.7 *Let (u,ϕ) be a solution of (99), such that $u \in L^\infty(\mathbf{R}^3)$, $u \geq 0$, and $\phi \in L^1_{unif}(\mathbf{R}^3)$. Then for any $R>0$, there exists a constant $\nu>0$ such that $\inf_{|x_3|<R} u \geq \nu$.*

Proof : We follow exactly the steps of Proposition 2.12, and arguing by contradiction, build $\psi \in L^1_{unif}(\mathbf{R}^3)$ solution to :

$$-\Delta\psi = 4\pi\mu(\cdot + x^0). \tag{117}$$

This is exactly where the proof differs : we are going to use here again a scaling argument, but the scaling function needs to be chosen differently.

Let $\xi_0 \in C^\infty(\mathbf{R})$, such that $\xi_0 = 1$ on $[-1,1]$, $\xi_0 = 0$ on $[-2,2]^c$, $|\xi_0''| \leq 4$, and $0 \leq \xi_0 \leq 1$. Let $\eta_R : \mathbf{R} \longrightarrow \mathbf{R}$ be defined by follows :

- $\eta_R = 1$ on [-1,1].
- $\eta_R(t) = 1 + \frac{1-|t|}{R-1}$ if $1 < |t| < R$.
- $\eta_R = 0$ on $[-R,R]^c$.

We denote by ξ_R the function $\xi_R(x) = \eta_R(x_3)\xi_0(\frac{r}{R})$. And we compute :

$$\begin{aligned} < -\Delta\psi, \xi_R > &= 4\pi < m_\infty, \xi_R > \\ &= 4\pi \sum_{k\in\mathbf{Z}^2} < m(\cdot + k), \xi_0(\frac{r}{R}) > \\ &\geq 4\pi \sum_{k\in\mathbf{Z}^2, |k|\leq 2R} < m(\cdot + k), \xi_0(\frac{r}{R}) > \\ &\geq CR^2. \end{aligned} \tag{118}$$

On the other hand, we have, denoting by Ω_R the set $\{r < 2R, |x_3| < R\}$ and by ω_R the set $\{r < R, |x_3| < 1\}$:

$$\begin{aligned} < -\Delta\psi, \xi_R > &= \int_{\Omega_R\setminus\omega_R} \nabla\psi\nabla\xi_R \\ &= \int_{\Omega_R\setminus\omega_R} \psi(-\Delta\xi_R) + \int_{|x_3|=R, r<2R} \psi\frac{\partial\xi_R}{\partial n} + \int_{|x_3|=1, r<R} \psi\frac{\partial\xi_R}{\partial n}. \end{aligned}$$

Since $-\Delta\xi_R = -\eta_R(x_3)\Delta\xi_0(\frac{r}{R}) = \eta_R(x_3)(\frac{1}{rR}\xi_0'(\frac{r}{R}) - \frac{1}{R^2}\xi_0''(\frac{r}{R}))$, the first term may be dealt with as follows :

$$\begin{aligned} \left|\int_{\Omega_R\setminus\omega_R} \psi(-\Delta\xi_R)\right| &\leq \frac{1}{R^2}\int_{\Omega_R} |\psi| + \int_{\Omega_R\setminus\omega_R} \frac{|\psi(x)|}{rR}dx \\ &\leq C\frac{R^3}{R^2} + \frac{C}{R}\left(\int_{\Omega_R\setminus\omega_R} |\psi|^2\right)^{1/2}\left(\int_R^{2R} R\frac{dr}{r}\right)^{1/2} \\ &\leq CR + C\frac{R^{3/2}}{R}(R\log 2)^{1/2} \ll R^2. \end{aligned} \tag{119}$$

Concerning the remaining terms, we have :

$$\left|\int_{|x_3|=R,r<2R} \psi \frac{\partial \xi_R}{\partial x_3}\right| \leq \int_{|x_3|=R,r<2R} |\psi| \frac{C}{R} \leq C\frac{R^2}{R} \ll R^2. \tag{120}$$

And :

$$\left|\int_{|x_3|=1,r<R} \psi \frac{\partial \xi_R}{\partial x_3}\right| \leq \int_{|x_3|=1,r<R} |\psi| \frac{C}{R} \leq C\frac{R^2}{R} \ll R^2. \tag{121}$$

Hence, collecting (118), (119), (120) and (121), we infer that (117) is in contradiction with the belonging of ψ to L^1_{unif}. $\Diamond$

We now state a uniqueness lemma that will allow us to conclude that u and ϕ are periodic.

Lemma 3.8 *Let (u,ϕ) and (v,ψ) be solutions to the system (99), satisfying the following :*

(i) $u, v \in L^\infty(\mathbf{R}^3)$, and $\phi, \psi \in L^1_{unif}(\mathbf{R}^3)$.

(ii) There exists a function $U \in L^2(\mathbf{R})$ such that $|\phi - \psi| + |u - v| \leq U(x_3)$.

Then $u = v$ and $\phi = \psi$.

Proof : The firsts steps of the proof are exactly those of Lemma 2.15. We thereby skip it, and start with equation (64), that is :

$$\int_{\mathbf{R}^3} \nu w^2 \xi^2 \leq \int_{\mathbf{R}^3} w^2 |\nabla \xi|^2 + \frac{1}{2}\int_{\mathbf{R}^3} (\phi - \psi)^2 |\nabla \xi|^2, \tag{122}$$

where ν is a positive function depending only on x_3, $w = u - v$, and ξ is any smooth function with compact support.

We apply inequality (122) to a sequence ξ_n converging to ξ defined by follows :

- $\xi(x) = 1 - \frac{r^\alpha}{R^\alpha}$ on the set $\{r < R\}$.
- $\xi(x) = 0$ elsewhere.

where $R > 0$ and $\alpha > 0$. Hence (122) is valid for this choice of ξ. For such a ξ, we compute that

$$|\nabla \xi|^2 = \alpha^2 \frac{r^{2\alpha-2}}{R^{2\alpha}}.$$

So we have :

$$\begin{aligned} \int_{\mathbf{R}^3} \nu w^2 \xi^2 &\leq \frac{3}{2}\int_{\mathbf{R}^3} \alpha^2 \frac{r^{2\alpha-2}}{R^{2\alpha}} U(x_3)^2 \\ &\leq \frac{3}{2}\|U\|_{L^2(\mathbf{R})} \int_0^R \alpha^2 \frac{r^{2\alpha-1}}{R^{2\alpha}} 2\pi dr \\ &\leq \frac{3}{2}\|U\|_{L^2(\mathbf{R})} \alpha\pi. \end{aligned} \tag{123}$$

We let now R go to infinity, deducing, from the monotone convergence theorem, that we have :

$$\int_{\mathbf{R}^3} \nu w^2 \leq \frac{3}{2}\pi\alpha \|U\|_{L^2(\mathbf{R})}.$$

Since this holds for any $\alpha > 0$, we let now α go to zero, and find that :

$$\int_{\mathbf{R}^3} \nu w^2 = 0.$$

This implies that $w = 0$, since ν is positive, hence that $\phi = \psi$. $\Diamond$

3.2.3 Convergence and identification of the limit

We recall the periodic variational problem I_{per} :

$$I_{per} = \inf\{E_{per}(\rho),\ \sqrt{\rho} \in X_{per},\ \int_{\Gamma_0} \rho = 1\}, \tag{124}$$

where E_{per} and X_{per} are defined as follows :

$$X_{per} = \{v \in H^1_{per}(\Gamma_0),\ (1+|x|)^{\frac{1}{2}} v \in L^2(\Gamma_0)\}.$$

$$\begin{aligned} E_{per}(\rho) = \quad & \textstyle\int_{\Gamma_0} |\nabla\sqrt{\rho}|^2 \quad + \int_{\Gamma_0} \rho^{5/3} - \int_{\Gamma_0} (G \star_{\Gamma_0} m_\infty)\rho \\ & + \qquad \frac{1}{2}\int_{\Gamma_0}\int_{\Gamma_0} \rho(x)\rho(y)G(x-y)dxdy. \end{aligned}$$

We are now able to state the following theorem :

Theorem 3.9 *Let $\Lambda = \Lambda_2 \times \{0\}$ be a Van Hove sequence in the first two directions, that is, Λ_2 is supposed to be a Van Hove sequence of $\mathbf{Z}^2$. Assume in addition that Λ is symmetric both with respect to x_1 and with respect to x_2 (in the smeared nuclei case, we also assume that the measure m is symmetric with respect to x_1 and x_2). Denote by $\rho_\Lambda = u_\Lambda^2$ the solution of I_Λ. Then u_Λ converges to u_{per} in $H^1(\Gamma_0)$, $\rho_{per} = u_{per}^2$ being the minimizer of the periodic problem I_{per}. Moreover, we have the following estimates :*

(i) $u_{per}(x) \leq \frac{C}{1+|x_3|^{3/2}}$ for some constant $C > 0$.

(ii) There exists a positive function ν depending only on x_3 such that we have : $\nu \leq u_{per}$.

Proof : We know that $(u_\Lambda, \phi_\Lambda)$ is bounded in $H^1(\Gamma_0) \times L^p_{unif}(\mathbf{R}^3)$, for all $p < 3$. Hence we may pass locally to the limit in the system (90)-(91). Denoting by $(u, \phi) \in H^1(\Gamma_0) \times L^p_{unif}(\mathbf{R}^3)$ the corresponding limit, we find a solution to the system (99), that is :

$$\begin{cases} -\Delta u + \frac{5}{3}u^{7/3} - u\phi = 0, \\ -\Delta\phi = 4\pi(m_\infty - u^2). \end{cases}$$

From the a priori bounds shown in Theorem 3.1, which shows in particular that $u \leq \frac{C}{1+|x_3|^{3/2}}$, and from Proposition 3.6, we know that, applying Lemma 3.8, we find :

$$\tau_1 \phi = \phi.$$

On the other hand, all the symmetries being also satisfied with respect to x_2, we deduce, denoting by $\tau_2\phi$ the function $\phi(\cdot + e_2)$,

$$\tau_2 \phi = \phi.$$

This implies that ϕ, hence u, are periodic with periodic cell Γ_0.

From the estimate of Theorem 3.1, we also deduce that $u \in X_{per}$. We are now going to prove that

$$\int_{\Gamma_0} u^2 = 1. \tag{125}$$

In order to do so, we introduce the functions :

$$\psi(x_3) = \int_{[-\frac{1}{2},\frac{1}{2}]^2} \phi(x) dx_1 dx_2.$$

and

$$f(x_3) = \int_{[-\frac{1}{2},\frac{1}{2}]^2} 4\pi(m_\infty(x) - u(x)^2) dx_3.$$

Those functions satisfy the differential equation

$$-\psi'' = f,$$

since $\int_{[-\frac{1}{2},\frac{1}{2}]^2} \left(\frac{\partial^2 \phi}{\partial x_1^2} + \frac{\partial^2 \phi}{\partial x_2^2}\right) dx_1 dx_2 = 0$ from the periodicity of ϕ.

Furthermore, $\phi \in L^\infty(\{|x_3| > 1\})$, hence $\psi \in L^\infty([-1,1]^c)$, so from the estimates on u, we deduce that

$$\psi\psi'' \in L^1([-1,1]^c).$$

On the other hand, $\psi'(t) - \psi'(1) = \int_1^t f$, for all $t > 1$. Hence we infer that

$$\psi' \in L^\infty([1,\infty)).$$

Those two properties, together with the equality

$$\int_1^t \psi\psi'' = \psi(t)\psi'(t) - \psi(1)\psi'(1) - \int_1^t \psi'^2,$$

show that

$$\psi' \in L^2([1,\infty)).$$

Repeating the same argument for $t < -1$, replacing 1 by -1, we conclude that

$$\psi' \in L^2([-1,1]^c).$$

But ψ' has a limit at infinity, namely $\psi'(1) + \int_1^\infty f$, so this limit must be 0. The same results holds concerning its limit at $-\infty$, so that we have :

$$\int_{\mathbf{R}} \psi'' = \lim_{\infty} \psi' - \lim_{-\infty} \psi' = 0.$$

This implies $\int_{\Gamma_0} -\Delta\phi = 0$, hence (125).

The next step is to show that

$$\phi = G \star_{\Gamma_0} (m_\infty - u^2) + d, \tag{126}$$

for some $d \in \mathbf{R}$. Noticing that $\phi - G \star_{\Gamma_0} (m_\infty - u^2)$ is harmonic over $\mathbf{R}^3$, and periodic with periodic cell Γ_0, we conclude that it is sufficient to show that $G \star_{\Gamma_0} (m_\infty - u^2) \in L^1_{unif}(\Gamma_0)$. And from Lemma 2.9, we know that

$$\left(G(x) - \frac{1}{|x|} + 2\pi|x_3| \right) \in L^\infty(\Gamma_0).$$

So we only need to prove that

$$\frac{1}{|x|} \star_{\Gamma_0} (m_\infty - u^2) \in L^1_{unif}(\Gamma_0) \tag{127}$$

and

$$|x_3| \star_{\Gamma_0} (m_\infty - u^2) \in L^1_{unif}(\Gamma_0). \tag{128}$$

(127) has been shown in the course of Lemma 2.20, so we only provide a proof of (128) :

Since we already know that the convolution product arising in (128) lies in $L^1_{loc}(\Gamma_0)$, we only need to bound it as $|x_3| \to \infty$. (125) implies that we have :

$$\int_{\Gamma_0} (m_\infty - u^2)(y)|x_3 - y_3|dy = \int_{\Gamma_0} (m_\infty - u^2)(y)(|x_3 - y_3| - |x_3|)dy.$$

Letting $R = \sqrt{|x_3|}$, we have, for $|y_3| < R$, and $|x_3| \to \infty$,

$$|x_3 - y_3| - |x_3| = -y_3 + O(\frac{R^2}{|x_3|}) = -y_3 + O(1).$$

Hence we may write :

$$\begin{aligned} \left| |x_3| \star_{\Gamma_0} (m_\infty - u^2) \right| &\leq \int_{\Gamma_0 \cap \{|y_3| > R\}} |m_\infty - u^2|(y) \big| |x_3 - y_3| - |x_3| \big| dy \\ &\quad + \int_{\Gamma_0 \cap \{|y_3| < R\}} |m_\infty - u^2|(y)(|y_3| + C)dy \\ &\leq \int_{\Gamma_0 \cap \{|y_3| > R\}} |m_\infty - u^2|(y)|y_3 - x_3 + x_3|dy \\ &\quad + \int_{\Gamma_0 \cap \{|y_3| < R\}} C|m_\infty - u^2|(y)(1 + |y_3|)dy. \end{aligned}$$

Those two terms are bounded because $u \in X_{per}$, so this concludes the proof of (128), hence of (126).

Now, this implies that u^2 is a solution of the Euler-Lagrange equation of the problem I_{per}, namely :

$$-\Delta\sqrt{\rho} + \frac{5}{3}\rho^{7/6} - \left(G \star_{\Gamma_0} (m_\infty - \rho) + \theta_{per}\right)\sqrt{\rho} = 0.$$

(θ_{per} is the Lagrange multiplier associated with the constraint in I_{per}.)

On the other hand, the problem I_{per} is convex because D_G is, since it is bilinear and positive, on the set of the test-functions of I_{per}. So u is the solution of I_{per}, which is unique. Thus, the convergence does not only occur for a subsequence of u_Λ, but for the whole sequence. $\Diamond$

3.2.4 Convergence of the energy

This paragraph is the exact analog of the corresponding one in Section 2. We start with the definition of interior domains, which is exactly the same as in Section 2.

Definition 3.10 *Let $\Lambda \subset \mathbf{Z}^2 \times \{0\}$ be a Van Hove sequence in the first two directions. Λ' will be said to be a sequence of interior domains, denoted by $\Lambda' \subset\subset \Lambda$, if it satisfies the following properties :*

(i) $\Lambda' \subset \Lambda$.

(ii) *For any finite subset A of $\mathbf{Z}^2$, there exists an $h_0 \in \mathbf{N}$ such that $\forall h \geq h_0$, $A \subset \Lambda'_h$.*

(iii) $\frac{|\Lambda'|}{|\Lambda|} \longrightarrow 1$ *as* $\Lambda \to \infty$.

(iv) $d(\Lambda', \partial\Gamma(\Lambda)) \longrightarrow \infty$ *as* $\Lambda \to \infty$.

For now on, we assume that the sequence Λ satisfies the hypotheses of Theorem 3.9, that is, in addition to the Van Hove hypotheses, Λ is supposed to be symmetric with respect to x_1 and x_2, and so is m.

Next, we state the following theorem :

Theorem 3.11 *For any sequence $\Lambda' \subset\subset \Lambda$ and any $R > 0$, we have :*

$$\|u_\Lambda - u_{per}\|_{L^\infty(\Gamma(\Lambda'))} \longrightarrow 0, \tag{129}$$

$$\|\phi_\Lambda - \phi_{per}\|_{L^\infty(\Gamma(\Lambda') \cap \{|x_3| < R\})} \longrightarrow 0, \tag{130}$$

as $\Lambda \longrightarrow \infty$. (We recall that $\phi_{per} = G \star_{\Gamma_0} (m - u_{per}^2) - \theta_{per}$)

Proof : The proof starts exactly as that of Theorem 2.25, except that Theorem 2.16 is not available here. Hence, we slightly modify the proof in the following way : $\overline{u}_\Lambda$ will not be $u_\Lambda(\cdot + x_\Lambda)$, but :

$$\overline{u}_\Lambda = u_\Lambda(\cdot + (x_\Lambda)_3 e_3).$$

Hence, the same convergence argument hold, except that we notice that $\overline{m}_\Lambda = m_\Lambda(\cdot + (x_\Lambda)_3 e_3)$ defines a Van Hove sequence, since $x_\Lambda \in \Gamma(\Lambda')$, and that it is symmetric with respect to both x_1 and x_2. Hence the proof carries through, replacing the use of Theorem 2.16 by that of Theorem 3.9, or (equivalently) by the fact that I_{per} has a unique solution. $\Diamond$

We end up by stating the energy convergence Theorem for thin films :

Theorem 3.12 *For any Van Hove sequence, symmetric with respect to x_1 and x_2, we have :*

$$\frac{I_\Lambda}{|\Lambda|} \longrightarrow I_{per} + \frac{M}{2}$$

as $\Lambda \to \infty$.

Proof : Here again, the proof is not different from that of Theorem 2.26, the only thing to check being that we have :

$$|\nabla u_\Lambda| \leq \frac{C}{1 + |x_3|^{3/2}}.$$

And this easy to prove from elliptic regularity, together with the bounds we have on u_Λ and ϕ_Λ. $\Diamond$

4 The Yukawa case

We give here without proof some results that can be obtained on the Yukawa case.

Replacing the Coulombian interaction potential $\frac{1}{|x|}$ by the Yukawa potential defined in (11), we get :

$$\begin{cases} -\Delta u_\Lambda + \frac{5}{3} u_\Lambda^{7/3} - u_\Lambda \phi_\Lambda = 0, \\ -\Delta \phi_\Lambda + a^2 \phi_\Lambda = 4\pi(m_\Lambda - u_\Lambda^2), \\ u_\Lambda \geq 0. \end{cases} \tag{131}$$

The limit system (9) being modified in an analogous way. Next, we notice that in this system, we have added a coercive term in the second equation. This fundamental difference allows us to show stronger uniqueness results, as the following one :

Theorem 4.1 *Let μ be a nonnegative measure, having its support in the set $\{|x_3| < 1\}$, and satisfying the following :*

(H_1) $\sup_{x \in \mathbf{R}^2 \times \{0\}} \mu(B_1 + x) < +\infty$.

(H_2) $\lim_{R \to \infty} \inf_{x \in \mathbf{R}^2 \times \{0\}} \frac{\mu(B_R + x)}{R} = +\infty$.

Then the system

$$\begin{cases} -\Delta u + \frac{5}{3}u^{7/3} - \phi u = 0, \\ -\Delta\phi + a^2\phi = 4\pi(\mu - u^2), \\ u \geq 0. \end{cases} \tag{132}$$

has a unique solution (u, ϕ) *in the set*

$$\{(u,\phi) \in L^{7/3}_{loc} \cap L^2_{unif}(\mathbf{R}^3) \times L^1_{unif}(\mathbf{R}^3),\ \forall h > 0,\ \inf_{\{|x_3|<h\}} u > 0\}.$$

Furthermore, this solution belongs to $W^{2,p}_{unif}(\mathbf{R}^3) \times L^p_{unif}(\mathbf{R}^3)$ *for all* $p < 3$*, and there exists a constant* C *such that* $u \leq \frac{C}{1+|x_3|^{3/2}}$.

A similar theorem is also valid in the one-dimensional case. This implies that we have convergence results in both cases (namely thin films and polymers), at least for the density, provided the finite problem I_Λ with Yukawa potential has a unique solution ρ_Λ. This is the case for instance (see [6]) if a is small enough.

On the other hand, the use of the Yukawa potential destroys the compactness of the sequence ρ_Λ (in the sense of (23) and (92)). In fact, this potential is too weak at infinity to prevent some of the electrons from escaping at infinity. Thus, the periodic variational problems I_{per}, in addition to the potential change, will bear a different mass constraint.

Alternatively, in the spirit of the results displayed in [6], Chapter 4, we have :

Theorem 4.2 *(Here* Γ_0 *denotes* $]-\frac{1}{2},\frac{1}{2}]^2 \times \mathbf{R}$*, and* r *the cylindrical radius* $\sqrt{x_1^2+x_2^2}$*.) Let* $p > 1$*,* Γ *a* Γ_0*-periodic potential lying in* $L^q_{loc}(\mathbf{R}^3)$ *for some* $q > \frac{3p}{2p-2}$*, such that* $\Gamma^+ \leq \frac{C}{|x_3|^2}$ *as* $|x_3| \to \infty$*. Assume that there exists* $R > 0$ *such that the first eigenvalue of the operator* $-\Delta - \Gamma$ *with periodic boundary conditions with respect to* (x_1, x_2) *and homogeneous Dirichlet conditions with respect to* x_3 *on* $\Gamma_0 \cap \{|x_3| < R\}$ *is negative. Then the equation*

$$-\Delta u + u^p - \Gamma u = 0 \tag{133}$$

has a unique nonnegative non trivial solution in the set

$$\{u \in H^1_{loc}(\mathbf{R}^3) \,/\, \forall x \in \mathbf{R}^3, u \in H^1(\Gamma_0 + x)\}.$$

This solution satisfies :

$$u(x) \leq \frac{C}{1 + |x_3|^{\frac{2}{p-1}}},$$

for some constant $C > 0$.

Here again, a similar result may be stated in the one-dimensional case.

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Chapitre 3

Optimisation de géométrie pour les cristaux périodiques

Ce chapitre, écrit en collaboration avec C. Le Bris, présente l'étude du problème de l'optimisation de géométrie pour un cristal périodique dans le cadre de la théorie TFW des solides. Le corps du chapitre a été publié dans Communications in Partial Differential Equations [P3]. Nous incluons en préambule une note aux Comptes Rendus de l'Académie des Sciences [P2] qui présente l'ensemble des chapitres 2 et 3.

Optimisation de géométrie dans le cadre des théories de type Thomas-Fermi pour les cristaux périodiques

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Résumé. Nous présentons dans cette Note l'étude du problème de l'optimisation de géométrie pour un cristal périodique dans le cadre du modèle TFW, c'est-à-dire le problème de minimisation de l'énergie de ce modèle en fonction du réseau qui définit le cristal. Nous montrons l'existence d'un tel minimum, définissant au passage des modèles de polymères linéiques et de films minces pour cette théorie.

Geometry optimization
for Thomas-Fermi type theories for solids

Abstract. *We study here the problem of geometry optimization for a crystal in the TFW solid-state setting, i.e the problem of minimizing the TFW energy with respect to the periodic lattice defining the positions of the nuclei. We show the existence of such a minimum. One step of our work consists in derivating TFW-type models for polymers and thin films.*

Abridged English Version - We consider here the Thomas-Fermi-von Weizsäcker model of solids as defined in [9, 10], which associates to a periodic lattice ℓ of basis (a_1, a_2, a_3) an energy $\mathcal{E}(\ell)$, recalled in equations (1)-(4). We investigate the problem of minimizing the energy with respect to the periodic lattice, as stated in (5). Note that the energy we want to minimize here is an energy per cell, that is per unit mass. This is consistent with the fact that it is the energy per unit mass which allows to derive macroscopic elasticity constants [2].

Referring to Teller's Lemma (see [16] or [19]), it is possible to show that in the TF case, such a problem have no solution, whereas in the TFW case, the stability theorems proved

in [11] indicate that the question is relevant.

In [6], we show the following :

Theorem *Any minimizing sequence of problem (5) is compact, up to extracting a subsequence. Therefore, this problem has at least one solution.*

For this purpose, we first show that the radii $R_i^n = |a_i^n|$ of any basis (a_1^n, a_2^n, a_3^n) of a minimizing sequence ℓ_n are bounded away from 0. This is based on Teller's Lemma (see [19] or [16]), and on the fact that the TFW energy is bounded from below by the TF energy. Next, we use the results of [12] to bound away from 0 the angles between the vectors of the basis. Hence, there only remains to show that the sequence of radii is bounded from above. Then, noticing that we may assume, without loss of generality, that $R_1^n \leq R_2^n \leq R_3^n$ for all n, we first show that R_1^n must be bounded by investigating the behaviour of $\mathcal{E}(\ell_n)$ as R_1^n goes to infinity :

Proposition *As R_1^n goes to infinity, the energy $\mathcal{E}(\ell_n)$ converges to the energy I_{at}^{TFW} of the atomic TFW model defined in (6) and (7).*

The proof of this Proposition is based firstly on the fact that the potential defined in (4) does converge to the potential $\frac{1}{|x|}$, weakly in L^2_{loc}, and secondly on bounds we obtain on this potential and on the associated electronic density.

Furthermore, by taking a particular sequence (a_1^n, a_2^n, a_3^n) (see Proposition 3.5 below concerning its exact definition) satisfying $R_1^n \longrightarrow \infty$ as $n \to \infty$, it is possible to show the bound (9), where $C_0 > 0$ is a universal constant, and m is the square root of the Lagrange multiplier of problem (6)-(7). Now, it is shown in [15] that this multiplier is positive. Hence we have shown that for any minimizing sequence, R_1^n must be bounded from above.

The final step of the proof consists in showing that the radii R_2^n and R_3^n must be bounded. The strategy is basically the same, comparing here the energy with some polymers and thin film models defined respectively in (10)-(12), where the polymer is defined by a set of nuclei reading $\{ka, \quad k \in \mathbf{Z}\}$, and (13)-(15), where the set of nuclei is $\{ka + jb, \quad k, j \in \mathbf{Z}\}$. In both cases, the energy reads exactly like (2)-(3). We derivate these models from a thermodynamic limit process and we show that they are mathematically well-posed in [7]. The same type of convergence as that of the above Proposition holds in this case, together with estimates of type (9). This concludes the proof of the Theorem.

It is to be emphasized that no additionnal property of the minimizer is known (uniqueness, symmetry, ...) and that many related questions remain open.

1 Introduction

Dans [9, 10], des modèles de type Thomas-Fermi-von Weizsäcker pour les cristaux ont été étudiés et justifiés par un procédé de limite thermodynamique à partir des modèles moléculaires correspondants. Fixant la position des noyaux par le choix d'un réseau périodique de $\mathbf{R}^3$, l'énergie fondamentale du cristal et la densité électronique associées sont définies comme les solutions d'un problème de minimisation posé sur la maille élémentaire du réseau. Une telle étude fait suite à des travaux analogues menés dans le cadre Thomas-Fermi

par E.H. Lieb et B. Simon [15, 16]. Nous nous intéressons ici au problème d'optimisation de géométrie dans ce cadre, c'est-à-dire, considérant l'énergie fondamentale comme une fonction du réseau définissant les positions des noyaux, nous nous posons la question de savoir s'il existe un réseau minimisant cette énergie. Nous considérons ici l'énergie par noyau, i.e par unité de masse du point de vue macroscopique, ce qui correspond à l'idée physique de considérer un nombre fixé (mais très grand) de particules, et de chercher le meilleur arrangement possible de ces particules en les supposant réparties périodiquement. Cette énergie massique permet en particulier de déterminer au niveau microscopique des constantes d'élasticité du cristal (voir [2]).

Considérant le théorème de Teller (voir [19] ou [16]), selon lequel aucun système moléculaire n'est stable dans le cadre de la théorie de Thomas-Fermi (TF en abrégé), il est possible de montrer (nous en fournirons une preuve dans [6]) que l'existence d'un tel réseau optimal ne peut avoir lieu dans le cadre TF. En revanche, dans le cas de la théorie de Thomas-Fermi-von Weizsäcker (TFW), les théorèmes de stabilité des molécules établis par I. Catto et P.-L. Lions [11] rendent pertinente l'étude d'une telle question. Bien que la généralisation au modèle Thomas-Fermi-Dirac-von Weizsäcker soit envisageable, nous nous restreindrons ici au cas TFW.

2 Le modèle de Thomas-Fermi-von Weizsäcker pour les cristaux

On représente un réseau périodique propre ℓ, i.e un sous-groupe discret de $\mathbf{R}^3$ engendré par trois vecteurs libres, par une base (a_1, a_2, a_3) de ce réseau vérifiant les propriétés suivantes :

(i) Les rayons $R_i = |a_i|, \quad i = 1, 2, 3$ satisfont $R_1 \leq R_2 \leq R_3$,

(ii) Les angles α_{ij} entre a_i et a_j sont tous dans l'intervalle $[\frac{\pi}{3}, \frac{\pi}{2}]$ pour $i \neq j$.

Nous renvoyons à [12] pour une preuve de l'existence d'une telle représentation. Nous noterons $\Gamma(\ell)$ la cellule périodique du réseau associée a cette base, i.e le domaine défini par :

$$\Gamma(\ell) = \left\{ xa_1 + ya_2 + za_3, \quad x, y, z \in [-\frac{1}{2}, \frac{1}{2}[\right\} \tag{1}$$

Fixant un tel réseau, nous définissons à l'aide de [9, 10] l'énergie TFW qui lui est associée :

$$\mathcal{E}(\ell) = \inf\left\{ E_\ell(\rho), \quad \rho \geq 0, \quad \sqrt{\rho} \in H^1_{per}(\Gamma(\ell)), \int_{\Gamma(\ell)} \rho = 1 \right\}, \tag{2}$$

où l'énergie E_ℓ est définie par :

$$E_\ell(\rho) = \int_{\Gamma(\ell)} |\nabla\sqrt{\rho}|^2 + \int_{\Gamma(\ell)} \rho^{5/3} - \int_{\Gamma(\ell)} G_\ell \rho + \frac{1}{2} \iint_{\Gamma(\ell)^2} G_\ell(x-y)\rho(x)\rho(y)dxdy, \tag{3}$$

et le potentiel d'interaction G_ℓ est l'unique solution ℓ-périodique du système :

$$\left\{ \begin{array}{l} -\Delta G_\ell = (\sum_{k\in\ell}\delta_k) - \frac{1}{|\Gamma(\ell)|}, \\ \lim_{x\to 0} G_\ell(x) - \frac{1}{|x|} = 0, \end{array} \right. \tag{4}$$

où $|\Gamma(\ell)|$ désigne le volume de la cellule $\Gamma(\ell)$. Pour ce qui concerne l'existence de $\mathcal{E}(\ell)$ et de sa solution ρ_ℓ, nous renvoyons à [9]. Nous étudions donc le problème de minimisation suivant :

$$I = \inf\left\{ \mathcal{E}(\ell), \ell \in \mathcal{L}_3(\mathbf{R}^3) \right\}, \tag{5}$$

où nous désignons par $\mathcal{L}_3(\mathbf{R}^3)$ l'ensemble des réseaux propres de $\mathbf{R}^3$.

3 Résultat et esquisse de démonstration

Nous démontrons dans [6] le résultat suivant :

Theorem 3.3 *Les suites minimisantes du problème (5) sont compactes à extraction près. En conséquence, ce problème admet au moins une solution.*

La première des choses à démontrer est que pour toute suite minimisante ℓ_n définie par $R^n = (R_1^n, R_2^n, R_3^n)$ et $\alpha^n = (\alpha_{23}^n, \alpha_{13}^n, \alpha_{12}^n)$ satisfaisant (i) et (ii) ci-dessus, il existe un rayon minimal r_0 tel que :

$$\forall n \in \mathbf{N}, \quad R_1^n \geq r_0.$$

Cette propriété se démontre essentiellement en minorant l'énergie TFW du cristal par son énergie TF, et en utilisant le théorème de Teller.

Ensuite, puisque α^n varie dans un compact ne contenant ni 0 ni π, il suffit donc de montrer que R^n est bornée. Pour cela, on commence par examiner la limite de l'énergie quand R_1^n tend vers $+\infty$:

Proposition 3.4 *Si R_1^n tend vers $+\infty$, alors $\mathcal{E}(\ell_n)$ tend vers l'énergie du modèle atomique TFW, à savoir :*

$$I_{at}^{TFW} = \inf\left\{ E_{at}^{TFW}(\rho), \quad \rho \geq 0, \quad \sqrt{\rho} \in H^1(\mathbf{R}^3), \quad \int_{\mathbf{R}^3} \rho = 1 \right\}, \tag{6}$$

$$E_{at}^{TFW}(\rho) = \int_{\mathbf{R}^3} |\nabla\sqrt{\rho}|^2 + \int_{\mathbf{R}^3} \rho^{5/3} - \int_{\mathbf{R}^3} \frac{\rho}{|x|} + \frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3} \frac{\rho(x)\rho(y)}{|x-y|} dxdy. \tag{7}$$

De plus, la densité électronique associée ρ_n converge vers l'unique minimiseur ρ_{at} de I_{at}^{TFW}.

Pour établir cette proposition, on commence par démontrer que la convergence faible suivante a lieu pour le potentiel $G_n = G_{\ell_n}$:

$$G_n \rightharpoonup \frac{1}{|x|} \quad \text{dans} \quad L^2_{loc}(\mathbf{R}^3), \quad \text{quand} \quad n \to \infty, \tag{8}$$

ce qui se fait en utilisant l'expression de G_n sous forme de série de Fourier. Comme cette convergence n'est pas suffisante pour passer à la limite dans l'expression de l'énergie, on établit ensuite des bornes asymptotiques sur la densité électronique ρ_n, dans l'esprit de [18], et sur G_n, qui permettent de contrôler les restes d'intégrales apparaissant dans les termes électrostatiques. Grâce à ces bornes, il est alors possible de passer à la limite dans l'énergie. La suite ρ_n apparaissant alors comme une suite minimisante (à restriction près) du problème atomique TFW, on obtient aussi sa convergence.

Ayant ainsi identifié la limite de $\mathcal{E}(\ell_n)$, nous montrons alors l'existence d'un réseau propre dont l'énergie est strictement inférieure à celle du modèle atomique :

Proposition 3.5 *Si* $\alpha^n = (\frac{\pi}{2}, \frac{\pi}{2}, \frac{\pi}{2})$ *et* $R_1^n = R_2^n = R_3^n \longrightarrow \infty$, *alors, pour* n *grand, on a :*

$$\mathcal{E}(\ell_n) \leq I_{at}^{TFW} - mC_0 e^{-mR_1^n} + o(e^{-mR_1^n}), \tag{9}$$

avec $C_0 > 0$, *et* $m = \sqrt{\theta_{at}}$, θ_{at} *étant le multiplicateur de Lagrange associé à* ρ_{at} *solution de* I_{at}^{TFW}.

Comme il a été montré dans [15] que $\theta_{at} > 0$, cette proposition permet alors de conclure que l'hypothèse de la proposition 3.4 ne peut être satisfaite pour une suite minimisante. La suite R_1^n est donc nécessairement bornée.

Il reste ensuite à établir de la même façon que les deux dernières composantes de R^n sont elles aussi nécessairement bornées. Pour cela, on utilise la même stratégie, en considérant des modèles de polymères linéiques (noté I_{pol}^{TFW}) et de films minces (noté I_{film}^{TFW}). Dans [7], nous définissons ces modèles avec précision sous une forme académique, bien que de nombreuses variantes soient possibles, en les justifiant par un procédé de limite thermodynamique, et nous prouvons qu'ils sont mathématiquement bien posés. Nous les introduisons ici rapidement :

Étant donné un réseau monodimensionnel ℓ de $\mathbf{R}^3$ défini par le vecteur a, on pose :

$$I_{pol}^{TFW}(\ell) = \mathcal{E}(\ell) = \inf\left\{ E_\ell(\rho), \quad \rho \geq 0, \quad \sqrt{\rho} \in H^1_{per}(\Gamma(\ell)), \quad \log(2+|x|)\rho \in L^1(\Gamma(\ell)) \right\}, \tag{10}$$

$$\Gamma(\ell) = \left\{ ta + x, \quad -\frac{1}{2} \leq t < \frac{1}{2}, \quad x \in \{a\}^\perp \right\}, \tag{11}$$

où E_ℓ s'écrit exactement comme (3), en transposant les notations, et en utilisant le potentiel défini par :

$$\begin{cases} -\Delta G_\ell = \sum_{k \in \mathbf{Z}} \delta_{ka}, \\ \lim_{x \to 0} (G_\ell(x) - \frac{1}{|x|}) = 0, \\ G_\ell(x) \sim -\frac{2}{|a|} \log |x'| \quad \text{quand} \quad |x'| \to \infty, \end{cases} \tag{12}$$

où $x' = x \wedge \frac{a}{|a|}$.

Le modèle I_{pol}^{TFW} est défini de la même façon : étant donné deux vecteurs libres (a,b) définissant un réseau bidimensionnel de $\mathbf{R}^3$, toujours noté ℓ,

$$I_{film}^{TFW}(\ell) = \mathcal{E}(\ell) = \inf\left\{ E_\ell(\rho), \quad \rho \geq 0, \quad \sqrt{\rho} \in H^1_{per}(\Gamma(\ell)), \quad |x|\rho \in L^1(\Gamma(\ell)) \right\}, \tag{13}$$

$$\Gamma(\ell) = \left\{ ta + sb + x, \quad t,s \in [-\frac{1}{2}, \frac{1}{2}[, \quad x \in \{a,b\}^\perp \right\}, \tag{14}$$

avec un potentiel G_ℓ défini par :

$$\left\{ \begin{array}{l} -\Delta G_\ell = \sum_{k,j\in\mathbf{Z}} \delta_{ka+jb}, \\ \lim_{x\to 0}(G_\ell(x) - \frac{1}{|x|}) = 0, \\ G_\ell(x) \sim -\frac{2\pi}{|a\wedge b|}|x''| \quad \text{quand} |x''| \to \infty, \end{array} \right. \tag{15}$$

où x'' est défini par : $x'' = x \cdot \frac{a\wedge b}{|a\wedge b|}$.

Il est alors possible d'établir les mêmes résultats de convergence que celui de la Proposition 3.4 :

Proposition 3.6 *Nous avons les propriétés suivantes :*

(i) Si R_1^n tend vers R_1 et si R_2^n tend vers $+\infty$ quand n tend vers $+\infty$, alors $\mathcal{E}(\ell_n)$ converge vers l'énergie $I_{pol}^{TFW}(R_1)$ d'un polymère linéique dont les noyaux sont espacés de la distance R_1.

(ii) Si (R_1^n, R_2^n) tend vers (R_1, R_2) et si α_{12}^n tend vers α_{12}, alors $\mathcal{E}(\ell_n)$ converge vers l'énergie $I_{film}^{TFW}(R_1, R_2, \alpha_{12})$ d'un film mince dont les noyaux sont répartis sur le réseau bidimensionnel défini par (R_1, R_2, α_{12}).

Après quoi on conclut, en établissant un résultat similaire à celui de la proposition 3.5, et qui nécessite d'établir la stricte positivité du multiplicateur pour ces modèles de polymères et films minces. Le théorème 3.3 est alors démontré.

Remarquons également que le théorème 3.3 assure l'existence d'un réseau périodique minimisant, mais ne fournit absolument aucun renseignement sur ses propriétés (symétries, invariances) ni sur son unicité, à part le fait qu'il s'agit d'un réseau propre. Des approches numériques pourraient peut-être répondre partiellement à ces questions.

L'existence d'un réseau minimisant pose la question d'un problème de type limite thermodynamique à géométrie optimisée : au lieu de considérer au départ des noyaux répartis sur certains points d'un réseau périodique, on considère un nombre N de noyaux répartis de telle façon que l'énergie de la molécule qu'ils forment soit minimale (voir [11]). La répartition des noyaux devient-elle périodique à la limite $N \to \infty$, et si oui, le réseau limite est-il un minimiseur du problème ci-dessus ? De telles questions restent ouvertes.

Geometry Optimization for crystals in Thomas-Fermi type theories of solids

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Abstract. We study here the problem of geometry optimization for a crystal in the TFW solid-state setting, i.e the problem of minimizing the TFW energy with respect to the periodic lattice defining the positions of the nuclei. We show the existence of such a minimum, and use for that purpose the TFW models of polymers and thin films defined in a previous work [7].

1 Introduction

We are interested here in the Thomas-Fermi-Von Weizsäcker (TFW) theory of solids, and more precisely in the geometry optimization problem, which may be stated in the following way : given the energy functional which to a periodic lattice associates its TFW energy (defined in [9]), does there exist a periodic lattice minimizing this energy ?

Let ℓ be a proper periodic lattice of $\mathbf{R}^3$, that is, a subgroup of $(\mathbf{R}^3,+)$ generated by three linearly independent vectors a, b, and c. We define the TFW energy of this lattice with respect to basis (a,b,c), i.e the TFW energy of a neutral crystal of lattice ℓ, with each nucleus of charge $+1$:

$$\mathcal{E}(\ell) = \inf\left\{ E^{TFW}_{(a,b,c)}(\rho), \quad \rho \geq 0, \quad \sqrt{\rho} \in H^1_{per}(\ell), \quad \int_{\Gamma_{(a,b,c)}} \rho = 1 \right\}, \tag{16}$$

where we used the following notation :

$$\Gamma_{(a,b,c)} = \left\{ ta + sb + rc, \quad t,r,s \in [-\frac{1}{2}, \frac{1}{2}[\right\}, \tag{17}$$

$$H^1_{per}(\ell) = \left\{ f \in H^1_{loc}(\mathbf{R}^3), \quad f \quad \text{is} \quad \ell - \text{periodic} \right\}, \tag{18}$$

and, skipping here the subscript (a,b,c) for $\Gamma_{(a,b,c)} = \Gamma$:

$$E^{TFW}_{(a,b,c)}(\rho) = \int_\Gamma |\nabla\sqrt{\rho}|^2 + \int_\Gamma \rho^{5/3} - \int_\Gamma G_\ell \rho + \int_\Gamma \int_\Gamma \rho(x)\rho(y) G_\ell(x-y)dxdy, \tag{19}$$

the potential G_ℓ being the ℓ-periodic solution of :

$$\begin{cases} -\Delta G_\ell = 4\pi\big((\sum_{k\in\ell}\delta_k) - \frac{1}{|\Gamma_{(a,b,c)}|}\big), \\ \lim_{x\to 0}\big(G_\ell(x) - \frac{1}{|x|}\big) = 0. \end{cases} \tag{20}$$

A preliminary observation is that these notations do not depend on the choice of the basis (a,b,c). This is stated in Proposition 2.2 below : equations (16), (19) and (20) do not depend on the choice of a basis of ℓ, but only on ℓ.

We now make precise the problem we are studying : denoting by $\mathcal{L}_3(\mathbf{R}^3)$ the set of proper periodic lattices of $\mathbf{R}^3$, does the problem

$$\mathcal{I} = \inf\left\{ \mathcal{E}(\ell), \quad \ell \in \mathcal{L}_3(\mathbf{R}^3) \right\} \tag{21}$$

have a solution ?

Our main result is :

Theorem 1.1 *Any minimizing sequence of problem (21) is relatively compact. Therefore, this problem has at least one solution.*

In order to show this result, we begin with recalling in Section 3 the definition and basic properties of what we call degenerate cases of the above solid state theory (16)-(19), namely the atomic model (26)-(27), and the linear polymer (31)-(33) and thin film (62)-(64) models. We refer to [4] and [11] for a study of the atomic model, and to [7] for a study of polymer and thin film models. Moreover, we show in Section 3 some further results similar to those of [11] : in particular we show the positiveness of the associated Lagrange multiplier, and give sharp estimates on the decay at infinity of the density. These estimates will be of crucial importance in the sequel.

In Section 4, we investigate the behavior of the minimizing sequences of problem (21). Up to rather technical complications that will be dealt with below but that we prefer to skip in this simplified presentation, it is sufficient to consider minimizing sequences of the form :

$$\ell_n = \left\{ iR_1^n a + jR_2^n b + kR_3^n c, \quad i,j,k \in \mathbf{Z} \right\}, \tag{22}$$

with $0 < R_1^n \leq R_2^n \leq R_3^n$, and (a,b,c) is a fixed basis such that $|a| = |b| = |c| = 1$.

Hence, showing Theorem 1.1 amounts to prove that R_i^n is bounded both from above and away from 0, for all $i = 1,2,3$. For this purpose, we show the following proposition :

Proposition 1.2

(i) If R_1^n goes to infinity as n goes to infinity, then the energy $\mathcal{E}(\ell_n)$ converges to the atomic TFW energy.

(ii) If R_1^n converges to some $R_1 > 0$, and R_2^n goes to infinity as n goes to infinity, then $\mathcal{E}(\ell_n)$ converges to the TFW energy of a linear polymer defined by $R_1 a$.

(iii) If (R_1^n, R_2^n) goes to (R_1, R_2), with $R_1, R_2 > 0$, and R_3^n goes to infinity as n goes to infinity, then $\mathcal{E}(\ell_n)$ converges to the TFW energy of a thin film defined by $(R_1 a, R_2 b)$.

Once this proposition is proved, we show with the help of the results of Section 3 that for any of the atomic, polymer and solid film TFW energies, there exists a proper lattice having strictly lower energy than those limits. This is done in Section 5, through the fact that the limits of Proposition 1.2 are asymptotically approached from below. Note that the positiveness of the Lagrange multiplier plays a key-role here. We also show in this Section, in order to complete the proof of Theorem 1.1, that the radii R_i^n are bounded away from 0, with the help of Teller's Lemma [15]. As a by-product of these proofs, we finally prove that in TF theory, any proper lattice has greater energy than the atomic TF energy, which shows that the analogue of problem (21) in the TF setting has no solution. This corroborates the fact that our whole argument in the TFW case is based on the positiveness of the Lagrange multiplier in the degenerate problems (atomic, polymer and solid film cases). Indeed, one may check that in the atomic TF model, the Lagrange multiplier is 0.

Remark 1.3 *Let us point out that here, we have used a different normalization than in [15] and [10, 9] for the potential G_ℓ. This is due to the fact that the constant M appearing in [15] and [10, 9] depends in fact on ℓ. Our renormalization (20) cancels M, or more precisely includes it in the expression of G_ℓ. This allows us to write $\mathcal{E}(\ell)$ as the exact limit of the energy per nuclei in the thermodynamic limit process, as may be seen in (99).*

Let us mention that the results detailed here have been announced in [8].

2 Notation and representation of lattices

Throughout this paper, we will use the following notation :

Definition 2.1

(i) A subset ℓ of $\mathbf{R}^3$ will be said to be a proper lattice, or a lattice of dimension 3 (or of rank 3), if there exists three independent vectors (a, b, c) such that $\ell = \{ia + jb + kc, \quad i, j, k \in \mathbf{Z}\}$. We denote by $\mathcal{L}_3(\mathbf{R}^3)$ the set of proper lattices of $\mathbf{R}^3$.

(ii) A subset of $\mathbf{R}^3$ of the form $\{ia + jb, \quad i, j \in \mathbf{Z}\}$, with a, b linearly independent will be called a lattice of dimension 2. The set of 2-dimensional lattices will be denoted by $\mathcal{L}_2(\mathbf{R}^3)$.

(iii) A subset ℓ of $\mathbf{R}^3$ will be said to be a lattice of dimension 1 if there exists $a \in \mathbf{R}^3 \setminus \{0\}$ such that $\ell = \{ia, \ i \in \mathbf{Z}\}$. We denote by $\mathcal{L}_1(\mathbf{R}^3)$ the set of lattices of dimension 1.

Identifying $\mathcal{L}_3(\mathbf{R}^3)$ with the quotient group $GL_3(\mathbf{R})/GL_3(\mathbf{Z})$, we define on $\mathcal{L}_3(\mathbf{R}^3)$ a topology. (We denote by $GL_3(\mathbf{Z})$ the set of matrices belonging to $GL_3(\mathbf{R})$, having integer entries, and such that their inverse have integer entries.) For this topology, $\mathcal{L}_3(\mathbf{R}^3)$ is a separated locally compact manifold. After having checked out that $\mathcal{E}$ is well-defined on $\mathcal{L}_3(\mathbf{R}^3)$, we then study its continuity on this manifold :

Proposition 2.2 *The function $\mathcal{E}$ defined in (16) and the potential defined in (20) do not depend on the choice of the basis (a, b, c).*

Proof : We choose two different basis (a, b, c) and (a', b', c') of the same proper lattice ℓ, and denote respectively by $\mathcal{E}$ and $\mathcal{E}'$ the associated energy. We know that there exists M in $GL_3(\mathbf{Z})$ such that $a' = Ma$, $b' = Mb$, and $c' = Mc$. M being invertible in the set $M_3(\mathbf{Z})$ of integer 3×3-matrices, its determinant must be invertible in $\mathbf{Z}$, so we have :

$$|\det M| = 1.$$

This implies in particular that $|\Gamma_{(a,b,c)}| = |\Gamma_{(a',b',c')}|$, so that the potential defined from (a, b, c) in (20) must be equal to the one defined by (a', b', c'). Next, we notice that for any ℓ-periodic function f, we have :

$$\int_{\Gamma_{(a,b,c)}} f = \int_{\Gamma_{(a',b',c')}} f.$$

This implies, for any $\rho \geq 0$ such that $\sqrt{\rho} \in H^1_{per}(\ell)$:

$$E^{TFW}_{(a,b,c)}(\rho) = E^{TFW}_{(a',b',c')}(\rho), \tag{23}$$

and

$$\int_{\Gamma_{(a,b,c)}} \rho = \int_{\Gamma_{(a',b',c')}} \rho. \tag{24}$$

(23) and (24) then imply that $\mathcal{E} = \mathcal{E}'$. $\Diamond$

Remark 2.3 *Note that one easily proves in the same fashion that for any orthogonal matrix M, the energy is unchanged under M, that is, $\mathcal{E}(\ell) = \mathcal{E}(M\ell)$. This will be useful in the sequel.*

Note also that up to minor modifications, Proposition 2.2 also holds for polymers and thin films models defined in Section 3.

Now that the function $\mathcal{E}$ is well-defined, we may show that it is continuous :

Proposition 2.4 *The function $\mathcal{E}$ is continuous with respect to the quotient topology of $\mathcal{L}_3(\mathbf{R}^3)$.*

Proof : The only thing to show here is that $\mathcal{E}$ is continuous as a function defined on $GL_3(\mathbf{R})$. This is easy to do by changing variables in the expression of $E^{TFW}_{(a,b,c)}$ and noticing that if (a,b,c) is close enough to (a',b',c'), then the norm $\|G_\ell - G_{\ell'}\|_{L^1(\Gamma_{(a,b,c)} \cup \Gamma_{(a',b',c')})}$ is small. (Here we denote by ℓ and ℓ' respectively the lattices of basis (a,b,c) and (a',b',c').) $\Diamond$

We now state a result on the representation of a lattice by one of its basis, referring to [12] for its proof :

Theorem 2.5 (Engel, [12]) *For any periodic lattice ℓ of rank 3, there exists a basis (a,b,c) of ℓ such that :*

$$\begin{cases} |a| \leq |b| \leq |c|, \\ \widehat{(a,b)}, \widehat{(a,c)}, \widehat{(b,c)} \in [\frac{\pi}{3}, \frac{\pi}{2}], \end{cases} \tag{25}$$

where $\widehat{(x,y)}$ denotes the angle between x and y.

We thus see that, according to Proposition 2.2 and Theorem 2.5, we may reduce any minimizing sequence to the form (22), up to the fact that (a,b,c) will not be fixed but satisfy conditions (25).

3 Preliminary results on the degenerate cases

We recall in this section the definitions of what we call here the degenerate models, namely thin film models, polymers models and atomic model in the TFW setting. We refer to [7] concerning precisions on the first two models, and to [15] and [11] for the latter. In the thin film and polymer cases, we also show further results, mainly on the asymptotic behavior of the density far away from the nuclei.

3.1 TFW theory of atoms

We first recall the definition and the main properties of the TFW theory of atoms : the ground state of an atom consisting of a point nucleus of charge +1 located at 0 and of an electron is determined by its electronic density, unique solution of the problem :

$$I_{at}^{TFW} = \inf\left\{ E_{at}^{TFW}(\rho), \quad \rho \geq 0, \quad \sqrt{\rho} \in H^1(\mathbf{R}^3), \quad \int_{\mathbf{R}^3} \rho = 1 \right\}, \tag{26}$$

where the energy functional E_{at}^{TFW} is defined by :

$$E_{at}^{TFW}(\rho) = \int_{\mathbf{R}^3} |\nabla\sqrt{\rho}|^2 + \int_{\mathbf{R}^3} \rho^{5/3} - \int_{\mathbf{R}^3} \frac{\rho}{|x|} + \frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3} \frac{\rho(x)\rho(y)}{|x-y|} dxdy. \tag{27}$$

Problem (26) has a unique solution ρ_{at} (see [15] or [4]), which is positive, and which square root $u_{at} = \sqrt{\rho_{at}}$ satisfies the following Euler-Lagrange equation, with a Lagrange multiplier $\theta = \theta_{at} > 0$:

$$-\Delta u_{at} + \frac{5}{3}u_{at}^{7/3} + \big(-\frac{1}{|x|} + u_{at}^2 \star \frac{1}{|x|}\big)u_{at} + \theta_{at}u_{at} = 0. \tag{28}$$

It is shown in [11] that the following estimates hold :

$$\rho_{at}(x) \sim \frac{a}{|x|^2} e^{-2\sqrt{\theta}|x|}, \quad \text{as} \quad |x| \longrightarrow \infty, \tag{29}$$

where a is a positive constant. The effective potential $\phi_{at} = \frac{1}{|x|} - \rho_{at} \star \frac{1}{|x|}$ satisfies :

$$\phi_{at}(x) \sim \frac{\pi a}{\theta|x|^2} e^{-2\sqrt{\theta}|x|}, \quad \text{as} \quad |x| \longrightarrow \infty. \tag{30}$$

3.2 TFW theory of polymers

We now consider the TFW model of polymers, as defined in [7], and which we recall here. Considering a periodic lattice of rank 1, that is some $\ell \in \mathcal{L}_1(\mathbf{R}^3)$, we may assume with no loss of generality that it is located on the vertical axis; that is, $\ell = \mathbf{Z}Re_3$, with $R \in \mathbf{R}_+^*$. We define its TFW energy as follows :

$$\begin{aligned} \mathcal{E}(\ell) = I_{pol}^{TFW}(\ell) \quad &= \quad \inf\Big\{ E_\ell^{TFW}(\rho), \quad \rho \geq 0, \quad \sqrt{\rho} \in H^1_{per}(\ell), \\ &\qquad \log(2+|x|)\rho \in L^1(\Gamma(\ell)), \quad \int_{\Gamma(\ell)} \rho = 1 \Big\}, \end{aligned} \tag{31}$$

where $\Gamma(\ell) = \{x \in \mathbf{R}^3, \quad x_3 \in [-\frac{R}{2}, \frac{R}{2}[\}$,

$$H^1_{per}(\ell) = \Big\{ f \in H^1_{loc}(\mathbf{R}^3) \cap H^1(\Gamma(\ell)), \quad f \quad \text{is} \quad \ell - \text{periodic} \Big\},$$

and the energy E_ℓ^{TFW} reads :

$$\begin{aligned} E_\ell^{TFW}(\rho) &= \int_{\Gamma(\ell)} |\nabla\sqrt{\rho}|^2 + \int_{\Gamma(\ell)} \rho^{5/3} - \int_{\Gamma(\ell)} G_\ell \rho \\ &+ \int_{\Gamma(\ell)} \int_{\Gamma(\ell)} \rho(x)\rho(y) G_\ell(x-y) dxdy, \end{aligned} \tag{32}$$

the periodic potential G_ℓ being defined by :

$$\begin{aligned} G_\ell(x) &= C_\ell - \frac{2}{R}\log|x'| + \sum_{k\in\ell}\left(\frac{1}{|x-ke_3|} - \frac{1}{R}\int_{-\frac{R}{2}}^{\frac{R}{2}} \frac{dt}{|x-(k+t)e_3|}\right) \\ &= C_\ell - \frac{2}{R}\log|x'| + \frac{1}{\pi R}\sum_{k\in\mathbf{Z}\setminus\{0\}} \int_{\mathbf{R}^2} \frac{e^{2i\pi(\frac{k}{R}x_3 + x'\cdot\xi)}}{\frac{k^2}{R^2}+|\xi|^2} d\xi, \end{aligned} \tag{33}$$

the constant C_ℓ being chosen so that we have $\lim_{x\to 0}(G_\ell(x) - \frac{1}{|x|}) = 0$, and x' denoting the vector (x_1, x_2). We recall a few properties of the potential G_ℓ shown in [7] :

Proposition 3.1 *We have :*

(i) G_ℓ *is smooth on* $\mathbf{R}^3 \setminus \ell$,

(ii) $G_\ell(x) = \frac{1}{|x|} + O(|x|)$ *as* $x \to 0$,

(iii) $G_\ell(x) = -\frac{2}{R}\log|x'| + C_\ell + O(\frac{1}{|x'|})$ *as* $|x'| \to \infty$, *uniformly with respect to* x_3.

We now show the following :

Proposition 3.2 *For any* $R > 0$, *the problem (31) has a unique solution* ρ_ℓ. *The function* $u_\ell = \sqrt{\rho_\ell}$ *is a solution of :*

$$-\Delta u_\ell + \frac{5}{3}u_\ell^{7/3} + (u_\ell^2 \star_{\Gamma(\ell)} G_\ell - G_\ell)u_\ell + \theta_\ell u_\ell = 0, \tag{34}$$

where $\star_{\Gamma(\ell)}$ *denotes the convolution product over the set* $\Gamma(\ell)$. *Moreover, the Lagrange multiplier* θ_ℓ *is positive.*

Proof : We refer to [7] for the proof of the existence and uniqueness of ρ_ℓ. Moreover, we recognize in (34) the Euler-Lagrange equation of problem (31). We now prove that θ_ℓ is positive.

Denoting by ϕ_ℓ the function

$$\phi_\ell = G_\ell - u_\ell^2 \star_{\Gamma_\ell} G_\ell,$$

it is possible to show the following a priori estimates (see [7], Proposition 2.5) :

$$0 < u_\ell \leq \frac{C}{1+|x'|^{3/2}}, \tag{35}$$

$$\phi_\ell - \theta_\ell \leq \frac{C}{1+|x'|^2} \quad \text{on} \quad \{|x'|>1\}. \tag{36}$$

We claim that

$$\phi_\ell \longrightarrow 0 \quad \text{as} \quad |x'| \to \infty. \tag{37}$$

In order prove our claim, we denote by G^0_ℓ the potential $G_\ell - C_\ell$, and notice that we have :

$$\phi_\ell = G^0_\ell - u^2_\ell \star_{\Gamma(\ell)} G^0_\ell.$$

Hence, we have :

$$\begin{aligned}
\phi_\ell(x) &= \int_{\Gamma(\ell)} (G^0_\ell(x) - G^0_\ell(x-y))u^2_\ell(y)dy, \\
&= \int_{\Gamma(\ell)\cap\{|y'|<|x'|^{1/2}\}} (G^0_\ell(x) - G^0_\ell(x-y))u^2_\ell(y)dy \\
&\quad + \int_{\Gamma(\ell)\cap\{|y'|>|x'|^{1/2}\}} (G^0_\ell(x) - G^0_\ell(x-y))u^2_\ell(y)dy.
\end{aligned}$$

If $|y'| < |x'|^{1/2} \ll |x'|$ as $|x'| \to \infty$, we have, from Proposition 3.1-(iii) :

$$G^0_\ell(x) - G^0_\ell(x-y) = -\frac{2}{R}\Big(\log(|x'|) - \log(|x'-y'|)\Big) + O(\frac{1}{|x'|}).$$

Developing this expression with respect to $\frac{|y|}{|x'|}$, we find :

$$\left|\int_{\Gamma(\ell)\cap\{|y'|<|x'|^{1/2}\}} \Big(G^0_\ell(x) - G^0_\ell(x-y)\Big)u^2_\ell(y)dy\right| \leq \frac{C}{|x'|^{1/2}}. \tag{38}$$

In order to deal with the second term, we use (35) and show that :

$$\left|\int_{\Gamma(\ell)\cap\{|y'|>|x'|^{1/2}\}} \Big(G^0_\ell(x) - G^0_\ell(x-y)\Big)u^2_\ell(y)dy\right| \leq \frac{C\log|x'|}{|x'|}.$$

This, together with (38), proves (37). Using estimate (36), we infer that

$$\theta_\ell \geq 0.$$

We assume from now on that we have $\theta_\ell = 0$, and try to reach a contradiction, which will conclude the proof.

Since there is no ambiguity here, we skip the subscript ℓ for the rest of the proof. From the uniqueness of u and the definition of ϕ, these functions depend on x' only through $|x'| = r$. We set

$$\overline{\phi}(r) = \frac{1}{R}\int_{-\frac{R}{2}}^{\frac{R}{2}} \phi(r, x_3)dx_3,$$

and

$$\overline{\rho}(r) = \frac{1}{R}\int_{-\frac{R}{2}}^{\frac{R}{2}} \rho(r, x_3)dx_3.$$

From the definition of ϕ, we have :

$$-\overline{\phi}'' - \frac{1}{r}\overline{\phi}' = -4\pi\overline{\rho}$$

on $\mathbf{R}_+ \setminus \{0\}$. Hence, using (35) :

$$0 \leq (r\overline{\phi}')' \leq \frac{C}{r^2}. \tag{39}$$

This shows that $(r\overline{\phi}')'$ is integrable on a neighborhood of $+\infty$. We now integrate (39) from $r > 0$ to ∞, and get :

$$r\overline{\phi}'(r) - \lim_{t\to\infty}(t\overline{\phi}'(t)) \leq 0.$$

Denoting by l the limit $\lim_{t\to\infty}(t\overline{\phi}'(t))$, which exists in virtue of (39), and assuming it to be different from 0, we deduce that $\overline{\phi}'(t) \sim \frac{l}{t}$ as t goes to infinity. This implies that $\overline{\phi}$ goes to $\pm\infty$ at infinity, which is a contradiction with estimate (36). Hence, $\overline{\phi}'$ is non-positive at infinity, which implies, in view of (37), that

$$\overline{\phi} \geq 0 \quad \text{for} \quad r \geq r_0. \tag{40}$$

It follows that :

$$\exists R_0 > 0, \quad \forall r \geq R_0, \quad \exists x_3 \in [-\frac{R}{2}, \frac{R}{2}[, \quad \phi(r, x_3) \geq 0. \tag{41}$$

On the other hand, we have, using Hölder estimates, for any ball B of radius 1, and any $v \in C^{2,\alpha}(B)$ for some $\alpha > 0$, (see [14] or [13])

$$\|\nabla v\|_{C^0(\frac{1}{2}B)} \leq \gamma\Big(\|\Delta v\|_{C^0(B)} + \|v\|_{C^0(B)}\Big),$$

where $\frac{1}{2}B$ denotes the ball of radius $\frac{1}{2}$ having the same center as B, and γ being a universal constant. Hence, from a scaling argument, we deduce that for any ball B_a of radius $a > 0$, and any $v \in C^{2,\alpha}(B_a)$,

$$\|\nabla v\|_{C^0(\frac{1}{2}B_a)} \leq \gamma\Big(a\|\Delta v\|_{C^0(B_a)} + \frac{1}{a}\|v\|_{C^0(B_a)}\Big). \tag{42}$$

Applying this inequality to ϕ, we find, for any ball B_a of radius $a > 0$ not containing 0 :

$$\|\nabla \phi\|_{C^0(\frac{1}{2}B_a)} \leq \gamma\Big(a\|\rho\|_{C^0(B_a)} + \frac{1}{a}\|\phi\|_{C^0(B_a)}\Big). \tag{43}$$

Using estimate (35) and the fact that ϕ is periodic and bounded as $r \to \infty$, and applying (43) with $a = \frac{|x|}{2}$, B_a centered at x, we thus find :

$$|\nabla \phi| \leq \frac{C}{r} \quad \text{as} \quad r \longrightarrow \infty.$$

In particular, we have this bound on $|\partial_3 \phi|$. Hence, from property (41), we infer that :

$$\phi(x) \geq -\frac{CR}{r} \quad \text{as} \quad r \longrightarrow \infty.$$

Inserting this information in (43), and using again (41), we find that $\phi \geq -\frac{C}{r^2}$ for sufficiently large r, hence, again from (36) :

$$|\phi(x)| \leq \frac{C}{r^2} \quad \text{as} \quad r \longrightarrow \infty.$$

We now apply again (43) on ϕ, but with $B_a = B_{\sqrt{r}}(x)$, and find that $\phi \geq -\frac{C}{r^{5/2}}$. Hence, using (36), we have :

$$-\frac{C}{r^{5/2}} \leq \phi(x) \leq \frac{C}{r^2} \quad \text{as} \quad r \to \infty. \tag{44}$$

With this result, we are going to show that $V = \frac{5}{3}u^{4/3} - \phi \leq \frac{1}{r^2}$.

This estimate, in the spirit of a work by Benguria and Yarur [5], will imply that $u \geq \frac{C}{r}$, which contradicts (35).

In view of equations (34) and (44), and the fact that $\theta = 0$, we infer that

$$-\Delta u + \frac{5}{3}u^{7/3} \geq -\frac{C}{r^4},$$

on the set $\{r > r_0\}$, for some $r_0 > 0$. Hence, denoting by u_0 the function $\frac{3}{10r^{3/2}}$, one computes easily :

$$-\Delta(u - u_0) + \frac{5}{3}(u^{7/3} - {u_0}^{7/3}) \geq (\frac{9}{4} - \frac{5}{3}(\frac{3}{10})^{7/3})\frac{1}{r^{7/2}} - \frac{C}{r^4}. \tag{45}$$

Since $\frac{9}{4} - \frac{5}{3}(\frac{3}{10})^{7/3} > 0$, it is then clear that there exists an $r_1 > 0$ such that on the set $\{r > r_1\}$, $v = u - u_0$ satisfies the following :

$$\Delta v \leq \frac{5}{3}(u^{7/3} - {u_0}^{7/3}).$$

Defining $F = \{r > r_1\} \cap \{v < 0\}$, we now show the following assertions :

(a) F is unbounded,

(b) F has no bounded connected component strictly included in $\{r > r_1\}$.

In order to show (a), we assume that F is bounded, and notice that then there exists r_2 such that $v \geq 0$ on $\{r > r_2\}$. Hence, on this set,

$$\Delta\phi \geq \frac{6\pi}{5r^3}.$$

This means in particular :

$$(r\overline{\phi}')' \geq \frac{6\pi}{5r^2}.$$

Integrating this inequality from r to $+\infty$, one finds $\overline{\phi}' \leq -\frac{6\pi}{5r^2}$, hence

$$\overline{\phi} \geq \frac{6\pi}{5r},$$

which is in contradiction with estimate (36).

We now show (b) by supposing that F has at least one bounded connected component F_0 such that $\{r = r_1\} \cap F_0 = \emptyset$. On F_0, $\Delta v < 0$, and $v = 0$ on ∂F_0. Hence from the maximum principle, v must be non-negative on F_0, which is contradictory.

Using (a) and (b), we deduce that (41) holds for $-v$:

$$\exists R_0 > 0, \quad \forall r \geq R_0, \quad \exists x_3 \in [-\frac{R}{2}, \frac{R}{2}[, \quad u(r, x_3) \leq \frac{3}{10r^{3/2}}.$$

Now, from the equation satisfied by u, it is clearly possible to show, using the same Hölder estimate as for ϕ, that

$$|\partial_3 u| \leq \frac{C}{r^{5/2}}.$$

This implies that, as $r \to \infty$, $u \leq \frac{3}{5r^{3/2}}$, and in particular :

$$V = \frac{5}{3}u^{4/3} - \phi \leq \frac{1}{r^2}.$$

The final step of the proof is merely a copy of Benguria and Yarur's proof [5] : $\overline{u}(r) = \int_{-\frac{R}{2}}^{\frac{R}{2}} u(r, x_3)dx_3$ satisfies :

$$-\overline{u}'' - \frac{1}{r}\overline{u}' + \frac{1}{r^2}\overline{u} \geq 0,$$

whenever $r > R_1$, for some $R_1 > 0$. Denoting by w the function $\overline{u} - \frac{\alpha}{r}$, where α is chosen so that $w > 0$ somewhere in $]R_1, \infty[$, we see that

$$-w'' - \frac{1}{r}w' + \frac{1}{r^2}w \geq 0 \tag{46}$$

on this set. And if w is negative at some point of $]R_1, \infty[$, it must have a negative minimum, which is in contradiction with (46). This shows that $u \geq \frac{C}{r}$. This is in contradiction with (35). $\Diamond$

Proposition 3.3 *The unique solution ρ_ℓ of problem (31) satisfies the following, where $a_\ell > 0$ depends only on ℓ :*

$$\rho_\ell(r, x_3) \sim a_\ell \frac{e^{-2\sqrt{\theta_\ell} r}}{r}, \quad as \quad r \longrightarrow \infty. \tag{47}$$

Moreover, setting $\phi_\ell = G_\ell - G_\ell \star_{\Gamma(\ell)} \rho_\ell$ the effective potential, there exists a finite set of complex numbers λ_k depending only on ℓ such that :

$$\left| \phi_\ell(r, x_3) - \sum_{0<\pi|k|\leq R\sqrt{\theta_\ell}} \lambda_k e^{2i\pi \frac{k}{R} x_3} W_{2\pi\frac{|k|}{R}}(r) \right| \leq b_{\ell,\epsilon} \frac{e^{-(2\sqrt{\theta_\ell}-\epsilon)r}}{\sqrt{r}}, \quad as \quad r \longrightarrow \infty, \tag{48}$$

for all $\epsilon > 0$. The constant $b_{\ell,\epsilon} > 0$ depends only on ℓ and ϵ, and W_a denotes the Yukawa potential of parameter $a > 0$ in $\mathbf{R}^2$, i.e the solution of $-\Delta f + a^2 f = 4\pi\delta_0$ in $\mathbf{R}^2$ vanishing at infinity.

Proof : We begin with a few properties of the Yukawa potential W_a of $\mathbf{R}^2$, with $a > 0$: W_a is the unique solution vanishing at infinity of :

$$-\Delta W_a + a^2 W_a = 4\pi\delta_0. \tag{49}$$

The potential W_a is spherically symmetric and satisfies the differential equation :

$$W_a'' + \frac{1}{r} W_a' - a^2 W_a = 0$$

on $\mathbf{R}_*^+$. Here $'$ denotes the radial derivative in $\mathbf{R}^2$. For all the following properties, we use the notation of [1], in which one may find these results. We refer to [20] concerning their proofs. The modified Bessel functions I_0 and K_0 are defined by :

$$I_0(t) = \sum_{n\geq 0} \left(\frac{t^n}{2^n n!} \right)^2,$$

$$K_0(t) = -\big(\log(\frac{t}{2}) + \gamma\big) I_0(t) + \sum_{n\geq 1} \left(\sum_{j=1}^{n} \frac{1}{j} \right) \left(\frac{t^n}{2^n n!} \right)^2,$$

where $\gamma = \lim_{n\to\infty} (\sum_{j=1}^{n} \frac{1}{j} - \log n)$ denotes the Euler constant. We have :

(a) The potential W_a is equal to the modified Bessel function K_0 :

$$W_a(t) = 2K_0(at).$$

(b) We denote by $\overline{W}_a$ the potential

$$\overline{W}_a(t) = 2K_0(at) + 2\pi I_0(at).$$

It is a solution of (49).

(c) The functions W_a and $\overline{W}_a$ are respectively decreasing and increasing, and satisfy the following estimates :

$$\begin{cases} W_a(t) \sim \sqrt{\frac{2\pi}{a}}\frac{e^{-at}}{\sqrt{t}} & \text{as} \quad t \to \infty, \\ W_a(t) \sim -2\log(t) & \text{as} \quad t \to 0. \end{cases} \tag{50}$$

$$\begin{cases} \overline{W}_a(t) \sim \sqrt{\frac{2\pi}{a}}\frac{e^{at}}{\sqrt{t}} & \text{as} \quad t \to \infty, \\ \overline{W}_a(t) \sim -2\log(t) & \text{as} \quad r \to 0. \end{cases} \tag{51}$$

$$\overline{W}_a' W_a - W_a' \overline{W}_a = \frac{4\pi}{t}. \tag{52}$$

Keeping these results in mind, we may now begin our proof.

We denote by V_ℓ the ℓ-periodic Yukawa potential with parameter $\sqrt{\theta_\ell}$:

$$V_\ell(x) = \sum_{k \in \ell} \frac{e^{-\sqrt{\theta_\ell}|x-k|}}{|x-k|}. \tag{53}$$

Comparing it with $W_{\sqrt{\theta_\ell}}(r)$, where $r = \sqrt{x_1^2 + x_2^2}$, and noticing that

$$W_{\sqrt{\theta_\ell}}(r) = \int_{\mathbf{R}} \frac{e^{-\sqrt{\theta}_\ell(r^2+z^2)}}{\sqrt{r^2+z^2}} dz,$$

one shows through a basic computation that $\frac{V_\ell}{W_{\sqrt{\theta_\ell}}} \to 1$ as $r \to \infty$, hence :

$$V_\ell(x) \sim \left(\sqrt{\frac{2\pi}{\sqrt{\theta_\ell}}}\right)\frac{e^{-\sqrt{\theta}_\ell r}}{\sqrt{r}}, \tag{54}$$

as r goes to infinity.

Denoting by f_ℓ the function $\frac{5}{3}{u_\ell}^{4/3} - \phi_\ell$, and using the bounds we have on u_ℓ and ϕ_ℓ, namely (35) and (44), we deduce that

$$|f_\ell| \leq \frac{C}{r^2}, \tag{55}$$

on $\{r > R_0\}$, for some $R_0 > 0$. Hence, we have there

$$-\Delta u_\ell + (\theta_\ell - \frac{C}{r^2})u_\ell \leq -\Delta u_\ell + (f_\ell + \theta_\ell)u_\ell = 0.$$

Now, denoting by v the function $\frac{e^{-\sqrt{\theta_\ell}r}}{\sqrt{r}}e^{-\mu/r}$, one easily finds that :

$$-\Delta v + (\theta_\ell - \frac{C}{r^2})v = (\frac{2\mu\sqrt{\theta_\ell} - \frac{1}{4} - C}{r^2} + \frac{2\mu}{r^3} - \frac{\mu^2}{r^4})v.$$

Hence, choosing $\mu > \frac{4C+1}{8\sqrt{\theta_\ell}}$, we have :

$$-\Delta v + (\theta_\ell - \frac{C}{r^2})v \geq 0$$

on some set $\{r > R_1\}$. Next, by a similar computation, setting $w(x) = \sqrt{R}\frac{e^{\sqrt{\theta_\ell}(|x|-R)}}{|x|}e^{-\frac{\mu}{|x|}}$, one easily shows w satisfies the same estimate. Hence, taking $v + w$ as a supersolution, and letting then R go to infinity, one can show that this implies :

$$u_\ell \leq Cv,$$

for some constant $C > 0$. In particular, we have

$$u_\ell \leq \frac{a}{\sqrt{r}}e^{-\sqrt{\theta_\ell}r}, \quad \text{at} \quad \text{infinity}, \tag{56}$$

for some $a > 0$. Now, an easy computation, in the spirit of [11], Proposition A.1, shows that, from this estimate, together with (54) and (55), we have :

$$(-f_\ell u_\ell) \star_{\Gamma(\ell)} V_\ell \sim \sqrt{a_\ell}\frac{e^{-\sqrt{\theta_\ell}r}}{\sqrt{r}}, \quad \text{as} \quad r \to \infty,$$

with $\sqrt{a_\ell} = \frac{1}{2\pi}\int_0^{2\pi} e^{\sqrt{\theta_\ell}\cos\theta}d\theta \int_{\Gamma(\ell)} -f_\ell u_\ell$. Note that this right-hand side is positive, since $-f_\ell u_\ell = -\Delta u_\ell + \theta_\ell u_\ell$. Hence, convoluting $-\Delta u_\ell + \theta_\ell u_\ell = -f_\ell u_\ell$ on both sides with V_ℓ, one finds (47).

We now prove (48) : we define a partial periodic Fourier transform by :

$$\tilde{f}(x', k) = \int_{-\frac{R}{2}}^{\frac{R}{2}} f(x)e^{-2i\pi\frac{k}{R}x_3}dx_3, \tag{57}$$

for any L^2_{loc} and ℓ-periodic function f. Applying this to ϕ_ℓ, and using the fact that $-\Delta\phi_\ell = 4\pi(\delta_0 - \rho_\ell)$ in $\Gamma(\ell)$, one finds :

$$-\Delta_T\tilde{\phi}_\ell(x', k) + 4\pi^2\frac{k^2}{R^2}\tilde{\phi}_\ell(x', k) = 4\pi(\delta_{r=0} - \tilde{\rho}_\ell(x', k)), \tag{58}$$

for all $k \in \mathbf{Z}$, where Δ_T denotes the Laplacian with respect to x'. We first notice that

$$|\tilde{\phi}_\ell(x', 0)| \leq C\frac{e^{-2\sqrt{\theta}_\ell r}}{r}, \tag{59}$$

since $\tilde{\phi}_\ell(\cdot, 0)$ is a radially symmetric function in $\mathbf{R}^2$ satisfying $(r\tilde{\phi}_\ell(r, 0)')' \sim a_\ell e^{-2\sqrt{\theta}_\ell r}$. Moreover, if $|k| \neq 0$, convoluting (58) with $W_{2\pi\frac{|k|}{R}}$, we have :

$$\tilde{\phi}_\ell = W_{2\pi\frac{|k|}{R}} - W_{2\pi\frac{|k|}{R}} \star_{\mathbf{R}^2} \tilde{\rho}_\ell.$$

We use here the following Lemma, which proof is postponed until the end of the present one :

Lemma 3.4 *Let a be a positive real, and let W_a and $\overline{W}_a$ be the potentials defined in (a) and (b) above. Then, for any spherically symmetric function $v \in L^1_{loc}(\mathbf{R}^2)$ such that $vW_a \in L^1(\mathbf{R}^2)$ and v has a trace on any circle of $\mathbf{R}^2$, we have :*

$$v \star W_a(x) = 8\pi^2 \left[\overline{W}_a(x) \int_{|y|>|x|} vW_a + W_a(x) \left(\int_{|y|<|x|} v\overline{W}_a - \int_{\mathbf{R}^2} vW_a \right) \right]. \qquad (60)$$

Applying this result to $a = 2\pi\frac{|k|}{R}$ and $v = \tilde{\rho}_\ell(\cdot, k)$, which is spherically symmetric in $\mathbf{R}^2$, and using estimates (47), (50) and (51), one easily finds :

$$\left(W_{2\pi\frac{|k|}{R}} \star_{\mathbf{R}^2} \tilde{\rho}_\ell \right)(r) = \left(\int_{\mathbf{R}^2} \tilde{\rho}_\ell \overline{W}_{2\pi\frac{|k|}{R}} \right) W_{2\pi\frac{|k|}{R}}(r) + O\left(\int_{|x'|>r} \tilde{\rho}_\ell \right),$$

whenever $2\pi\frac{|k|}{R} < 2\sqrt{\theta_\ell}$. Thus, for such a k, setting $\lambda_k = \frac{1}{R} - \frac{1}{R}\int_{\mathbf{R}^2} \tilde{\rho}_\ell \overline{W}_{2\pi\frac{|k|}{R}}$,

$$\begin{aligned} \tilde{\phi}_\ell(x', k) &= R\lambda_k W_{2\pi\frac{|k|}{R}}(r) e^{2i\pi\frac{kx_3}{R}} + O\left(\int_{|x'|>r} \tilde{\rho}_\ell \right) \\ &= R\lambda_k W_{2\pi\frac{|k|}{R}}(r) e^{2i\pi\frac{kx_3}{R}} + O\left(\frac{e^{-2\sqrt{\theta_\ell} r}}{\sqrt{r}} \right). \end{aligned}$$

We next use Plancherel's formula and write :

$$\begin{aligned} \phi_\ell(x) &= \sum_{k\in\mathbf{Z}} \frac{1}{R} \tilde{\phi}_\ell(x', k) e^{2i\pi\frac{kx_3}{R}} \\ &= \sum_{0<\pi|k|\le R\sqrt{\theta_\ell}} \lambda_k W_{2\pi\frac{|k|}{R}}(r) e^{2i\pi\frac{kx_3}{R}} + \sum_{\pi|k|>R\sqrt{\theta_\ell}} \frac{1}{R} \tilde{\phi}_\ell(x', k) e^{2i\pi\frac{kx_3}{R}} \\ &\quad + O\left(\frac{e^{-2\sqrt{\theta_\ell} r}}{\sqrt{r}} \right). \end{aligned}$$

Denoting by ψ_ℓ the function

$$\psi_\ell = \sum_{\pi|k|>R\sqrt{\theta_\ell}} \frac{1}{R} \tilde{\phi}_\ell(x', k) e^{2i\pi\frac{k}{R}x_3},$$

proving (48) amounts to show that

$$|\psi_\ell| \le C_\epsilon \frac{e^{-(2\sqrt{\theta_\ell}-\epsilon)r}}{\sqrt{r}},$$

for all $\epsilon > 0$. For this purpose, we notice that, using (60) again, we have, for all $|k| > \frac{R\sqrt{\theta_\ell}}{\pi}$:

$$|\tilde{\psi}_\ell(x', k)| = |\tilde{\phi}_\ell(x', k)| \le C \frac{e^{-2\sqrt{\theta_\ell} r}}{\sqrt{r}}.$$

On the other hand, from the fact that $\Delta\psi_\ell$ is smooth and that ψ_ℓ is bounded on $\{r>1\}$, ψ_ℓ is bounded in $C^p(\Gamma(\ell)\cap\{r>1\})$, for all $p\in\mathbf{N}$, so that we have :

$$|\tilde{\psi}_\ell(x',k)|\leq C_p\frac{1}{|k|^p},$$

for all $p>0$, with C_p depending only on p. Those two bounds, together with the definition of ψ_ℓ, allow to write, for any $\beta<1$:

$$\begin{aligned}\int_{r=R_0}|\psi_\ell|^2dx_3 &= \frac{1}{R}\sum_{\pi|k|>R\sqrt{\theta}_\ell}|\tilde{\psi}(R_0,k)|^2\\ &\leq C\frac{e^{-4\beta\sqrt{\theta}_\ell R_0}}{R_0}\sum_{\pi|k|>\sqrt{\theta}_\ell}\frac{C_p^{(2-2\beta)}}{|k|^{p(2-2\beta)}}+O(\frac{e^{-4\sqrt{\theta}_\ell R_0}}{R_0}).\end{aligned}$$

This is valid for all R_0 sufficiently large. We then choose $\beta=1-\frac{\epsilon}{2\sqrt{\theta}_\ell}$ and $p>\frac{1}{2-2\beta}$, and finally conclude through elliptic regularity and the fact that $|\Delta\psi_\ell|\leq C\frac{e^{-\sqrt{\theta_\ell}r}}{\sqrt{r}}$. $\Diamond$

Proof of Lemma 3.4 : We denote by $F(x)$ the function defined in (60). F is spherically symmetric, and using estimates (c) above, one easily shows that F vanishes at infinity. Hence, it is sufficient to prove that $-\Delta F+a^2F=8\pi^2v$. For this purpose, we notice that :

$$-\Delta F=-F''-\frac{1}{|x|}F'.$$

We then compute :

$$F'(|x|)=\overline{W}_a'(|x|)\int_{|y|>|x|}vW_a+W_a'(|x|)\Big(\int_{|y|<|x|}v\overline{W}_a-\int_{\mathbf{R}^n}vW_a\Big).$$

Thus, we have :

$$\begin{aligned}-\Delta F &= -\Delta\overline{W}_a\int_{|y|>|x|}vW_a-\Delta W_a\Big(\int_{|y|<|x|}v\overline{W}_a-\int_{\mathbf{R}^n}vW_a\Big)\\ &\quad+\overline{W}_a'\int_{|y|=|x|}vW_a-W_a'\int_{|y|=|x|}v\overline{W}_a.\end{aligned}$$

This implies the following :

$$-\Delta F+a^2F=v2\pi|x|(\overline{W}_a'W_a-W_a'\overline{W}_a).$$

We then use (52) and conclude the proof. $\Diamond$

Estimate (48) has been proved for ϕ_ℓ, but what will be really useful is the same estimate on the partial derivative $\partial_r\phi_\ell$, with $r=\sqrt{x_1^2+x_2^2}$. Since the estimates we have used on ρ_ℓ also hold for $\partial_r\rho_\ell$, an easy adaptation of Proposition 3.3 shows :

Proposition 3.5 *Let ρ_ℓ be the unique solution of problem (31), and $\phi_\ell = G_\ell - G_\ell \star_{\Gamma(\ell)} \rho_\ell$. There exists a finite set of complex numbers μ_k depending only on ℓ such that :*

$$\left| \partial_r \phi_\ell(r, x_3) - \sum_{0<\pi|k|\leq R\sqrt{\theta}_\ell} \mu_k e^{2i\pi \frac{k}{R} x_3} W_{2\pi\frac{|k|}{R}}(r) \right| \leq b'_{\ell,\epsilon} \frac{e^{-(2\sqrt{\theta}_\ell - \epsilon)r}}{\sqrt{r}}, \quad as \quad r \to \infty, \tag{61}$$

for all $\epsilon > 0$, the constant $b'_{\ell,\epsilon}$ depending only on ℓ and ϵ.

3.3 TFW theory of thin films

We recall the TFW model for thin films defined in [7] : considering a periodic lattice ℓ of rank 2, we may assume that it is included in the plane generated by the two first vectors of the canonical basis (e_1, e_2, e_3). In other words, there exists $R_1 > 0$ and $b = b_1 e_1 + b_2 e_2$, such that $a = R_1 e_1$ and b generate ℓ :

$$\ell = \{ia + jb, \quad i, j \in \mathbf{Z}^2\}.$$

We define its TFW energy by :

$$\begin{aligned} \mathcal{E}(\ell) = I^{TFW}_{film} &= \Big\{ E^{TFW}_\ell(\rho), \quad \rho \geq 0, \quad , \sqrt{\rho} \in H^1_{per}(\ell), \\ &\qquad (1 + |x_3|)\rho \in L^1(\Gamma(\ell)), \quad \int_{\Gamma(\ell)} \rho = 1 \Big\}, \end{aligned} \tag{62}$$

where $\Gamma(\ell) = \{ua + vb + we_3, \quad u, v \in [-\frac{1}{2}, \frac{1}{2}[, \quad w \in \mathbf{R}\}$,

$$H^1_{per}(\ell) = \Big\{ f \in H^1_{loc}(\mathbf{R}^3) \cap H^1(\Gamma(\ell)), \quad f \quad \text{is} \quad \ell - \text{periodic} \Big\},$$

and the energy E^{TFW}_ℓ reads :

$$\begin{aligned} E^{TFW}_\ell(\rho) &= \int_{\Gamma(\ell)} |\nabla\sqrt{\rho}|^2 + \int_{\Gamma(\ell)} \rho^{5/3} - \int_{\Gamma(\ell)} G_\ell \rho \\ &+ \int_{\Gamma(\ell)} \int_{\Gamma(\ell)} \rho(x)\rho(y) G_\ell(x-y) dx dy, \end{aligned} \tag{63}$$

the periodic potential G_ℓ being the analogue of (33), with $a \wedge b$ denoting the inner product of the two vectors a and b :

$$\begin{aligned} G_\ell(x) &= C_\ell - \frac{2\pi}{|a \wedge b|}|x_3| + \sum_{k \in \ell} \left(\frac{1}{|x-k|} - \frac{1}{|a \wedge b|} \int_{\Gamma(\ell) \cap \{x_3 = 0\}} \frac{dy}{|x - k - y|} \right) \\ &= C_\ell - \frac{2\pi}{|a \wedge b|}|x_3| + \frac{1}{\pi |a \wedge b|} \sum_{k \in \ell^* \setminus \{0\}} \int_{\mathbf{R}} \frac{e^{2i\pi(k \cdot x + x_3 \xi)}}{|k|^2 + \xi^2} d\xi, \end{aligned} \tag{64}$$

where C_ℓ is chosen so that $\lim_{x \to 0}(G_\ell(x) - \frac{1}{|x|}) = 0$, and ℓ^* is the reciprocal lattice to ℓ in the plane (e_1, e_2), that is, ℓ^* is the periodic lattice generated by the basis (a', b') of $\{x_3 = 0\}$ defined by $a \cdot a' = b \cdot b' = 1$, and $a \cdot b' = b \cdot a' = 0$.

Here again, we have the analogue of Proposition 3.1, proven in [7] :

Proposition 3.6 *We have :*

(i) G_ℓ *is smooth on* $\mathbf{R}^3 \setminus \ell$,

(ii) $G_\ell(x) = \frac{1}{|x|} + O(|x|)$ *as* $x \to 0$,

(iii) $G_\ell(x) = -\frac{2\pi}{|a \wedge b|}|x_3| + C_\ell + O(\frac{1}{|x_3|})$ *as* $|x_3| \to \infty$, *uniformly with respect to* (x_1, x_2).

We also have the following :

Proposition 3.7 *For any basis* (a, b) *of the plane generated by* (e_1, e_2), *the problem (62) has a unique solution* ρ_ℓ. *Setting* $u_\ell = \sqrt{\rho_\ell}$, u_ℓ *is a solution of :*

$$-\Delta u_\ell + \frac{5}{3}u_\ell^{7/3} + (u_\ell^2 \star_{\Gamma(\ell)} G_\ell - G_\ell)u_\ell + \theta_\ell u_\ell = 0, \tag{65}$$

with $\theta_\ell > 0$.

Proof : We skip this proof, since it is a straightforward adaptation of Proposition 3.2's. ◊

Next, we mimic the proof of Proposition 3.3 and find :

Proposition 3.8 *The solution* ρ_ℓ *of problem (62) satisfies the following estimate, where* a_ℓ *is a positive constant depending only on* ℓ *:*

$$\rho_\ell(x) \sim a_\ell e^{-2\sqrt{\theta_\ell}|x_3|}, \quad as \quad |x_3| \longrightarrow \infty. \tag{66}$$

Denoting by $\phi_\ell = G_\ell - G_\ell \star_{\Gamma(\ell)} \rho_\ell$ *the effective potential, there exists complex numbers* μ_k *such that, for all* $\epsilon > 0$,

$$\left| \partial_3 \phi_\ell(r, x_3) - \sum_{0 < \pi|k| \leq \sqrt{\theta_\ell}, k \in \ell^*} \mu_k e^{2i\pi k \cdot x'} e^{-2\pi|k||x_3|} \right| \leq b_{\ell,\epsilon} e^{-(2\sqrt{\theta_\ell} - \epsilon)|x_3|}, \tag{67}$$

as $|x_3| \to \infty$, *with* $b_{\ell,\epsilon} > 0$ *depending only on* ℓ *and* ϵ.

Proof : The only necessary change is to show the above estimate for the Yukawa potential :

$$V_\ell(x) = \sum_{k \in \ell} \frac{e^{-\sqrt{\theta_\ell}|x-k|}}{|x-k|} \sim \frac{2\pi}{\sqrt{\theta_\ell}} e^{-\sqrt{\theta_\ell}|x_3|} \quad \text{as} \quad |x_3| \to \infty,$$

which is easy to prove by comparing it to the one-dimensional Yukawa potential with respect to x_3, namely $\frac{2\pi}{\sqrt{\theta_\ell}} e^{-\sqrt{\theta_\ell}|x_3|}$. The partial Fourier transform defined in (57) is adapted as follows :

$$\tilde{f}(k, t) = \int_{\Gamma(\ell) \cap \{x_3 = t\}} f(x) e^{-2i\pi k \cdot x'} dx', \tag{68}$$

for all $k \in \ell^*$. And the role of $\overline{W}_a$ is played here by $e^{a|x_3|}$. ◊

4 Behavior of unbounded sequences

We investigate in this section the behavior of the TFW energy of unbounded sequences. By unbounded sequences, we mean sequences of periodic lattices for which some sequence of basis satisfying (25) is unbounded.

We first establish some bounds on the electronic density ρ_ℓ that are uniform with respect to ℓ.

4.1 Bounds on ρ_ℓ for $\ell \in \mathcal{L}_3(\mathbf{R}^3)$

Throughout this section, ℓ denotes a proper lattice, and $\Gamma(\ell)$ is a cell of ℓ associated to a basis $(a_i)_{1\leq i\leq 3}$ satisfying (25), and the following :

$$0 < R_0 \leq \min_{i=1,2,3} |a_i| = \min_{i=1,2,3} R_i. \tag{69}$$

In the spirit of [3] and [18], we define, for a radius $R > 0$, the ground state e_R of the Laplace operator with Dirichlet condition on B_R, and set $g_R = e_R^2$.

Lemma 4.1 *For all $R > 0$, u_ℓ and ϕ_ℓ denoting the solutions of the Euler-Lagrange equation of (16), namely*

$$\begin{cases} -\Delta u_\ell + \frac{5}{3} {u_\ell}^{7/3} - \phi_\ell u_\ell = 0, \\ -\Delta \phi_\ell = 4\pi(\sum_{k\in\ell} \delta_k - {u_\ell}^2), \end{cases} \tag{70}$$

we have, $\star$ denoting a convolution product over $\mathbf{R}^3$:

$$g_R \star \phi_\ell(x) \leq \frac{5}{3} g_R \star {u_\ell}^{4/3}(x) + \frac{\pi^2}{R^2}, \tag{71}$$

for all $x \in \Gamma(\ell)$. Moreover, if $0 \notin x + B_R$, i.e if $|x| > R$, $\phi_\ell(x) \leq (g_R \star \phi_\ell)(x)$.

Proof : We simply copy here the proof of [18], pointing out that it does not depend on ℓ. Since u_ℓ is non-negative and satisfies (70), the operator $-\Delta + \frac{5}{3}{u_\ell}^{4/3} - \phi_\ell$, with homogeneous Dirichlet boundary conditions on $B_R + x$, is positive. Hence, for all $\chi \in H_0^1(B_R + x)$,

$$\int_{\Gamma(\ell)} |\nabla \chi|^2 + \int_{\Gamma(\ell)} (\frac{5}{3} {u_\ell}^{4/3} - \phi_\ell)\chi^2 \geq 0.$$

We apply this inequality with $\chi = e_R(x - \cdot)$, and find (71).

Assuming that $|x| > R$, ϕ_ℓ is then subharmonic on $B_R + x$, hence from the mean-value inequality and the fact that $\int_{\mathbf{R}^3} g_R = 1$, $\phi_\ell(x) \leq (g_R \star \phi_\ell)(x)$. $\Diamond$

Proposition 4.2 *For any solution (u_ℓ, ϕ_ℓ) of (70), we have the following estimate, valid in $\Gamma(\ell) \cap \{|x| > 2\}$:*

$$\phi_\ell(x) \leq \frac{b}{|x|^2} + \sum_{k\in\ell} \frac{a}{|x-k|^4}, \tag{72}$$

$a, b > 0$ being universal constants.

Proof : Here again, we merely check out that [18]'s proof carries through this case, with minor modifications. Using estimate (71), together with Hölder inequality, we have :

$$g_R \star \phi_\ell - \frac{\pi^2}{R^2} \leq \frac{5}{3}\left(g_R \star {u_\ell}^2\right)^{2/3}.$$

Denoting by $\tilde{\phi}_\ell$ the function $\tilde{\phi}_\ell = g_R \star \phi_\ell - \frac{\pi^2}{R^2}$, we then have $-\Delta\tilde{\phi}_\ell = 4\pi(\sum_{k\in\ell} g_R(\cdot - k) - g_R \star {u_\ell}^2)$, hence :

$$-\Delta\tilde{\phi}_\ell + (\frac{3}{5}\tilde{\phi}_\ell)_+^{3/2} \leq 4\pi \sum_{k\in\ell} g_R(\cdot - k).$$

We now introduce the corresponding periodic TF-potential $\widehat{\phi}_\ell$, that is, the positive solution of :

$$-\Delta\widehat{\phi}_\ell + \frac{5}{3}\widehat{\phi}_\ell^{3/2} = 4\pi \sum_{k\in\ell} g_R(\cdot - k).$$

It is thus clear, from a comparison argument, that we have : $\tilde{\phi}_\ell \leq \widehat{\phi}_\ell$. Now, on the one hand, from Theorem V.12 of [16], we know that $\widehat{\phi}_\ell \leq \sum_{k\in\ell} \widehat{\phi}(\cdot - k)$, where $\widehat{\phi}$ is the solution of :

$$-\Delta\widehat{\phi} + \frac{5}{3}(\widehat{\phi})^{3/2} = 4\pi g_R.$$

On the other hand, Lemma 11 of [18] shows that

$$\widehat{\phi} \leq \frac{a}{|x|^4} \quad \text{on} \quad \{|x| > R+1\},$$

where $a > 0$ is a universal constant. Collecting those results and taking, for $|x| > 2$, $R = \frac{1}{2}|x|$, we find (72). $\Diamond$

Proposition 4.3 *For any solution (u_ℓ, ϕ_ℓ) of (70), we have the following estimate, for $x \in \Gamma(\ell) \cap \{|x| > 2\}$:*

$$u_\ell^{4/3} \leq \frac{b'}{|x|^2} + a' \sum_{k\in\ell} \frac{1}{|x-k|^4}, \tag{73}$$

where $a', b' > 0$ depend only on R_0 defined in (69), and not on the R_i.

Proof : We first remark that the proof of Propositions 3.5 and 3.10 of [9] do not in fact depend on the periodic lattice, as far as its radii R_i satisfy (69), and that we thus have :

$$0 < u_\ell \leq c,$$

where $c > 0$ is a constant depending on R_0, and not on ℓ. We define the function :

$$f(x) = \beta \sum_{k\in\ell} \frac{1}{|x-k|^4} + \frac{\gamma}{|x|^2} + \frac{\delta {R'}^2}{(|x|^2 - {R'}^2)^2}.$$

An easy but tedious computation shows that :

$$-\Delta f \geq \beta \sum_{k\in\ell} \frac{-12}{|x-k|^6} - \frac{2\gamma}{|x|^4} - 12\delta R'^2 \frac{|x|^2+R'^2}{(|x|^2-R'^2)^4}.$$

We also have :

$$f(x)^2 \geq \beta^2 \sum_{k\in\ell} \frac{1}{|x-k|^8} + \frac{\gamma^2}{|x|^4} + 2\beta\gamma \sum_{k\in\ell} \frac{1}{|x-k|^4|x|^2} + \frac{\delta^2 R'^4}{(|x|^2-R'^2)^4}.$$

Hence, choosing $\gamma \geq 6$, $\beta \geq 12$ and $\delta \geq 24$, we have, in $B_{R'}$:

$$-\Delta f + f^2 \geq 0. \tag{74}$$

Now, we also have : $\Delta(u_\ell^{4/3}) \geq \frac{4}{3}(\frac{5}{3}u_\ell^{4/3} - \phi_\ell)u_\ell^{4/3}$. Thus, denoting by S the set $S = \{u_\ell^{4/3} > f\}$, which is open, bounded and included in $\{|x| > 2\} \cap B_{R'}$ as far as $\beta \geq 16c$, from the definition of f and (72), we notice that on S, $u_\ell^{4/3} \geq \frac{\inf(\beta,\gamma)}{\sup(a,b)}\phi_\ell$. Hence

$$\Delta u_\ell^{4/3} \geq \frac{4}{3}\left(\frac{5}{3} - \frac{\sup(a,b)}{\inf(\beta,\gamma)}\right)(u_\ell^{4/3})^2.$$

In addition to the above conditions on β and γ, we may impose the inequality $\beta, \gamma > 2\sup(a,b)$, so that, on S :

$$\Delta(u_\ell^{4/3} - f) \geq (u_\ell^{4/3})^2 - f^2 > 0.$$

The function $u_\ell^{4/3} - f$ is thus subharmonic on S, and cancels on ∂S. From the maximum principle, we infer that $u_\ell^{4/3} - f$ is non-positive on S, which is impossible. Hence, $S = \emptyset$. Letting then R' go to infinity, we find (73). $\Diamond$

4.2 Convergence of G_ℓ

Considering unbounded sequences, we investigate here the behavior of the associated potential G_ℓ.

4.2.1 The Thin film case

We consider here the case of a sequence $(\ell_n)_{n\geq 0}$ such that only one of its radii R_i^n is unbounded, and the others are bounded away from 0 as well as bounded from above. That is, we consider a sequence $(\ell_n)_{n\in\mathbf{N}}$ such that for all $n \in \mathbf{N}$, ℓ_n has a basis $(a_i^n)_{1\leq i\leq 3}$ satisfying the conclusion of Theorem 2.5 together with :

(1) $a_1^n \longrightarrow a_1 \neq 0$ as n goes to infinity,

(2) $a_2^n \longrightarrow a_2 \neq 0$ as n goes to infinity,

(3) $|a_3^n| = R_3^n \longrightarrow \infty$ as n goes to infinity.

Moreover, we may assume, changing the system of coordinates if necessary, that for all $n \geq 0$, the plane generated by (a_1^n, a_2^n) as well as the one generated by (a_1, a_2), is included in (hence equal to) the one generated by (e_1, e_2). Note that since the angle between a_1^n and a_2^n is confined in $[\frac{\pi}{3}, \frac{\pi}{2}]$, so is the angle between a_1 and a_2, and these two vectors must be linearly independent.

We denote by G_n the periodic potential associated to ℓ_n, defined in (20), and which may be written as :

$$G_n(x) = C_n + \frac{1}{\pi|\Gamma(\ell_n)|} \sum_{k \in \ell_n^* \setminus \{0\}} \frac{e^{2i\pi k \cdot x}}{|k|^2}, \tag{75}$$

where $C_n = \frac{1}{|\Gamma(\ell_n)|} \int_{\Gamma(\ell_n)} G_n$ is such that $\lim_{x \to 0}(G_{\ell_n}(x) - \frac{1}{|x|}) = 0$, and ℓ_n^* is the periodic lattice reciprocal to ℓ_n, i.e the lattice of basis (b_1^n, b_2^n, b_3^n) satisfying :

$$a_i^n \cdot b_j^n = \delta_{ij}, \quad \forall i, j \in \{1, 2, 3\}.$$

The potential G_∞ denotes the potential associated to the lattice ℓ_∞ generated by (a_1, a_2), as defined in (64). We now show the following :

Proposition 4.4 *The potentials G_n and G_∞ satisfy, for all $x \in \Gamma(\ell_n)$:*

$$|G_n(x) - G_\infty(x)| \leq C(1 + |x_3|), \tag{76}$$

where $C > 0$ is a constant independent of n.

Proof : The strategy of the proof is the following : writing G_n through its Fourier series, we isolate singular terms, and deal with them separately, whereas in the remaining terms, we recognize a Riemann sum converging to the Fourier coefficients of G_∞, as defined in (64).

We denote by $(\tilde{a}_i^n)$ the renormalized basis associated to (a_i^n), that is, $\tilde{a}_i^n = \frac{a_i^n}{R_i^n} = \frac{a_i^n}{|a_i^n|}$. We thus have, setting $\delta_n = |\tilde{a}_1^n \cdot (\tilde{a}_2^n \wedge \tilde{a}_3^n)| = |\det(\tilde{a}_1^n, \tilde{a}_2^n, \tilde{a}_3^n)|$:

$$G_n(x) = C_n + \frac{1}{\pi R_1^n R_2^n R_3^n \delta_n} \sum_{k \in \mathbf{Z}^3 \setminus \{0\}} \frac{e^{2i\pi(k_1 b_1^n + k_2 b_2^n + k_3 b_3^n) \cdot x}}{|k_1 b_2^n + k_2 b_2^n + k_3 b_3^n|^2}. \tag{77}$$

Hence, isolating the terms where $k_1 = k_2 = 0$, and denoting by $\tilde{b}_3^n$ the vector $\tilde{b}_3^n = R_3^n b_3^n$:

$$\begin{aligned} G_n(x) &= C_n + \frac{R_3^n}{\pi R_1^n R_2^n \delta_n} \sum_{k_3 \neq 0} \frac{e^{2i\pi k_3 \frac{\tilde{b}_3^n \cdot x}{R_3^n}}}{k_3^2 |\tilde{b}_3^n|^2} \\ &+ \frac{1}{\pi R_1^n R_2^n R_3^n \delta_n} \sum_{(k_1, k_2) \in \mathbf{Z}^2 \setminus \{0\}} \sum_{k_3 \in \mathbf{Z}} \frac{e^{2i\pi(k_1 b_1^n + k_2 b_2^n + k_3 \frac{\tilde{b}_3^n}{R_3^n}) \cdot x}}{|k_1 b_1^n + k_2 b_2^n + k_3 \frac{\tilde{b}_3^n}{R_3^n}|^2}. \end{aligned}$$

Next, considering the fact that (a_1, a_2) is a basis of the plane generated by (e_1, e_2), together with the definition of b_i^n, we infer that $\tilde{b}_3^n = \lambda_n e_3$, with $\lambda_n \in \mathbf{R}$ bounded away from 0 as well as bounded from above. Next, we notice that the first sum is easily computable, since $\sum_{k\in\mathbf{Z}\setminus\{0\}} \frac{e^{2i\pi kt}}{k^2} = \frac{\pi^2}{3} + 2\pi^2|t|(|t|-1)$ for $|t| \leq \frac{1}{2}$. Hence, for all $x \in \Gamma(\ell)$:

$$\begin{aligned} G_n(x) &= C_n + \frac{\pi R_3^n}{3R_1^n R_2^n \delta_n \lambda_n^2} + \frac{2\pi x_3^2}{\delta_n R_1^n R_2^n R_3^n} - \frac{2\pi|x_3|}{R_1^n R_2^n \delta_n \lambda_n} \\ &+ \frac{1}{\pi R_1^n R_2^n R_3^n \delta_n} \sum_{(k_1,k_2)\in\mathbf{Z}^2\setminus\{0\}} \sum_{k_3\in\mathbf{Z}} \frac{e^{2i\pi((k_1 b_1^n + k_2 b_2^n)\cdot x + \frac{\lambda_n x_3}{R_3^n})}}{|k_1 b_1^n + k_2 b_2^n + k_3 \frac{\lambda_n e_3}{R_3^n}|^2}. \end{aligned}$$

We denote by $G_{(a_1^n, a_2^n)}$ the thin film potential associated to the lattice of basis (a_1^n, a_2^n). Denoting by $\overline{G}_n$ the function

$$\overline{G}_n(x) = \overline{C}_n - \frac{2\pi}{R_1^n R_2^n \lambda_n \delta_n}|x_3| + \frac{1}{\pi R_1^n R_2^n \lambda_n \delta_n} \sum_{k\in\mathbf{Z}^2\setminus\{0\}} \int_{\mathbf{R}} \frac{e^{2i\pi((k_1 b_1^n + k_2 b_2^n)\cdot x + \xi x_3)}}{|k_1 b_1^n + k_2 b_2^n + \xi e_3|^2},$$

with $\overline{C}_n$ chosen so that $\overline{G}_n(x) - \frac{1}{|x|}$ cancels at 0, and computing its Laplacian, we find that $\overline{G}_n - G_{(a_1^n, a_2^n)}$ is harmonic, bounded (from Proposition 3.6-(iii)), has value 0 at the origin. Thus, $\overline{G}_n = G_{(a_1^n, a_2^n)}$. We then have, denoting by F_n the function $G_n - G_\infty$:

$$\begin{aligned} F_n(x) &= G_{(a_1^n, a_2^n)}(x) - G_\infty(x) - \overline{C}_n + C_n \\ &+ \frac{\pi R_3^n}{3R_1^n R_2^n \delta_n \lambda_n^2} + \frac{2\pi x_3^2}{\delta_n R_1^n R_2^n R_3^n} \\ &- \frac{1}{\pi R_1^n R_2^n \delta_n \lambda_n} \sum_{(k_1,k_2)\neq(0,0)} e^{2i\pi(k_1 b_1^n + k_2 b_2^n)\cdot x} \left(\int_{\mathbf{R}} \frac{e^{2i\pi\xi x_3}}{|k_1 b_1^n + k_2 b_2^n + \xi e_3|^2} \right. \\ &- \left. \frac{\lambda_n}{R_3^n} \sum_{k_3\in\mathbf{Z}} \frac{e^{2i\pi \frac{\lambda_n k_3 x_3}{R_3^n}}}{|k_1 b_1^n + k_2 b_2^n + k_3 \frac{\lambda_n e_3}{R_3^n}|^2} \right). \end{aligned} \tag{78}$$

Using estimate (ii) and (iii) of Proposition 3.6, it is clear that

$$\left| G_{(a_1^n, a_2^n)}(x) - G_\infty(x) \right| \leq C(1 + |x_3|) \tag{79}$$

in $\Gamma(\ell_n)$, for n sufficiently large. We now deal with the sum appearing in (78) : we denote it by $F_n'(x)$, omitting the factor $\frac{1}{\pi R_1^n R_2^n \delta_n \lambda_n}$ since it is bounded, and write $F_n' = F_n^1 + F_n^2$, where :

$$F_n^1(x) = \sum_{(k_1,k_2)\neq(0,0)} \sum_{k_3\in\mathbf{Z}} \frac{\left(\frac{\lambda_n}{R_3^n} - \int_{(k_3-\frac{1}{2})\frac{\lambda_n}{R_3^n}}^{(k_3+\frac{1}{2})\frac{\lambda_n}{R_3^n}} e^{2i\pi x_3(\xi - \frac{\lambda_n k_3}{R_3^n})} d\xi \right) e^{2i\pi(k_1 b_1^n + k_2 b_2^n + \frac{k_3\lambda_n}{R_3^n} e_3)\cdot x}}{|k_1 b_1^n + k_2 b_2^n + \frac{k_3\lambda_n}{R_3^n} e_3|^2}, \tag{80}$$

$$F_n^2(x) = \sum_{(k_1,k_2)\neq(0,0)} e^{2i\pi(k_1 b_1^n + k_2 b_2^n)\cdot x} \sum_{k_3\in\mathbf{Z}} \int_{(k_3-\frac{1}{2})\frac{\lambda_n}{R_3^n}}^{(k_3+\frac{1}{2})\frac{\lambda_n}{R_3^n}} \Big(\frac{1}{|k_1 b_1^n + k_2 b_2^n + \frac{k_3\lambda_n}{R_3^n} e_3|^2} - \frac{1}{|k_1 b_1^n + k_2 b_2^n + \xi e_3|^2} \Big) e^{2i\pi\xi x_3} d\xi. \quad (81)$$

And we have $F_n^1(x) = \overline{F}_n^1(x)(\frac{\lambda_n}{R_3^n} - \frac{\sin(\pi\frac{\lambda_n x_3}{R_3^n})}{\pi x_3})$, with

$$\overline{F}_n^1(x) = \sum_{(k_1,k_2)\neq(0,0)} \sum_{k_3\in\mathbf{Z}} \frac{e^{2i\pi(k_1 b_1^n + k_2 b_2^n + \frac{k_3\lambda_n}{R_3^n} e_3)\cdot x}}{|k_1 b_1^n + k_2 b_2^n + \frac{k_3\lambda_n}{R_3^n} e_3|^2}.$$

One computes easily :

$$\|\overline{F}_n^1\|^2_{L^2(\Gamma(\ell_n))} = C(R_3^n)^2 \sum_{(k_1,k_2)\neq(0,0)} \frac{1}{R_3^n} \sum_{k_3\in\mathbf{Z}} \frac{1}{|k_1 b_1^n + k_2 b_2^n + \frac{k_3\lambda_n}{R_3^n} e_3|^4},$$

and since the sum over k_3 is a Riemann sum converging to $\int_{\mathbf{R}} \frac{d\xi}{|k_1 b_1^n + k_2 b_2^n + \xi e_3|^4} \leq \frac{C}{|k_1 b_1^n + k_2 b_2^n|^3}$ as R_3^n goes to infinity, we infer that :

$$\|\overline{F}_n^1\|_{L^2(\Gamma(\ell_n))} \leq C R_3^n,$$

where C does not depend on n. This implies :

$$\|F_n^1\|_{L^2(\Gamma(\ell_n))} \leq C, \quad (82)$$

with C independent of n. We now turn to F_n^2 : noticing that

$$\Big| \int_{(k_3-\frac{1}{2})\frac{\lambda_n}{R_3^n}}^{(k_3+\frac{1}{2})\frac{\lambda_n}{R_3^n}} \Big(\frac{1}{|k_1 b_1^n + k_2 b_2^n + \frac{k_3\lambda_n}{R_3^n} e_3|^2} - \frac{1}{|k_1 b_1^n + k_2 b_2^n + \xi e_3|^2} \Big) e^{2i\pi\xi x_3} d\xi \Big| \leq C\big(\frac{\lambda_n}{R_3^n}\big)^2 \frac{1}{|k_1 b_1^n + k_2 b_2^n + \frac{k_3\lambda_n}{R_3^n} e_3|^3},$$

we deduce, according to (81), that we have :

$$\begin{aligned} \|F_n^2\|^2_{L^2(\Gamma(\ell))} &\leq C R_3^n \sum_{(k_1,k_2)\neq(0,0)} \Big(\sum_{k_3\neq 0} \big(\frac{\lambda_n}{R_3^n}\big)^2 \frac{1}{|k_1 b_1^n + k_2 b_2^n + \frac{k_3\lambda_n}{R_3^n} e_3|^3} \Big)^2 \\ &\leq C \frac{\lambda_n^4}{(R_3^n)^2} \sum_{(k_1,k_2)\neq(0,0)} \frac{1}{(k_1^2+k_2^2)^2}. \end{aligned}$$

This shows that

$$\|F_n^2\|_{L^2(\Gamma(\ell_n))} \leq \frac{C}{R_3^n}, \quad (83)$$

with C independent of n. With (82), we get :

$$\|F_n'\|_{L^2(\Gamma(\ell_n))} \leq C, \tag{84}$$

the constant C not depending on n. Next, since F_n' is harmonic in $\Gamma(\ell_n)$, standard elliptic regularity results show that F_n' is necessarily bounded in $L^\infty(\Gamma(\ell_n))$. Since $F_n(0) = 0$, this also shows that $C_n - C_{(a_1^n, a_2^n)} + \frac{\pi R_3^n}{3R_1^n R_2^n \lambda_n \delta_n}$ is bounded, and we finally get (76). $\Diamond$

Next, looking closely at F_n', we notice that its $L^\infty(\Gamma(\ell_n) \cap \{|x_3| \leq R\})$ norm satisfies (83), for any fixed $R > 0$. Indeed, if $|x_3| \leq R$, $|\frac{\lambda_n}{R_3^n} - \frac{\sin(\pi \frac{\lambda_n x_3}{R_3^n})}{\pi x_3}| \leq \frac{CR^2}{(R_3^n)^3}$, so that (82) then becomes :

$$\|F_n^1\|_{L^2(\Gamma(\ell_n))} \leq \frac{C}{(R_3^n)^2}.$$

Hence, with the help of (78),the last bound we have obtained may be improved :

$$C_n - \overline{C}_n + \frac{\pi R_3^n}{3R_1^n R_2^n \lambda_n \delta_n} \longrightarrow 0. \tag{85}$$

This implies the following :

Proposition 4.5 *As n goes to infinity, we have, for any fixed $R > 0$:*

$$\|G_n - G_\infty\|_{L^\infty(\Gamma(\ell_n) \cap \{|x_3| < R\})} \longrightarrow 0 \quad \text{as} \quad n \to \infty.$$

Proof : From the above remark (85), we only need to improve (79), and show that this quantity is not only bounded, but goes to zero as n goes to infinity when $|x_3|$ is bounded. In order to do so, we only need to show it for the Fourier series, since the term of the form $\alpha_n |x_3|$ does converge. And the Fourier series may be dealt with in the same way as F_n'. This completes the proof. $\Diamond$

Remark 4.6 *In all the above bounds, we have omitted for simplicity the factor $\frac{1}{R_1^n R_2^n}$, since it is bounded from above. Rigorously, it should appear in all bounds, so that in fact (76) may very well read :*

$$|G_n(x) - G_\infty(x)| \leq C(1 + \frac{|x_3|}{R_1^n R_2^n}), \tag{86}$$

with C independent of n. This will be useful in the sequel.

4.2.2 The polymer case

We use here the same notation as in Section 4.2.1, except that only R_1^n is bounded. In other words, we have :

(1) $a_1^n \longrightarrow a_1 \neq 0$ as n goes to infinity,

(2) $R_2^n \longrightarrow \infty$ as n goes to infinity,

(3) $R_3^n \longrightarrow \infty$ as n goes to infinity.

Changing coordinates if necessary, we may assume that a_1^n is collinear to e_3, for all $n \in \mathbf{N}$. Next, we may rotate the system of coordinates so that the angle between a_2^n and e_1 is lower than $\frac{\pi}{6}$. Hence, from (25), the angle between a_3^n and e_2 is necessarily bounded, and there exists a constant C independent of n such that :

$$|a_2^n \cdot e_1| \geq CR_2^n, \quad \text{and} \quad |a_3^n \cdot e_2| \geq CR_3^n.$$

Here the lattice ℓ_∞ is the one generated by $a_1 = R_1 e_3$, and G_∞ is thus defined by (33).

Proposition 4.7 *There exists a constant C independent of n such that for all x in $\Gamma(\ell_n)$, we have :*

$$|G_n(x) - G_\infty(x)| \leq C\left(1 + \frac{|x_2|}{R_2^n} + \log(2 + |x'|)\right). \tag{87}$$

Moreover, $G_n - G_\infty$ goes to 0 in $L^\infty(\Gamma(\ell_n) \cap \{r < R\})$, for any $R > 0$.

Proof : Writing G_n through its Fourier coefficients, we argue exactly as in the proof of Proposition 4.4 concerning the Fourier series F_n'. The argument carries through this case. Hence, we only study the residual term, that is,

$$\begin{aligned} A_n(x) &= \frac{1}{\pi\delta_n R_1^n R_2^n R_3^n} \sum_{(k_2,k_3)\neq(0,0)} \frac{e^{2i\pi(k_2 b_2^n + k_3 b_3^n)\cdot x}}{|k_2 b_2^n + k_3 b_3^n|^2} \\ &\quad + C_n - C_{a_1^n} + \frac{2}{R_1^n}\log|x'| + G_{a_1^n}(x) - G_\infty(x), \end{aligned}$$

where $G_{a_1^n}$ is the polymer potential associated to a lattice of basis (a_1^n), and $C_{a_1^n}$ the corresponding constant appearing in (33). We use estimates (ii)-(iii) of Proposition 3.1 to deal with $G_{a_1^n}(x) - G_\infty(x)$, finding :

$$\left|G_{a_1^n}(x) - G_\infty(x)\right| \leq C(1 + \log(2 + |x'|)), \tag{88}$$

in $\Gamma(\ell_n)$. Next, we need a bound on the remaining term. Unfortunately, we do not have, as in the preceding case, an exact expression of this Fourier series. But we know that it depends only on $x' = (x_1, x_2)$, since a_1^n is collinear to e_3, and we may compute its Laplacian in the plane $\{x_3 = 0\}$:

$$-\Delta\left(\frac{1}{\pi R_1^n R_2^n} \sum_{(k_2,k_3)\neq(0,0)} \frac{e^{2i\pi(k_2 b_2^n + k_3 b_3^n)\cdot x}}{|k_2 b_2^n + k_3 b_3^n|^2}\right) = 4\pi(\delta_0 - \frac{1}{R_1^n R_2^n}),$$

and this function is periodic. Its periodic cell is defined by the basis $(\overline{a}_2^n, \overline{a}_3^n)$ reciprocal to (b_2^n, b_3^n). It is thus clear that $\overline{a}_2^n$ and $\overline{a}_3^n$ are respectively the projection of a_2^n and a_3^n on the plane $\{x_3 = 0\}$, so that their norms $\tilde{R}_2^n$ and $\tilde{R}_3^n$ go to infinity as n goes to infinity. Two cases are then possible :

Case 1 : $\tilde{R}_2^n/\tilde{R}_3^n$ is bounded. We reduce this case to $\tilde{R}_2^n = \tilde{R}_3^n = R^n$, the general case being a rather technical adaptation of this one. We then have, denoting by $B_n(x')$ the above function,

$$B_n(x') = B(\frac{x'}{R^n}),$$

where B is the function B_n with $R^n = 1$. Hence, we have, denoting by $\tilde{\Gamma}_n$ the set $\{t\tilde{a}_1^n + u\tilde{a}_2^n, \quad -\frac{1}{2} < t, u \leq \frac{1}{2}\}$:

$$\|B_n + 2\log\frac{|x'|}{R^n}\|_{L^\infty(\tilde{\Gamma}_n)} = \|B + 2\log|x'|\|_{L^\infty(\frac{1}{R^n}\tilde{\Gamma}_n)} \leq C,$$

C being a constant independent of n. This gives a bound on $A_n(x) - C_n + C_{a_1^n} - \log(R^n)$ in $L^\infty(\Gamma(\ell_n))$, hence on $G_n - G_\infty - C_n + C_{a_1^n} - \log(R^n)$. Pointing out that $G_n - G_\infty$ cancels at 0, we thus deduce a bound on $-C_n + C_{a_1^n} - \log(R^n)$, and conclude the proof of (87).

If now $\tilde{R}_2^n \neq \tilde{R}_3^n$, we may re-scale by $\tilde{R}_2^n$ in the same way as above, and thus get a periodic Green function on a periodic cell of the form $\frac{1}{\tilde{R}_n^2}\tilde{\Gamma}_n$. The above bounds are then still valid, since the domain is bounded independently of n.

Case 2 : $\tilde{R}_2^n/\tilde{R}_3^n$ is unbounded. We may then assume that this quotient goes to infinity. Re-scaling by R_2^n as in Case 1, we then have a problem of the same kind as Proposition 4.5's, except that it is in two dimensions and not in three. Nevertheless, it may be dealt with in the same way. As pointed out in Remark 4.6, we then get the right coefficient with $|x_2|$. This concludes the proof of (87).

The L^∞ convergence is then proved by pointing out that the same remarks as in Proposition 4.5's proof are available. $\Diamond$

Remark 4.8 *Here again, we have omitted the coefficient $\frac{1}{R_1^n}$ in front of all terms, but it will be useful to keep in mind that it is implicit in the constant C of (87).*

4.2.3 The atomic case

We now consider the case when all radii go to infinity :

$$R_3^n \geq R_2^n \geq R_1^n \longrightarrow \infty.$$

We assume (changing coordinates if necessary, here again) that a_1^n is collinear to e_1, and that the angle between a_2^n and e_2 is not larger than $\frac{\pi}{6}$. This also implies that the angle between a_3^n and e_3 is bounded, and that :

$$|a_2^n \cdot e_2| \geq CR_2^n, \quad \text{and} \quad |a_3^n \cdot e_3| \geq CR_3^n.$$

In this case, we have the following :

Proposition 4.9 *There exists a constant C independent of n such that :*

$$|G_n(x) - \frac{1}{|x|}| \leq C(1 + \frac{\log(2+|x'|)}{R_1^n} + \frac{|x_3|}{R_1^n R_2^n}). \tag{89}$$

Moreover, $G_n - \frac{1}{|x|}$ converges to 0 in $L^\infty_{loc}(\mathbf{R}^3)$.

Proof : We first assume that $\frac{R_3^n}{R_1^n}$ is bounded. In this case, we may assume that this ratio, together with $\frac{R_2^n}{R_1^n}$, converge. Thus, denoting by $\overline{G}_n$ the function

$$\overline{G}_n(x) = R_1^n G_n(R_1^n x), \tag{90}$$

a direct computation shows that $\overline{G}_n$ is the periodic potential associated to the lattice of basis $(\frac{a_1^n}{R_1^n}, \frac{a_2^n}{R_1^n}, \frac{a_3^n}{R_1^n})$. Next, we notice that $\overline{G}_n - \frac{1}{|x|}$ has its Laplacian identically equal to 1 in $\frac{1}{R_1^n}\Gamma(\ell_n)$ and that G_n is bounded in $L^2(\Gamma(\ell_n))$ (from its Fourier coefficients), independently of n, so that we have :

$$\left\| \overline{G}_n - \frac{1}{|x|} \right\|_{L^\infty(\frac{1}{R_1^n}\Gamma(\ell_n))} \leq C.$$

This implies :

$$\left\| G_n - \frac{1}{|x|} \right\|_{L^\infty(\Gamma(\ell_n))} \leq \frac{C}{R_1^n},$$

and (89) follows, as well as the L^∞_{loc} convergence.

We next consider the possibility :

$$\frac{R_3^n}{R_1^n} \longrightarrow \infty, \quad \text{with} \quad \frac{R_2^n}{R_1^n} \quad \text{bounded.}$$

Here again, we rescale the potential G_n with respect to R_1^n, according to (90), and find ourselves in the case of Proposition 4.4, and using the same tricks, we show (76) for $\overline{G}_n$ and $R_1^n G_\infty(R_1^n x)$. Next, we notice that, from the same reasons as in the first case,

$$\left| R_1^n G_\infty(R_1^n x) - \frac{1}{|x|} \right| \leq \frac{C}{R_1^n}$$

in $\Gamma(\ell_n)$. Therefore :

$$|G_n(x) - \frac{1}{|x|}| \leq C(\frac{1}{R_1^n} + \frac{|x_3|}{R_1^n R_2^n}).$$

Here again, this shows (89) as well as the L^∞_{loc} convergence.

The last case is the following :

$$\frac{R_3^n}{R_1^n} \longrightarrow \infty, \quad \text{and} \quad \frac{R_2^n}{R_1^n} \longrightarrow \infty.$$

Here again, we rescale and find the polymer case. Adapting the corresponding proof, our Proposition is proved. $\Diamond$

Remark 4.10 *Formally, the above estimates assert that the convergence of G_n to G_∞ is a good one if it is isotropic. When it is not, the convergence defect behaves like the corresponding intermediate potential. For example, in the case of the convergence towards $\frac{1}{|x|}$, it $G_n - \frac{1}{|x|}$ converges to 0 in $L^\infty(\Gamma(\ell_n))$ if $R_1^n = R_2^n = R_3^n$, whereas if $R_1^n = R_2^n \ll R_3^n$, a residual term appears, which has the same behavior as the thin film potential associated to the basis (a_1^n, a_2^n).*

4.3 Convergence of the energy

According to the bounds we have shown in the preceding sections, we are now in position to show the following :

Theorem 4.11 *Let ℓ_n be a sequence of proper lattices, with basis (a_i^n) satisfying conclusions of Theorem 2.5. Assume in addition that there exists an R_0 such that*

$$\forall n \geq 0, \quad \forall i = 1, 2, 3, \quad R_i^n = |a_i^n| \geq R_0.$$

Then we have :

(i) If $R_3^n \longrightarrow \infty$ and $a_i^n \longrightarrow a_i$, $i \neq 3$, as $n \to \infty$, then the energy $\mathcal{E}(\ell_n)$ converges to $\mathcal{E}(\ell_\infty)$, where ℓ_∞ is the periodic lattice of rank 2 generated by (a_1, a_2),

(ii) If $R_2^n \longrightarrow \infty$ as $n \to \infty$, and if a_1^n converges to some $a_1 \neq 0$, then $\mathcal{E}(\ell_n)$ converges to the energy $\mathcal{E}(\ell_\infty)$ of the polymer defined by a_1,

(iii) If $R_1^n \longrightarrow \infty$ as $n \to \infty$, then $\mathcal{E}(\ell_n)$ converges to the atomic energy I_{at}^{TFW}.

Proof : We first prove (i) : in this case, we may assume (as has been done in the proof of Proposition 4.4) that a_1^n and a_2^n belong to the plane $\{x_3 = 0\}$. We first show that :

$$\limsup_{n\to\infty} \mathcal{E}(\ell_n) \leq \mathcal{E}(\ell_\infty). \tag{91}$$

For this purpose, we fix a $\rho \geq 0$, such that $\sqrt{\rho} \in C^\infty(\mathbf{R}^3)$, $\sqrt{\rho}$ has compact support with respect to x_3, and is ℓ_∞-periodic, and has total mass one over $\Gamma(\ell_\infty)$. We denote by M_n the unique matrix satisfying :

$$M_n a_i^n = a_i, \quad i = 1, 2, \quad \text{and} \quad M_n e_3 = e_3.$$

It is clear that M_n converges to the identity matrix as n goes to infinity. Moreover, if n is large enough to ensure that $\mathrm{Supp}\rho \subset \{|x_3| \leq R_3^n\}$, $\rho_n = |\det M_n| \rho \circ M_n$ is a test-function for the variational problem I_n defining $\mathcal{E}(\ell_n)$. Hence :

$$E_{\ell_n}^{TFW}(\rho_n) \geq \mathcal{E}(\ell_n).$$

We then study separately the four terms appearing in $E_{\ell_n}^{TFW}(\rho_n)$.

Considering the term $\int_{\Gamma(\ell_n)} |\nabla\sqrt{\rho}_n|^2$, we notice that we have $\nabla\sqrt{\rho}_n = |\det M_n|^{1/2} M_n \cdot \nabla(\sqrt{\rho}) \circ M_n$, so that, changing variables in this term, we have :

$$\int_{\Gamma(\ell_n)} |\nabla\sqrt{\rho}_n|^2 = \int_{\Gamma(\ell_\infty)} \left|M_n \cdot \nabla\sqrt{\rho}\right|^2,$$

which converges to $\int_{\Gamma(\ell_\infty)} |\nabla\sqrt{\rho}|^2$ as n goes to infinity. The second term may be dealt with exactly in the same way, and we then turn to the electrostatic terms :

$$\begin{aligned}
\int_{\Gamma(\ell_n)} \rho_n G_n &= \int_{\Gamma(\ell_\infty)} \rho\, G_n \circ M_n^{-1} \\
&= \int_{\Gamma(\ell_\infty)} \rho(G_n \circ M_n^{-1} - G_\infty \circ M_n^{-1}) + \int_{\Gamma(\ell_\infty)} \rho G_\infty \circ M_n^{-1}.
\end{aligned}$$

Since $\int_{\Gamma(\ell_\infty)} \rho G_\infty \circ M_n^{-1} = \int_{\Gamma(\ell_n)} |\det M_n| (\rho \circ M_n) G_\infty$, the fact that G_∞ is bounded in $L^2_{loc}(\Gamma(\ell_n))$ together with the convergence of ρ_n towards ρ in $L^2(\Gamma(\ell_\infty))$ and the fact that ρ has compact support with respect to x_3, shows that

$$\int_{\Gamma(\ell_\infty)} \rho\, G_\infty \circ M_n^{-1} \longrightarrow \int_{\Gamma(\ell_\infty)} \rho\, G_\infty.$$

On the other hand, we have, choosing R so that $\mathrm{Supp}\rho \subset \{|x_3| < R\}$:

$$\begin{aligned} \int_{\Gamma(\ell_\infty)} \left|\rho(G_n \circ M_n^{-1} - G_\infty \circ M_n^{-1})\right| &\leq \|(G_n - G_\infty) \circ M_n^{-1}\|_{L^\infty(\Gamma(\ell_\infty)\cap\{|x_3|\leq R\})} \\ &\leq \|G_n - G_\infty\|_{L^\infty(\Gamma(\ell_n)\cap\{|x_3|\leq R\})}, \end{aligned}$$

which vanishes as $n \to \infty$ from Proposition 4.5. Since the remaining term of the energy follows then exactly in the same way, we have proved that

$$\limsup_{n\to\infty} \mathcal{E}(\ell_n) \leq E^{TFW}_{\ell_\infty}(\rho).$$

This is valid for all ℓ_∞-periodic ρ such that $\sqrt{\rho} \in C^\infty(\mathbf{R}^3)$ and $\mathrm{Supp}\rho$ is compact with respect to x_3. Since this subspace of $H^1_{per}(\ell_\infty)$ is dense, we conclude that (91) holds.

The next step consists in showing :

$$\liminf_{n\to\infty} \mathcal{E}(\ell_n) \geq \mathcal{E}(\ell_\infty). \tag{92}$$

We denote by ρ_n the unique solution of problem (16) defining $\mathcal{E}(\ell_n)$, and by $u_n = \sqrt{\rho}_n$ its square root. From (91), we know that the energy $E^{TFW}_{\ell_n}(\rho_n)$ is bounded. Moreover, if we fix an $R > 2$ and choose n large enough to have $\Gamma(\ell_n) \cap \{|x_3| > R\} \neq \emptyset$, we have :

$$\int_{\Gamma(\ell_n)} \rho_n |G_n - G_\infty| \leq \|G_n - G_\infty\|_{L^\infty(\Gamma(\ell_n)\cap\{|x_3|<R\})} + \int_{\Gamma(\ell_n)\cap\{|x_3|>R\}} \rho_n |G_n - G_\infty|.$$

We infer from Propositions 4.3 and 4.4 :

$$\rho_n \leq C\left(\frac{1}{|x|^2} + \sum_{k\in\ell_n} \frac{1}{|x-k|^4}\right)^{3/2} \leq C\left(\frac{1}{|x|^2} + \sum_{j\in\mathbf{Z}} \frac{1}{|x - jR_3^n e_3|^2}\right)^{3/2},$$

in $\Gamma(\ell_n) \cap \{|x_3| > R\}$, hence :

$$\begin{aligned} \int_{\Gamma(\ell_n)} \rho_n |G_n - G_\infty| &\leq \|G_n - G_\infty\|_{L^\infty(\Gamma(\ell_n)\cap\{|x_3|<R\})} \\ &\quad + C\int_R^{R_3^n} t\left(\frac{1}{t^2} + \sum_{j\neq 0} \frac{1}{t^2 + j^2 R_3^{n\,2}}\right)^{3/2} dt. \end{aligned}$$

Using the convergence result of Proposition 4.5, we thus have :

$$\begin{aligned}\int_{\Gamma(\ell_n)} \rho_n |G_n - G_\infty| &\leq o(1) + C\int_R^{R_3^n} t\left(\frac{1}{t^2} + \frac{1}{tR_3^n}\right)^{3/2} dt \\ &\leq o(1) + C\int_R^{R_3^n} t\left(\frac{1}{t^{3/2}} + \frac{1}{(R_3^n t)^{3/4}}\right)^2 \\ &\leq o(1) + \frac{C}{R} + \frac{C}{R_3^n},\end{aligned}$$

where $o(1)$ denotes a function which goes to 0 as n goes to infinity. Letting n, then R, go to infinity, this shows that :

$$\int_{\Gamma(\ell_n)} \rho_n (G_n - G_\infty) \longrightarrow 0. \tag{93}$$

Repeating exactly the same kind of argument, one easily shows :

$$\int_{\Gamma(\ell_n)} \int_{\Gamma(\ell_n)} \rho_n(x)\rho_n(y)(G_n(x-y) - G_\infty(x-y))dxdy \longrightarrow 0. \tag{94}$$

Now, it is not difficult, from estimate (73) of Proposition 4.3 together with Proposition 3.6-(ii)-(iii), to show that the quantities $\int_{\Gamma(\ell_n)} \rho_n G_\infty$ and $\int_{\Gamma(\ell_n)} \int_{\Gamma(\ell_n)} \rho_n(x)\rho_n(y)G_\infty(x-y)dxdy$ are bounded independently of n. With the fact that $E_{\ell_n}^{TFW}(\rho_n)$ is bounded, this implies that u_n is bounded in $H^1_{loc}(\mathbf{R}^3)$. Extracting a subsequence if necessary, u_n then converges weakly to some $\sqrt{\rho} = u \in H^1_{loc}(\mathbf{R}^3)$. Then, letting $\Omega \subset\subset \Gamma(\ell_\infty)$, we have, taking n large enough to have $\Omega \subset \Gamma(\ell_n)$,

$$\int_{\Gamma(\ell_n)} |\nabla u_n|^2 \geq \int_\Omega |\nabla u_n|^2,$$

so that

$$\liminf_{n\to\infty} \int_{\Gamma(\ell_n)} |\nabla u_n|^2 \geq \liminf_{n\to\infty} \int_\Omega |\nabla u_n|^2 \geq \int_\Omega |\nabla u|^2.$$

This is valid for any $\Omega \subset\subset \Gamma(\ell_\infty)$, so that :

$$\liminf_{n\to\infty} \int_{\Gamma(\ell_n)} |\nabla u_n|^2 \geq \int_{\Gamma(\ell_\infty)} |\nabla u|^2. \tag{95}$$

With a slight adaptation of this argument, we have :

$$\liminf_{n\to\infty} \int_{\Gamma(\ell_n)} \rho_n^{5/3} \geq \int_{\Gamma(\ell_\infty)} \rho^{5/3}. \tag{96}$$

The weak convergence in H^1_{loc} implies a strong one in L^2_{loc}, up to extracting a subsequence, so that, with estimate (73), it is easy to show that :

$$\int_{\Gamma(\ell_n)} \rho_n G_\infty \longrightarrow \int_{\Gamma(\ell_\infty)} \rho G_\infty, \tag{97}$$

with a similar result concerning the convolution term. Hence, collecting (93), (94), (95), (96) and (97), and pointing out that the total mass of ρ_n is conserved from the L^2_{loc} convergence and estimate (73), we prove (92). This concludes the proof of (i).

The proofs of (ii) and (iii) follow exactly the same pattern : we show (91), by the very same argument. Showing (92) in cases (ii)-(iii) requires sharper estimates, precisely those shown in Propositions 4.7 and 4.9. $\Diamond$

5 Compactness of the minimizing sequences

We show in this Section our main result, namely Theorem 1.1, that we recall here :

Theorem 5.1 *Let $\mathcal{E}$ be the functional defined by (16), and denote by $\mathcal{I}$ the minimization problem (21), that is :*

$$\mathcal{I} = \inf\left\{\mathcal{E}(\ell), \quad \ell \in \mathcal{L}_3(\mathbf{R}^3)\right\}.$$

Then any minimizing sequence of $\mathcal{I}$ is relatively compact in $\mathcal{L}_3(\mathbf{R}^3)$, so that this problem has at least one solution.

In order to show this compactness result, we consider a minimizing sequence ℓ_n, and intend to prove that there exists a basis (a_i^n) of ℓ_n satisfying (25), together with :

(a) The sequences $R_i^n = |a_i^n|$ are bounded from below : $\exists R_0 > 0$, s.t $\forall i = 1,2,3$, $\forall n \in \mathbf{N}$, $R_i^n \geq R_0$.

(b) The sequences R_i^n are bounded from above, i.e $\exists R_1 > 0$, s.t $\forall i = 1,2,3$, $\forall n \in \mathbf{N}$, $R_i^n \leq R_1$.

We start with the proof of assertion (a).

5.1 Bound from below

Proposition 5.2 *Let $\ell \in \mathcal{L}_3(\mathbf{R}^3)$, and $(a_i)_{i=1,2,3}$ one of its basis. Denote by $R_i = |a_i|$ the associated radii, and assume that $R_1 \leq R_2 \leq R_3$. Then we have the following :*

$$\mathcal{E}(\ell) \geq \frac{1}{4R_1} + a, \tag{98}$$

the constant $a \in \mathbf{R}$ being independent of ℓ.

Proof : We go back to the thermodynamic limit process (see [9, 10]), and recall that taking $\Lambda_n = \left\{\sum_{i=1}^3 k_i a_i, k_i \in \{-n, -n+1, \ldots, n, n+1\}\right\}$, we have :

$$\mathcal{E}(\ell) = \lim_{n\to\infty} \frac{I^{TFW}_{\Lambda_n}}{|\Lambda_n|}, \tag{99}$$

where $|\Lambda_n| = (2n+2)^3$ is the cardinal of Λ_n, and $I^{TFW}_{\Lambda_n}$ is the TFW energy defined by :

$$I^{TFW}_{\Lambda_n} = \inf\Big\{ E^{TFW}_{\Lambda_n}(\rho) + \frac{1}{2}\sum_{k\neq j\in\Lambda_n}\frac{1}{|k-j|}, \quad \rho\geq 0, \\ \sqrt{\rho}\in H^1(\mathbf{R}^3), \quad \int_{\mathbf{R}^3}\rho = (2n+2)^3\Big\},$$

with

$$E^{TFW}_{\Lambda_n}(\rho) = \int_{\mathbf{R}^3}|\nabla\sqrt{\rho}|^2 + \int_{\mathbf{R}^3}\rho^{5/3} - \sum_{k\in\Lambda_n}\int_{\mathbf{R}^3}\frac{\rho(x)}{|x-k|}dx \\ +\frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3}\frac{\rho(x)\rho(y)}{|x-y|}dxdy.$$

In particular, we may bound this energy from below by the corresponding TF energy :

$$E^{TFW}_{\Lambda_n}(\rho)\geq E^{TF}_{\Lambda_n}(\rho) = \int_{\mathbf{R}^3}\rho^{5/3} - \sum_{k\in\Lambda}\int_{\mathbf{R}^3}\frac{\rho(x)}{|x-k|}dx + \frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3}\frac{\rho(x)\rho(y)}{|x-y|}dxdy,$$

so that

$$I^{TFW}_{\Lambda_n}\geq I^{TF}_{\Lambda_n},$$

$I^{TF}_{\Lambda_n}$ being defined by

$$I^{TF}_{\Lambda_n} = \inf\Big\{ E^{TF}_{\Lambda_n}(\rho) + \frac{1}{2}\sum_{k\neq j\in\Lambda_n}\frac{1}{|k-j|}, \quad \rho\geq 0, \\ \rho\in L^1\cap L^{5/3}(\mathbf{R}^3), \quad \int_{\mathbf{R}^3}\rho = (2n+2)^3\Big\}.$$

We now invoke Teller's Lemma [16], which we recall here :

Lemma 5.3 (Teller) *Let $\Lambda = \Lambda_a\cup\Lambda_b$ be a finite subset of $\mathbf{R}^3$, with (Λ_a,Λ_b) a partition of Λ. Then we have :*

$$I^{TF}_{\Lambda} > I^{TF}_{\Lambda_a} + I^{TF}_{\Lambda_b}.$$

Separating Λ_n into $4(n+1)^3$ sets of two points which distance is equal to R_1, as shown in Figure 1 we then have :

$$I^{TFW}_{\Lambda_n}\geq I^{TF}_{\Lambda_n} > 4(n+1)^3 I^{TF}_{\Lambda_0},$$

with $\Lambda_0 = \{0, a_1\}$. Hence considering (99), it is sufficient to prove (98) for $I^{TF}_{\Lambda_0}$, i.e :

$$E^{TF}_{\{0,a_1\}}(\rho)\geq a, \quad \forall\rho\in L^1\cap L^{5/3}, \quad \int_{\mathbf{R}^3}\rho = 2, \tag{100}$$

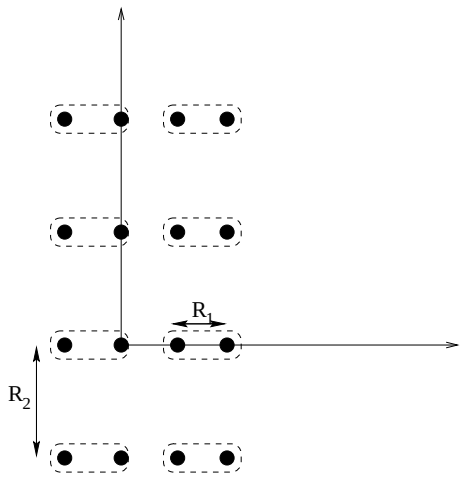

Figure 1: The set Λ_n and its subdivision into diatomic molecules (in only two dimensions).

with a independent of a_1. In order to do so, we notice that $\frac{1}{|x|} \in L^{5/2}_{loc}(\mathbf{R}^3)$, and thus :

$$\int_{\mathbf{R}^3} \frac{1}{|x|}\rho \leq \int_{|x|>1} \rho + (8\pi)^{2/5}\left(\int_{|x|<1} \rho^{5/3}\right)^{3/5} \leq 2 + (8\pi)^{2/5}\left(\int_{\mathbf{R}^3} \rho^{5/3}\right)^{3/5}.$$

This implies that :

$$E^{TF}_{\Lambda_0}(\rho) \geq \int_{\mathbf{R}^3} \rho^{5/3} - 2(8\pi)^{2/5}\left(\int_{\mathbf{R}^3} \rho^{5/3}\right)^{3/5} - 4 \geq a,$$

for some universal constant $a \in \mathbf{R}$. This implies (100), and thus concludes the proof. $\Diamond$

At this stage, we would like to make some comment on the Thomas-Fermi case (see [15, 16]). It is worth noticing that we may use directly Teller's Lemma on the TF energy, in order to obtain (since the analogous result to (99) is valid in the TF setting, see [16]), that

$$\mathcal{E}^{TF}(\ell) = \lim_{n\to\infty} \frac{I^{TF}_{\Lambda_n}}{|\Lambda_n|} \geq \frac{1}{2} I^{TF}_{\Lambda_0} > I^{TF}_{at},$$

where $I^{TF}_{\Lambda_0}$ is the TF energy of the diatomic molecule with nuclei at positions 0 and a_1, and I^{TF}_{at} is the atomic TF energy (defined exactly as in (26)-(27), but without the gradient term). Since the same convergence results as those of Theorem 4.11 may be shown in the TF setting, we have the following :

Theorem 5.4 *In the Thomas-Fermi case, problem (21) has no solution. Moreover, for any* $\ell \in \mathcal{L}_3(\mathbf{R}^3)$, $\mathcal{E}(\ell) > I^{TFW}_{at}$.

A direct consequence of Proposition 5.2 is the following :

Proposition 5.5 *For any minimizing sequence* $(\ell_n)_{n\in\mathbf{N}}$ *of problem (21), any sequence of basis* (a^n_i) *of* ℓ_n *satisfy :*

$$\exists R_0 > 0, \quad |a^n_i| \geq R_0.$$

5.2 Bound from above

We now turn to the proof of (b). We assume that there exists an unbounded minimizing sequence $(\ell_n)_{n\in\mathbf{N}}$, and try to reach a contradiction. For that purpose, we denote by (a_i^n) a basis of ℓ_n given by Theorem 2.5, by $R_i^n = |a_i^n|$ the corresponding radii, and notice that, up to extracting a subsequence, only three cases may occur :

(1) R_1^n goes to infinity as n goes to infinity,

(2) a_1^n converges to some a_1 and R_2^n goes to infinity as n goes to infinity,

(3) (a_1^n, a_2^n) converges to some (a_1, a_2) and R_3^n goes to infinity as n goes to infinity.

Using Theorem 4.11, we know that respectively in case (1), (2), (3), $\mathcal{E}(\ell_n)$ converges to the atomic energy, the polymer energy associated to a_1, or the thin film energy associated to (a_1, a_2). It is thus sufficient to prove that in all three cases, there exists a proper lattice having a lower energy than those limits. This is our aim in the following subsections.

5.2.1 The thin film case

We show here that for any $\ell \in \mathcal{L}_2(\mathbf{R}^3)$, $\mathcal{E}(\ell)$ cannot be a minimum of $\mathcal{E}$, therefore excluding occurrence (3).

Proposition 5.6 *For any $\ell \in \mathcal{L}_2(\mathbf{R}^3)$, there exists an $\ell_0 \in \mathcal{L}_3(\mathbf{R}^3)$ such that :*

$$\mathcal{E}(\ell_0) < \mathcal{E}(\ell).$$

Proof : We fix an $\ell \in \mathcal{L}_2(\mathbf{R}^3)$, of basis (a_1, a_2), that we may assume to be in the plane $\{x_3 = 0\}$. For any $R > 0$, we define $\ell_R \in \mathcal{L}_3(\mathbf{R}^3)$ the proper lattice of basis (a_1, a_2, Re_3). We intend to show the following :

$$\mathcal{E}(\ell_R) \leq \mathcal{E}(\ell) - Ce^{-\sqrt{\theta_\ell}R} + o(e^{-\sqrt{\theta_\ell}R}), \quad \text{as} \quad R \longrightarrow \infty, \tag{101}$$

with $C > 0$, and where $\theta_\ell > 0$ is the Lagrange multiplier of problem (62). For this purpose, we denote by ρ the unique electronic density associated to the lattice ℓ, and set $\rho_R = \frac{\rho|_{\Gamma(\ell_R)}}{\|\rho\|_{L^1(\Gamma(\ell_R))}}$. Since ρ is even with respect to x_3, ρ_R is ℓ_R-periodic, thus is a test function for the variational problem defining $\mathcal{E}(\ell_R)$. Denoting by $\varepsilon_R = \int_{\Gamma(\ell)\cap\{|x_3|>R\}} \rho$, we have, from Proposition 3.8,

$$\varepsilon_R \sim a_\ell \frac{|a_1 \wedge a_2|}{2\sqrt{\theta_\ell}} e^{-\sqrt{\theta_\ell}R} = \alpha e^{-\sqrt{\theta_\ell}R}, \quad \text{as} \quad R \longrightarrow \infty.$$

We now study each terms of the energy functional :

$$\int_{\Gamma(\ell_R)} |\nabla\sqrt{\rho}_R|^2 \leq \frac{1}{1-\varepsilon_R} \int_{\Gamma(\ell)} |\nabla\sqrt{\rho}|^2 \leq (1+\varepsilon_R) \int_{\Gamma(\ell)} |\nabla\sqrt{\rho}|^2 + o(\varepsilon_R). \tag{102}$$

Likewise,

$$\int_{\Gamma(\ell_R)} \rho_R^{5/3} \leq (1+\frac{5}{3}\varepsilon_R) \int_{\Gamma(\ell)} \rho^{5/3} + o(\varepsilon_R). \tag{103}$$

We then turn to the electrostatic terms : setting

$$E_{\ell_R}^{TFW,el}(\rho_R) = -\int_{\Gamma(\ell_R)} \rho_R G_{\ell_R} + \frac{1}{2}\int_{\Gamma(\ell_R)}\int_{\Gamma(\ell_R)} \rho_R(x)\rho_R(y) G_{\ell_R}(x-y)dxdy,$$

and denoting by h_R the function $G_\ell - G_{\ell_R}$, we have :

$$\begin{aligned} E_{\ell_R}^{TFW,el}(\rho_R) &= -\int_{\Gamma(\ell_R)} \rho_R G_\ell + \frac{1}{2}\int_{\Gamma(\ell_R)}\int_{\Gamma(\ell_R)} \rho_R(x)\rho_R(y) G_\ell(x-y)dxdy \\ &\quad + \int_{\Gamma(\ell_R)} \rho_R h_R - \frac{1}{2}\int_{\Gamma(\ell_R)}\int_{\Gamma(\ell_R)} \rho_R(x)\rho_R(y) h_R(x-y)dxdy \\ &\quad + o(\varepsilon_R). \end{aligned}$$

Hence, developing in the same fashion as above :

$$\begin{aligned} E_{\ell_R}^{TFW,el}(\rho_R) &= -(1+\varepsilon_R)\int_{\Gamma(\ell_R)} \rho G_\ell + \int_{\Gamma(\ell_R)} \rho_R h_R \\ &\quad + (\frac{1}{2}+\varepsilon_R)\int_{\Gamma(\ell_R)}\int_{\Gamma(\ell_R)} \rho(x)\rho(y) G_\ell(x-y)dxdy \\ &\quad - \frac{1}{2}\int_{\Gamma(\ell_R)}\int_{\Gamma(\ell_R)} \rho_R(x)\rho_R(y) h_R(x-y)dxdy + o(\varepsilon_R). \end{aligned}$$

We are now going to show that :

$$\begin{aligned} -\int_{\Gamma(\ell_R)} \rho G_\ell &+ \frac{1}{2}\int_{\Gamma(\ell_R)}\int_{\Gamma(\ell_R)} \rho(x)\rho(y) G_\ell(x-y)dxdy \leq \\ &- \int_{\Gamma(\ell)} \rho G_\ell + \frac{1}{2}\int_{\Gamma(\ell)}\int_{\Gamma(\ell)} \rho(x)\rho(y) G_\ell(x-y)dxdy \end{aligned} \tag{104}$$

and

$$\int_{\Gamma(\ell_R)} \rho_R h_R - \frac{1}{2}\int_{\Gamma(\ell_R)}\int_{\Gamma(\ell_R)} \rho_R(x)\rho_R(y) h_R(x-y)dxdy \leq o(\varepsilon_R) \tag{105}$$

We begin with (104), and write the difference of these two expressions as :

$$\begin{aligned} -\int_{\Gamma(\ell_R)} \rho G_\ell &+ \frac{1}{2}\int_{\Gamma(\ell_R)}\int_{\Gamma(\ell_R)} \rho(x)\rho(y) G_\ell(x-y)dxdy \\ +\int_{\Gamma(\ell)} \rho G_\ell &- \frac{1}{2}\int_{\Gamma(\ell)}\int_{\Gamma(\ell)} \rho(x)\rho(y) G_\ell(x-y)dxdy \\ &= \int_{\Gamma(\ell)\setminus\Gamma(\ell_R)} \rho\big(G_\ell - \frac{1}{2} G_\ell \star_{\Gamma(\ell)} (\rho_{|\Gamma(\ell_R)} + \rho)\big). \end{aligned}$$

Hence, proving that $G_\ell - \frac{1}{2} G_\ell \star_{\Gamma(\ell)} (\rho_{|\Gamma(\ell_R)} + \rho) \leq 0$ on $\Gamma(\ell) \setminus \Gamma(\ell_R)$, for R sufficiently large, will conclude the proof of (104). For this purpose, we use Proposition 3.6 and write :

$$-\alpha|x_3| + \beta - \frac{\gamma}{|x|} \leq G_\ell(x) \leq -\alpha|x_3| + \beta + \frac{\gamma}{|x|} \tag{106}$$

in $\Gamma(\ell)$, where α, β and γ are positive constants independent of R. From this and the fact that $\frac{1}{2}(\rho + \rho_{|\Gamma(\ell_R)})$ has total mass $1 - \frac{\varepsilon_R}{2}$ over $\Gamma(\ell)$, we deduce that :

$$\left\{ \begin{array}{l} -\alpha(1 - \frac{\varepsilon_R}{2})|x_3| + \beta(1 - \frac{\varepsilon_R}{2}) - \frac{\gamma'}{|x|} \leq \frac{1}{2} G_\ell \star_{\Gamma(\ell)} (\rho + \rho_{|\Gamma(\ell_R)}) \\ \frac{1}{2} G_\ell \star_{\Gamma(\ell)} (\rho + \rho_{|\Gamma(\ell_R)}) \leq -\alpha(1 - \frac{\varepsilon_R}{2})|x_3| + \beta(1 - \frac{\varepsilon_R}{2}) + \frac{\gamma'}{|x|}, \end{array} \right.$$

with a constant $\gamma' > 0$ independent of R. This, together with (106), proves that

$$G_\ell - \frac{1}{2} G_\ell \star_{\Gamma(\ell)} (\rho_{|\Gamma(\ell_R)} + \rho) \leq (1 - \frac{\varepsilon_R}{2})(\beta - \alpha|x_3|) \leq 0$$

whenever $|x_3|$ is sufficiently large. This proves our claim, and thus completes the proof of (104).

We now turn to (105), and set $\phi_R = G_\ell - G_\ell \star_{\Gamma(\ell)} \rho_R$. We have :

$$-\Delta \phi_R = 4\pi(\delta_0 - \rho_R).$$

Since h_R cancels at 0, and $-\Delta \phi_R = \rho_R - \delta_0$,we have :

$$\begin{aligned} -\int_{\Gamma(\ell_R)} \rho_R h_R \;\; + \;\; & \frac{1}{2} \int_{\Gamma(\ell_R)} \int_{\Gamma(\ell_R)} \rho_R(x) \rho_R(y) h_R(x-y) dx dy \\ = \;\; & \frac{1}{2} \int_{\Gamma(\ell_R)} \int_{\Gamma(\ell_R)} h_R(x-y) \Big(-\Delta \phi_R(x) \Big) \Big(-\Delta \phi_R(y) \Big) dx dy. \end{aligned}$$

We now integrate by parts this expression, and find :

$$\begin{aligned} -\int_{\Gamma(\ell_R)} \rho_R h_R \;\; + \;\; & \frac{1}{2} \int_{\Gamma(\ell_R)} \int_{\Gamma(\ell_R)} \rho_R(x) \rho_R(y) h_R(x-y) dx dy \\ = \;\; & \frac{1}{2} \int_{\partial\Gamma(\ell_R)} \int_{\partial\Gamma(\ell_R)} \frac{\partial \phi_R}{\partial n}(x) \frac{\partial \phi_R}{\partial n}(y) h_R(x-y) dx' dy'. \end{aligned}$$

From the ℓ-periodicity of ϕ_R, this boundary integral reduces to an integral over the set $\partial\Gamma(\ell_R) \cap \{|x_3| = \frac{R}{2}\}$. And using the fact that ϕ_R and h_R are even with respect to x_3, we thus have :

$$\begin{aligned} -\int_{\Gamma(\ell_R)} \rho_R h_R \;\; + \;\; & \frac{1}{2} \int_{\Gamma(\ell_R)} \int_{\Gamma(\ell_R)} \rho_R(x) \rho_R(y) h_R(x-y) dx dy \\ = \;\; & \int_{\{x_3 = \frac{R}{2}\} \cap \overline{\Gamma(\ell)}} \int_{\{y_3 = \frac{R}{2}\} \cap \overline{\Gamma(\ell)}} \partial_3 \phi_R(x) \partial_3 \phi_R(y) h_R(x-y) dx' dy' \\ - \;\; & \int_{\{x_3 = \frac{R}{2}\} \cap \overline{\Gamma(\ell)}} \int_{\{y_3 = -\frac{R}{2}\} \cap \overline{\Gamma(\ell)}} \partial_3 \phi_R(x) \partial_3 \phi_R(y) h_R(x-y) dx' dy'. \end{aligned}$$

In order to bound this term, we write :

$$\phi_R = \phi + \frac{1}{1-\varepsilon_R}\rho_{|\Gamma(\ell_R)^c} \star G_\ell - \frac{\varepsilon_R}{1-\varepsilon_R}\rho \star G_\ell = \phi + \hat{\phi}_R,$$

where the convolution products are over $\Gamma(\ell)$, and $\phi = G_\ell - \rho \star G_\ell$. We are going to prove (105) for all those terms. The second one may be dealt with as follows : we first notice that

$$|\rho \star G_\ell(x_3 = \pm\frac{R}{2})| \leq CR, \tag{107}$$

and

$$\begin{aligned} |(\rho_{|\Gamma(\ell_R)^c} \star G_\ell)(x_3 = \pm\frac{R}{2})| &= \left| \int_{\{|y_3| \geq \frac{R}{2}\} \cap \Gamma(\ell_R)} \rho(y) G_\ell(x-y)dy \right| (x_3 = \pm\frac{R}{2}) \\ &\leq \int_{\{|y_3| \geq \frac{R}{2}\} \cap \Gamma(\ell_R)} \frac{\rho(y)}{|x-y|}dy \\ &\quad + \int_{\{|y_3| \geq \frac{R}{2}\} \cap \Gamma(\ell_R)} \rho(y)|x-y|dy \\ &\leq CR\varepsilon_R. \end{aligned} \tag{108}$$

(107) and (108) imply that :

$$|\hat{\phi}_R(x_3 = \pm\frac{R}{2})| \leq CR\varepsilon_R. \tag{109}$$

On the other hand, $|-\Delta\hat{\phi}_R(x_3 = \pm\frac{R}{2})| \leq |\rho_R(x_3 = \pm\frac{R}{2})| \leq C\varepsilon_R$, so that we have :

$$|\nabla\hat{\phi}_R(x_3 = \pm\frac{R}{2})| \leq CR\varepsilon_R.$$

Since we also know that $|\nabla\phi(x_3 = \pm\frac{R}{2})| \leq Ce^{-aR}$, for some $a > 0$ independent of R, (105) is proved for $\hat{\phi}_R$ and for the crossing term. Thus, the proof of (105) amounts to show :

$$\begin{aligned} &\int_{\{x_3 = \frac{R}{2}\} \cap \Gamma(\ell)} \int_{\{y_3 = \frac{R}{2}\} \cap \Gamma(\ell)} \partial_3\phi(x)\partial_3\phi(y)h_R(x-y)dx'dy' \\ -&\int_{\{x_3 = \frac{R}{2}\} \cap \Gamma(\ell)} \int_{\{y_3 = -\frac{R}{2}\} \cap \Gamma(\ell)} \partial_3\phi(x)\partial_3\phi(y)h_R(x-y)dx'dy' \quad \geq \quad o(\varepsilon_R). \end{aligned} \tag{110}$$

To prove this, we expand h_R as a Fourier series with respect to x'. Using (64) and (75), one easily computes :

$$h_R(x) = H_R(x_3) - c_\ell \sum_{k \in \ell^* \setminus \{0\}} \frac{e^{2i\pi k \cdot x'}}{|k|} \sum_{k_3 \in \mathbf{Z} \setminus \{0\}} e^{-|k|2\pi|x_3 - k_3 R|}, \tag{111}$$

with $|H_R(t)| \leq C(1+|t|)$, C being independent of R, and $c_\ell > 0$. Here we have used the fact that

$$\int_{\mathbf{R}} \frac{e^{2i\pi x_3 \xi}}{|k|^2+\xi^2} d\xi = \frac{2\pi}{|k|} e^{-2\pi|k||x_3|},$$

and the corresponding periodic equality, that is :

$$\frac{2\pi}{|k|} \sum_{k_3 \in \mathbf{Z}} \frac{e^{2i\pi \frac{k_3}{R} x_3}}{|k|^2 + \frac{k_3^2}{R^2}} = \sum_{k_3 \in \mathbf{Z}} e^{-|k|2\pi|x_3 - k_3 R|}.$$

We then insert (111) into the left-hand side of (110), which we denote by A_R, and find :

$$\begin{aligned} A_R &= \int_{x_3=\frac{R}{2}} \int_{y_3=\frac{R}{2}} \partial_3\phi(x)\partial_3\phi(y) H_R(x_3-y_3) dx'dy' \\ &\quad - \int_{x_3=\frac{R}{2}} \int_{y_3=-\frac{R}{2}} \partial_3\phi(x)\partial_3\phi(y) H_R(x_3-y_3) dx'dy' \\ &\quad - c_\ell \sum_{k\in\ell^*} \left(\tilde{\partial_3\phi}(k,\frac{R}{2}) \tilde{\partial_3\phi}(-k,\frac{R}{2}) \sum_{k_3\neq 0} e^{-2\pi|k||k_3|R} \right) \\ &\quad + c_\ell \sum_{k\in\ell^*} \left(\tilde{\partial_3\phi}(k,\frac{R}{2}) \tilde{\partial_3\phi}(-k,-\frac{R}{2}) \sum_{k_3\neq 0} (e^{-2\pi|k||1-k_3|R}) \right), \end{aligned}$$

where the $\tilde{}$ -transform is defined by (68). We next use estimate (67)of Proposition 3.8, with $\epsilon < \sqrt{\theta_\ell}$ to show that the first two integrals of the above sum may be bounded by $O(R^2 e^{-2(\sqrt{\theta_\ell}-\epsilon)R}) = o(\varepsilon_R)$, and that up to terms of the same order, the sum reduces to a sum over $K = \ell^* \cap \{0 < \pi|k| < \sqrt{\theta_\ell}\}$. We thus have, μ_k being defined in (67) :

$$\begin{aligned} A_R &= -c_\ell \sum_{k\in K} \sum_{k_3\neq 0} \mu_k \mu_{-k} e^{-2\pi|k|R} (e^{-2\pi|k||k_3|R} - e^{-2\pi|k||1-k_3|R}) + o(\varepsilon_R) \\ &= -c_\ell \sum_{k\in K} \mu_k \mu_{-k} e^{-2\pi|k|R} (-1 + e^{-2\pi|k|R}) + o(\varepsilon_R). \end{aligned}$$

Then, noticing that since $\partial_3\phi$ is a real-valued function, we infer that $\mu_{-k} = \overline{\mu}_k$, so that we may write the above sum as :

$$A_R = c_\ell \sum_{k\in K} |\mu_k|^2 e^{-2\pi|k|R} (-e^{-2\pi|k|R} + 1) \geq 0,$$

for R large enough, since K does not depend on R. This proves (110), hence (105).

We now collect (102), (103), (104) and (105), and find :

$$\begin{aligned} E^{TFW}_{\ell_R}(\rho_R) &\leq E^{TFW}_\ell(\rho) + \varepsilon_R \left(\int_{\Gamma(\ell)} |\nabla\rho|^2 + \frac{5}{3} \int_{\Gamma(\ell)} \rho^{5/3} \right. \\ &\quad \left. - \int_{\Gamma(\ell)} G_\ell \rho + \int_{\Gamma(\ell)} \int_{\Gamma(\ell)} \rho(x)\rho(y) G_\ell(x-y) dxdy \right) + o(\varepsilon_R). \end{aligned}$$

Integrating the Euler-Lagrange equation of the minimization problem defining $\mathcal{E}(\ell)$, we find that :

$$\int_{\Gamma(\ell)} |\nabla\rho|^2 + \frac{5}{3}\int_{\Gamma(\ell)} \rho^{5/3} - \int_{\Gamma(\ell)} G_\ell\rho + \int_{\Gamma(\ell)}\int_{\Gamma(\ell)} \rho(x)\rho(y)G_\ell(x-y)dxdy = -\theta_\ell,$$

so that we infer that :

$$\mathcal{E}(\ell_R) \leq \mathcal{E}(\ell) - \varepsilon_R\theta_\ell + o(\varepsilon_R).$$

This concludes the proof. $\Diamond$

5.2.2 The polymer case

We now turn to case (2) :

Proposition 5.7 *For any $\ell \in \mathcal{L}_1(\mathbf{R}^3)$, there exists $\ell_0 \in \mathcal{L}_3(\mathbf{R}^3)$ such that :*

$$\mathcal{E}(\ell_0) < \mathcal{E}(\ell).$$

Proof : We use exactly the same trick as for Proposition 5.6, defining ℓ_R as the lattice of basis (Re_1, Re_2, a), where a is the basis of ℓ, and is collinear to e_3 (this is always possible to do by change of coordinates). We intend to show estimate (101) in this case. We define ρ_R and ε_R exactly in the same way, so that (102) and (103) follow immediately. (Note that from Proposition 3.3, ε_R satisfies exactly the same estimate as in the thin film case.)

A straightforward adaptation of (104)'s proof shows that this estimate also holds (just replace $|x_3|$ by $\log|x'|$). To prove (105), the same ϕ_R-trick works, and we are here again reduced to show bounds on integrals over the set $\{|x_1| = \frac{R}{2}\} \cup \{|x_2| = \frac{R}{2}\}$. Here again, the same type of estimates are available, namely (33), (75) and (61), so that the above proof can be easily adapted, replacing the function $e^{-a|x_3|}$ by $W_a(x')$ defined in (49) $\Diamond$

5.2.3 The atomic case

We deal here with case (3) :

Proposition 5.8 *There exists an $\ell \in \mathcal{L}_3(\mathbf{R}^3)$ satisfying the following :*

$$\mathcal{E}(\ell) < I_{at}^{TFW}.$$

Proof : We follow step by step the proof of Proposition 5.6, with $\ell_R = R\mathbf{Z}^3$, and find out that difficulties might only occur in the electrostatic terms. We introduce here again the function $\phi_R = \frac{1}{|x|} - \frac{1}{|x|} \star \rho_{R|\Gamma(\ell_R)}$, and using the same tricks, conclude the proof. Note that here, the proof is simpler since the eigenmodes appearing in the polymer and thin film case with coefficients μ_k vanish, so that the proof of (105) is simplified. $\Diamond$

This concludes the proof of Theorem 1.1, since, considering a minimizing sequence ℓ_n of problem (21), Proposition 5.5 shows that there exists an $R_0 > 0$ such that for any basis $(a_i^n)_{i=1,2,3}$ of ℓ_n, we have :

$$|a_i^n| \geq R_0, \quad \forall i \in \{1,2,3\}, \forall n \in \mathbf{N}.$$

On the other hand, Theorem 4.11 together with Propositions 5.6, 5.7 and 5.8, show that there exists a sequence of basis of ℓ_n which is bounded in $\mathbf{R}^3$, and hence is relatively compact.

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Chapitre 4

Le “Crystal Problem” en dimension 1

Ce chapitre a été écrit en collaboration avec C. Le Bris, et accepté pour publication dans Nonlinear Analysis T.M.A. [P4]. Nous y étudions le modèle de Thomas-Fermi-von Weizsäcker en dimension 1, et montrons que la solution du problème d'optimisation de géométrie converge vers une géométrie périodique.

Periodicity of the infinite-volume ground state of a one-dimensional quantum model

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Abstract We study a one-dimensional molecular system consisting of N nuclei and N electrons, modeled by a quantum mechanical model, namely the Thomas-Fermi-von Weizsäcker (TFW) model. For each N fixed, we consider the ground state of this system. Then we investigate its behavior in the limit $N \to \infty$. We show that the system converges to a periodic system, and that its energy per atom converges to the energy of a periodic TFW model. This implies that for any periodic configuration of nuclei (with an arbitrary number n of identical atoms per cell), the minimum of energy per atom is reached for the periodic configuration with *one* atom per cell.

Key words: quantum chemistry, periodicity, crystalline order, ground state, nonlinear.

1 Introduction

It is an unsolved problem in the study of matter to understand why matter is in a crystalline state at low temperature [14]. So far as we know, this "crystal problem" has been tackled by Radin [13, 8] in a classical framework and in one dimension. Our aim here is to address the same kind of problem when we take into account the quantum feature of the electrons.

We consider a set of N identical pointwise nuclei, of charge $+1$ and positions $\{X_i\}_{1\leq i\leq N}$, together with N electrons, defined through their density ρ. We assume that the system is in its ground state, which means that it is a solution of:

$$I_N = \inf\left\{ E^{TFW}(\rho, \{X_i\}),\ \rho \geq 0,\ \sqrt{\rho} \in H^1(\mathbf{R}),\ |x|\rho \in L^1(\mathbf{R}),\ \int_{\mathbf{R}} \rho = N \right\}, \tag{1}$$

where the energy E^{TFW} is defined by:

$$\begin{aligned} E^{TFW}(\rho, \{X_i\}) &= \int_{\mathbf{R}} (\sqrt{\rho}\,')^2 + \int_{\mathbf{R}} \rho^p + \sum_{i=1}^{N} \int_{\mathbf{R}} \frac{1}{2}|x - X_i|\rho(x)dx \\ &- \frac{1}{4} \iint_{\mathbf{R}^2} \rho(x)|x-y|\rho(y)dxdy - \sum_{i<j} \frac{|X_i - X_j|}{2}. \end{aligned} \tag{2}$$

The potential $-\frac{|x|}{2}$ is the Coulombic interaction potential in one dimension, and the exponent p is strictly greater than one. Note that since the term $\int \rho^p$ is a homogeneous gas approximation of the kinetic energy, p should be equal to $\frac{d+2}{d} = \frac{1+2}{1} = 3$ in this one-dimensional model. On the other hand, if one considers that we deal with a three-dimensional model which is invariant with respect to two variables, then p should be equal to $\frac{5}{3}$. Both cases are contained in the present study. The minimization problem (1) with respect to ρ, with $\{X_i\}$ fixed, is called the electronic problem:

$$I(\{X_i\}) = \inf\left\{ E^{TFW}(\rho, \{X_i\}),\ \rho \geq 0,\ \sqrt{\rho} \in H^1(\mathbf{R}),\ |x|\rho \in L^1(\mathbf{R}),\ \int_{\mathbf{R}} \rho = N \right\}, \tag{3}$$

The global one, also equal to

$$I_N = \inf\left\{ I(\{X_i\}), \quad X_i \in \mathbf{R} \right\}, \tag{4}$$

is called the geometry optimization problem. The first point is, one can reorder the nuclei so that $X_i \leq X_{i+1}$, for all $i \in \{1, \ldots, N-1\}$. Next, a straightforward adaptation of [1] (see also [3]) shows that the electronic problem (3) is convex with respect to ρ, and has a unique solution. Also, adapting the proofs of [7] to this one-dimensional case, one easily shows that the geometry optimization problem (1) has a solution. Our interest lies in showing that in the limit $N \to \infty$, the system converges (in some sense to be made precise below) to a periodic system. For this purpose, we introduce the following periodic geometry optimization problem:

$$I_{per} = \inf\left\{ E^{TFW}_{per,R}(\rho), \quad R > 0, \quad \rho \geq 0, \quad \sqrt{\rho} \in H^1_{per}(]0, R[), \quad \int_0^R \rho = 1 \right\}, \tag{5}$$

where $H^1_{per}(]0,R[)$ is the set of H^1_{loc} functions which are periodic of period R, and the energy $E^{TFW}_{per,R}$ is defined by:

$$\begin{aligned} E^{TFW}_{per,R}(\rho) &= \int_{-\frac{R}{2}}^{\frac{R}{2}} (\sqrt{\rho}\,')^2 + \int_{-\frac{R}{2}}^{\frac{R}{2}} \rho^p - \int_{-\frac{R}{2}}^{\frac{R}{2}} G_R(x)\rho(x)dx \\ &\quad + \frac{1}{2}\int_{-\frac{R}{2}}^{\frac{R}{2}}\int_{-\frac{R}{2}}^{\frac{R}{2}} \rho(x)G_R(x-y)\rho(y)dxdy, \end{aligned} \tag{6}$$

where the potential G_R represents the coulombic interaction between neutral R-periodic distribution of charges. Actually, we have:

$$G_R(x) = \sum_{k\neq 0} R\frac{e^{\frac{2i\pi kx}{R}}}{4\pi^2k^2}. \tag{7}$$

Here again, the minimization problem (5) may be splitted into electronic and geometry optimization problem, namely:

$$I_{per,R} = \inf\left\{ E^{TFW}_{per,R}(\rho), \quad \rho \geq 0, \quad \sqrt{\rho} \in H^1_{per}(]0,R[), \quad \int_0^R \rho = 1 \right\}, \tag{8}$$

$$I_{per} = \inf\left\{ I_{per,R}\,, \quad R > 0 \right\}. \tag{9}$$

As shown in [3], problem (8) is convex with respect to ρ and has a unique solution ρ_R. Moreover, (9), has at least one solution $\overline{R}$, by [4, 2].

Our first result is the convergence in energy:

Theorem 1.1 *The sequence $\frac{I_N}{N}$ which models the energy per atom converges to the periodic energy I_{per}.*

Next, we show a convergence result on the electronic density and on the nuclei positions:

Theorem 1.2 *Let $(\rho_N, \{X^N_i\})$ be any solution of problem (1). Then there exists a sequence $(i_N)_{N\in\mathbf{N}}$ such that:*

(i) $i_N \longrightarrow \infty, \quad N - i_N \longrightarrow \infty,$

(ii) There exists a solution (ρ_R, R) of (5) such that $\forall j \in \mathbf{Z}, \quad X^N_{i_N+j} - X^N_{i_N} \longrightarrow jR$, and $\rho_N(\cdot - X^N_{i_N}) - \rho_R(\cdot - X^N_{i_N})$ converges to 0 uniformly on any compact subset of $\mathbf{R}$.

Note that it will become clear in the course of the proof of Theorem 1.2 (Section 4) that condition (i) is in fact a necessary condition, implied by (ii).

Before entering the details of the proofs, let us point out that similar results were obtained by Gardner and Radin [8, 12] in a classical framework, where the atoms are supposed to interact with each other through a Lennard-Jones type two-body potential.

In the same spirit, Nijboer and Ventevogel [16, 10, 11] obtained an analogous result to that of Corollary 5.1 (see below) in this case. In [12], Radin also proves that a ground state configuration of N particles, in the limit $N \to \infty$, is indeed a ground state in a local sense: assuming that the energy of the system $\mathcal{S}$ is defined by a density of energy $e(\mathcal{S})$, an infinite system $\mathcal{S}$ is a local ground state if for any interval I and any system $\mathcal{T}$ equal to $\mathcal{S}$ on $\mathbf{R} \setminus I$, we have:

$$\int_I e(\mathcal{T}) \geq \int_I e(\mathcal{S}).$$

In the present case, the existence of e, i.e the local feature of the energy, is not that obvious because of the electrostatic terms, although it may be re-written in a local form (this is in fact what is done in the proof of Theorem 1.1).

2 A priori estimates

We first show that two nuclei can never have the same position, and study the Euler-Lagrange equations of problem (1).

Proposition 2.1 *The minimization problem (1) has at least one solution* $(\rho_N, \{X_i^N\})$. *Without loss of generality, we may assume that this solution satisfies* $X_i^N \leq X_{i+1}^N$, *for all* $1 \leq i \leq N-1$. *Moreover, any such solution satisfies:*

$$X_1^N < X_2^N < \cdots < X_N^N, \quad \text{and}$$

$$\int_{X_i^N}^{X_{i+1}^N} \rho_N = 1, \quad \int_{-\infty}^{X_1^N} \rho_N = \int_{X_N^N}^{\infty} \rho_N = \frac{1}{2}. \tag{10}$$

Proof: Consider any solution of (1), which we denote by $(\rho_N, \{X_i^N\})$. In particular, ρ_N is the solution of the minimization problem with $\{X_i^N\}$ fixed. It consequently satisfies the Euler-Lagrange equation of the corresponding problem, namely, setting $u_N = \sqrt{\rho}_N$:

$$-u_N'' + p u_N^{2p-1} + \left(\frac{1}{2} \sum_{i=1}^{N} |x - X_i^N| - \frac{1}{2}|x| \star u_N^2 \right) u_N + \theta u_N = 0,$$

where $\star$ denotes the convolution product over $\mathbf{R}$, and θ is the Lagrange multiplier associated to the constraint $\int_{\mathbf{R}} \rho_N = N$. Using Harnack inequality, one then easily shows that u_N never cancels. Moreover, since $\sqrt{\rho}_N \in H^1(\mathbf{R})$, ρ_N is a continuous and bounded function. Next, differentiating the function E^{TFW} with respect to X_i^N on the set $\{X_1^N < \cdots < X_N^N\}$, one finds :

$$\frac{\partial E^{TFW}}{\partial X_i^N}(\rho_N, \{X_i^N\}) = \frac{1}{2} \int_{\mathbf{R}} \operatorname{sgn}(X_i^N - x) \rho_N(x) dx - \frac{1}{2} \sum_{j=1}^{N} \operatorname{sgn}(X_i^N - X_j^N), \tag{11}$$

where sgn denotes the sign function, with the convention that $\mathrm{sgn}(0) = 0$. Since $X_i^N < X_{i+1}^N$, $\frac{1}{2}\sum_{j=1}^N \mathrm{sgn}(X_i^N - X_j^N) = i - \frac{N+1}{2}$. Hence, one easily finds that

$$\frac{\partial^2 E^{TFW}}{\partial {X_i^N}^2} = \rho_N(X_i^N), \quad \frac{\partial^2 E^{TFW}}{\partial X_i^N \partial X_j^N} = 0 \quad i \neq j.$$

This in particular shows that E^{TFW} is strictly convex with respect to $\{X_i^N\}$. Next, consider the system $\{Y_i\}$ defined by (10): it satisfies $Y_i < Y_{i+1}$, and it is a critical point of $E^{TFW}(\rho_N, \cdot)$. Hence, it is the unique solution of the convex variational problem defining $\{X_i^N\}$. As a consequence, $X_i^N = Y_i$, hence $X_i^N < X_{i+1}^N$, for all i, and $(\rho_N, \{X_i^N\})$ satisfies (11), for all i. Summing these inequalities, we find (10). $\Diamond$

Studying the Euler-Lagrange equation satisfied by ρ_N, we define

$$\phi_N = \frac{1}{2}\rho_N \star |x| - \frac{1}{2}\sum_{i=1}^N |x - X_i^N| - \theta, \tag{12}$$

and thus have:

$$\begin{cases} -u_N'' + p u_N^{2p-1} - \phi_N u_N = 0, \\ -\phi_N'' = \sum_{i=1}^N \delta_{X_i^N} - u_N^2. \end{cases} \tag{13}$$

Proposition 2.2 *For any $(\rho_N = u_N^2, \{X_i^N\})$ solution of (1), denoting by ϕ_N the function defined in (12), $u_N \in C^2(\mathbf{R})$, $\phi_N \in C^\infty(\mathbf{R} \setminus \{X_i^N\})$, and ϕ_N admits left and right derivatives at X_i^N, which satisfy:*

$$\forall i, \quad \phi_N'(X_i^{N-}) = -\phi_N'(X_i^{N+}) = \frac{1}{2}. \tag{14}$$

Moreover,

$$\frac{1}{2}{\phi_N'}^2 + \rho_N^p = \phi_N \rho_N + {u_N'}^2. \tag{15}$$

Proof: The regularity of u_N and ϕ_N follow from standard elliptic regularity and equations (13). Let $x \in]-\infty, X_1^N[$. According to (13), $\phi_N'(x) = \int_{-\infty}^x u_N^2(t)dt$, so that using (10), $\phi_N'(X_1^{N-}) = \frac{1}{2}$. Due to the presence of a Dirac mass at X_1^N, one immediately deduces that $\phi_N'(X_1^{N+}) = -\frac{1}{2}$. Next, we carry on this integration procedure until X_2^N, then X_3^N, and so on, to finally get (14). We then turn to the proof of (15): multiplying the first equation of (13) by u_N' and the second one by ϕ_N', we substract the results and get, on each interval $]X_i^N, X_{i+1}^N[$:

$$-u_N'' u_N' + p u_N^{2p-1} u_N' - \phi_N u_N u_N' + \phi_N' \phi_N'' = u_N^2 \phi_N',$$

which implies:

$$\left(-\frac{1}{2}{u_N'}^2 + \frac{1}{2}u_N^{2p} + \frac{1}{4}{\phi_N'}^2 - \frac{1}{2}\phi_N u_N^2\right)' = 0.$$

Its derivative being identically 0, this function is thus a constant on each of the intervals $]X_i^N, X_{i+1}^N[$. Moreover, since u'_N, u_N, ϕ_N are continuous, and since, according to (14), $(\phi'_N)^2$ is continuous at X_i^N, $-{u'_N}^2 + u_N^{2p} + \frac{1}{2}{\phi'_N}^2 - \phi_N u_N^2$ is constant on $\mathbf{R}$. To show that this constant is 0, we only need to show that $\lim_{-\infty}(-{u'_N}^2 + u_N^{2p} + \frac{1}{2}{\phi'_N}^2 - \phi_N u_N^2) = 0$. In order to do so, we point out that $u_N \to 0$ at infinity since $u_N \in H^1(\mathbf{R})$. Next, writing $\phi'_N(x) = \int_{-\infty}^x u_N^2(t)dt$, one easily shows that the same property holds for ϕ'_N. Next, we point out that, for $x \leq y < X_1^N$,

$$\phi_N(y) - \phi_N(x) = \int_x^y \int_{-\infty}^t u_N^2(s)dsdt = (y-x)\int_{-\infty}^x u_N^2 + \int_x^y (y-t)u_N^2(t)dt,$$

So that, using the fact that $|x|u_N^2 \in L^1(\mathbf{R})$,

$$|\phi_N(y) - \phi_N(x)| \leq \int_{-\infty}^y |t-y|u_N^2(t)dt \longrightarrow 0 \quad \text{as} \quad y \to -\infty.$$

This implies that ϕ_N has a limit at infinity, hence is bounded on a neighborhood of $-\infty$. Hence $\phi_N u_N$ vanishes at $-\infty$, and from the first equation of (13), ${u''_N}^2$ is integrable on a neighborhood of $-\infty$. Hence, u'_N goes to 0 at $-\infty$. $\Diamond$

Corollary 2.3 *Let $(\rho_N, \{X_i^N\})$ be a solution of (1), and ϕ_N be the effective potential (12). Then we have:*

(i) $|\phi'_N| \leq \frac{1}{2}$, *and this value is reached only at the X_i^Ns,*

(ii) $\rho_N \leq \left(\frac{1}{8(p-1)}\right)^{1/p}$,

(ii) $X_{i+1}^N - X_i^N \geq \left(8(p-1)\right)^{1/p}$, *for all* $i \in \{1, \ldots, N-1\}$.

Proof: Since ϕ_N satisfies the second equation of (13), ϕ''_N is strictly positive on each $]X_i^N, X_{i+1}^N[$, which means that ϕ'_N is strictly increasing on these intervals, and thus ranges from $-\frac{1}{2}$ to $\frac{1}{2}$ monotonically. Next, on $]-\infty, X_1^N[$, knowing that $\phi'_N(x) = \int_{-\infty}^x u_N^2(t)dt$, we find that ϕ'_N ranges monotonically from 0 to $\frac{1}{2}$ on this interval. Using the same kind of argument on $]X_N^N, \infty[$, this proves (i). We turn to the proof of (ii): u_N is a positive C^2 bounded function vanishing at infinity. Hence, there exists a point $x_0 \in \mathbf{R}$ which is the maximum of u_N. Moreover, at this point, u'_N cancels and u''_N is non-positive. Hence, $\phi_N(x_0)\rho_N(x_0) \geq p\rho_N^p(x_0)$, and $\frac{1}{2}{\phi'_N}^2(x_0) + \rho_N^p(x_0) = \phi_N(x_0)\rho_N(x_0)$. It follows that:

$$(p-1)\rho_N^p(x_0) \leq \frac{1}{2}{\phi'_N}^2(x_0). \tag{16}$$

Using (i), this implies (ii). Then, using (10), we have $\|\rho\|_{L^\infty}(X_{i+1} - X_i) \geq \int_{X_i}^{X_{i+1}} \rho = 1$, from which (iii) follows. $\Diamond$

Proposition 2.4 *Let $(u_N^2, \{X_i^N\})$ be a solution of (1), and ϕ_N the corresponding effective potential (12). Let $(i_N)_{N\in\mathbf{N}}$ be a sequence of indexes (such that $0 \leq i_N \leq N$). Then, for any $L > 0$, there exists a constant C_L independent of N such that*

$$\|\phi_N\|_{L^\infty(X_{i_N}^N - L, X_{i_N}^N + L)} \leq C_L \tag{17}$$

Proof: Let J_N denote the interval $[X_{i_N}^N - L, X_{i_N}^N + L]$. The first step of the proof is to show that u_N' is bounded. Indeed, let x_0 be the point where it reaches its maximum (since $u_N' \longrightarrow 0$ at infinity, as the proof of Proposition 2.2 shows, such a point exists). Then $u_N''(x_0) = 0$, so that using (13), $\phi_N\rho_N = p\rho_N^p$. Hence, using (15), one finds that

$$(u_N')^2(x_0) = (1-p)\rho_N^p(x_0) + \frac{1}{2}(\phi_N')^2(x_0) \leq \frac{1}{8},$$

which proves our claim. We next show (17). Such a bound clearly holds for a general C_L depending on N, since ϕ_N has a limit at infinity and satisfies the second equation of (13). We now assume that it does not hold uniformly with respect to N. We then have an interval $[a, b] \subset J_N$ on which $|\phi_N| \longrightarrow \infty$ as $N \to \infty$. Since ϕ_N' is bounded independently of N, either $\phi_N \longrightarrow +\infty$ on J_N, or $\phi_N \longrightarrow -\infty$ on the whole interval J_N. We now set $\overline{\phi}_N = \frac{1}{2L}\int_{J_N}\phi_N$. We then have

$$\|\phi_N - \overline{\phi}_N\|_{L^\infty(J_N)} \leq \|\phi_N'\|_{L^\infty(J_N)} \leq \frac{1}{2}.$$

Hence, $\overline{\phi}_N\rho_N = \frac{1}{2}{\phi_N'}^2 + \rho_N^p - {u_N'}^2 - (\phi_N - \overline{\phi}_N)\rho_N$ is bounded on J_N. As a consequence,

$$\rho_N \longrightarrow 0 \quad \text{in} \quad L^\infty(J_N).$$

This also implies that u_N' and u_N'' converge to 0 in $\mathcal{D}'(J_N)$. Using (13), this implies that $\phi_N u_N \longrightarrow 0$ in $\mathcal{D}'(J_N)$. A similar result then holds for $\phi_N\rho_N$. Using (15), we then have

$$\frac{1}{2}{\phi_N'}^2 - {u_N'}^2 \longrightarrow 0 \quad \text{in} \quad \mathcal{D}'(J_N).$$

On the other hand, $2(u_N u_N'' + {u_N'}^2) = \rho_N'' \longrightarrow 0$ in $\mathcal{D}'(J_N)$. Since we already know that $u_N u_N'' = pu_N^{2p} - \phi_N\rho_N$ satisfies this property, we deduce that

$${\phi_N'}^2 \longrightarrow 0 \quad \text{in} \quad \mathcal{D}'(J_N).$$

This contradicts the fact that $\phi_N'' + \delta_{X_i^N} = \rho_N \longrightarrow 0$ in $L^\infty([X_{i_N}^N - \varepsilon, X_{i_N}^N + \varepsilon])$ for any $0 < \varepsilon < (8(p-1))^{1/p}$. $\Diamond$

Remark 2.5 *Note that in the case where $1 < p \leq 2$, it is possible to adapt the technics used in [15] to show that there exists a constant C independent of N such that $|\phi_N| \leq C$ on the whole real line.*

3 Convergence of the energy

We start by showing that the energy per atom does converge to some real number:

Proposition 3.1 *Let I_N be defined by (1). Then the sequence $\frac{I_N}{N}$ converges.*

Proof: The point is that the sequence I_N satisfies:

$$I_{N+P} < I_N + I_P, \quad \forall N, P \in \mathbf{N}. \tag{18}$$

This follows from an easy adaptation of the proofs of [7] or [2], and consists roughly in pointing out that if a system of $N+P$ atoms divides into two parts of respectively N and P atoms, its energy converges to the sum of the energies of the subsystems. Then, fixing a $P \in \mathbf{N}$, we have, for all $N \in \mathbf{N}$, $N = PQ + R$, with $R < P$. Using (18), we infer:

$$I_N < QI_P + I_R.$$

Hence, $\frac{I_N}{N} < \frac{QI_P}{PQ+R} + \frac{I_R}{N}$. Letting N go to infinity, we get: $\limsup \frac{I_N}{N} \leq \frac{I_P}{P}$. We deduce from this that $\limsup \frac{I_N}{N} \leq \liminf \frac{I_N}{N}$. $\Diamond$

We are now in position to prove Theorem 1.1:

Proof of Theorem 1.1: We first show that:

$$\lim_{N\to\infty} \frac{I_N}{N} \leq I_{per}, \tag{19}$$

where I_{per} is defined in (5). Consider $\overline{R} \in \mathbf{R}$ a solution of I_{per}, and define $Y_i^N = (i - N)\overline{R}, \quad i = 1, \ldots, 2N$. Consider the density $\rho_N = \eta_N$ solution of the electronic problem with nuclei Y_i^N, together with its energy J_{2N}. An easy adaptation of [5, 6] shows that $\frac{J_{2N}}{2N}$ converges to $I_{per,\overline{R}} = I_{per}$. Moreover, the system $(\eta_N, \{Y_i^N\})$ is a test system for the minimization problem I_{2N}, hence

$$\frac{I_{2N}}{2N} \leq \frac{J_{2N}}{2N} \longrightarrow I_{per}.$$

This proves (19). We now show:

$$\lim_{N\to\infty} \frac{I_N}{N} \geq I_{per}. \tag{20}$$

In order to do so, we re-write the energy I_N: let $(\rho_N, \{X_i^N\})$ be a solution of I_N, and ϕ_N the associated effective potential (12). Then,

$$I_N = E^{TFW}(\rho_N, \{X_i^N\}) = \int_{\mathbf{R}} (\sqrt{\rho_N}\,')^2 + \int_{\mathbf{R}} \rho_N^p + \frac{1}{2}\int_{\mathbf{R}} (\phi_N')^2,$$

according to the definition of ϕ_N. Thus, we have:

$$\begin{aligned} I_N \;=\; & \int_{-\infty}^{X_1^N} (\sqrt{\rho_N}\,')^2 + \rho_N^p + \frac{1}{2}(\phi_N')^2 + \int_{X_N^N}^{+\infty} (\sqrt{\rho_N}\,')^2 + \rho_N^p + \frac{1}{2}(\phi_N')^2 \\ & + \sum_{i=1}^{N-1} \int_{X_i^N}^{X_{i+1}^N} (\sqrt{\rho_N}\,')^2 + \rho_N^p + \frac{1}{2}(\phi_N')^2. \end{aligned}$$

First, we prove that for any $i \in \{1, \dots, N-1\}$,

$$\int_{X_i^N}^{X_{i+1}^N} (\sqrt{\rho_N}\,')^2 + \rho_N^p + \frac{1}{2}(\phi_N')^2 \geq I_{per}. \tag{21}$$

In order to do so, we introduce Y_i^N as the unique point in $]X_i^N, X_{i+1}^N[$ such that $\phi_N'(Y_i^N) = 0$. It exists since ϕ_N' ranges monotonically from $-\frac{1}{2}$ to $\frac{1}{2}$ on $]X_i^N, X_{i+1}^N[$. We then consider the function ρ_i defined by:

$$\rho_i(x) = \begin{cases} \rho_N(x) & \text{if} \quad X_i^N \leq x \leq Y_i^N, \\ \rho_N(X_i^N - x) & \text{if} \quad 2X_i^N - Y_i^N \leq x \leq X_i^N. \end{cases} \tag{22}$$

This defines a function ρ_i on $[2X_i^N - Y_i^N, Y_i^N]$ satisfying periodic boundary conditions (see figure 1). We define ϕ_i in the same way, namely

$$\phi_i(x) = \begin{cases} \phi_N(x) & \text{if} \quad X_i^N \leq x \leq Y_i^N, \\ \phi_N(X_i^N - x) & \text{if} \quad 2X_i^N - Y_i^N \leq x \leq X_i^N, \end{cases} \tag{23}$$

and prolong these two functions by periodicity. Thanks to (14), one then easily finds that $-\phi_i'' = \delta_{X_i^N} - \rho_i$ on $[2X_i^N - Y_i^N, Y_i^N]$, together with periodic boundary conditions. This implies, from the definition of $G_{2(X_i^N - Y_i^N)}$ (7), that

$$\phi_i(x) = \left(G_{2(X_i^N - Y_i^N)} - \rho_i \star_{[-(Y_i^N - X_i^N), Y_i^N - X_i^N]} G_{2(X_i^N - Y_i^N)} \right)(x + X_i^N) + a,$$

where a is a constant. Thus, the derivatives of these two effective potentials are equal, and

$$\begin{aligned} \int_{X_i^N}^{Y_i^N} (\sqrt{\rho_N}\,')^2 + \rho_N^p + \frac{1}{2}(\phi_N')^2 &= \frac{1}{2}\int_{2X_i^N - Y_i^N}^{Y_i^N} (\sqrt{\rho_i}\,')^2 + \rho_i^p + \frac{1}{2}(\phi_i')^2 \\ &= \frac{1}{2} E_{per,R}^{TFW}(\rho_i) \geq \frac{1}{2} I_{per}, \quad \text{with} \quad R = Y_i^N - X_i^N. \end{aligned} \tag{24}$$

A similar treatment may be done concerning the integral over $[Y_i^N, X_{i+1}^N]$, which proves (21).

We then prove that $\displaystyle\int_{-\infty}^{X_1^N} (\sqrt{\rho_N}\,')^2 + \rho_N^p + \frac{1}{2}(\phi_N')^2 \geq \frac{1}{2} I_1$. Consider the function ρ_0 defined by

$$\rho_0(x) = \begin{cases} \rho_N(x) & \text{if} \quad x \leq X_1^N, \\ \rho_N(X_1^N - x) & \text{if} \quad x > X_1^N. \end{cases}$$

Define ϕ_0 in the same way from ϕ_N. We then have $\phi_0'' = \delta_{X_1^N} - \rho_0$, and ϕ_0 converges to some constant at infinity. This implies in particular that $\phi_0 = \phi_0^0 + a$, where $a \in \mathbf{R}$ and $\phi_0^0 = \frac{1}{2}\rho_1 \star |x| - \frac{1}{2}|x - X_1^N|$. As a consequence, ${\phi_0}' = {\phi_0^0}'$, hence

$$\begin{aligned} \int_{-\infty}^{X_1^N} (\sqrt{\rho_N}\,')^2 + \rho_N^p + \frac{1}{2}(\phi_N')^2 &= \frac{1}{2}\int_{\mathbf{R}} (\sqrt{\rho_1}\,')^2 + \rho_1^p + \frac{1}{2}({\phi_1^0}')^2 \\ &= \frac{1}{2} E^{TFW}(\rho_1, X_1^N) \geq \frac{1}{2} I_1. \end{aligned}$$

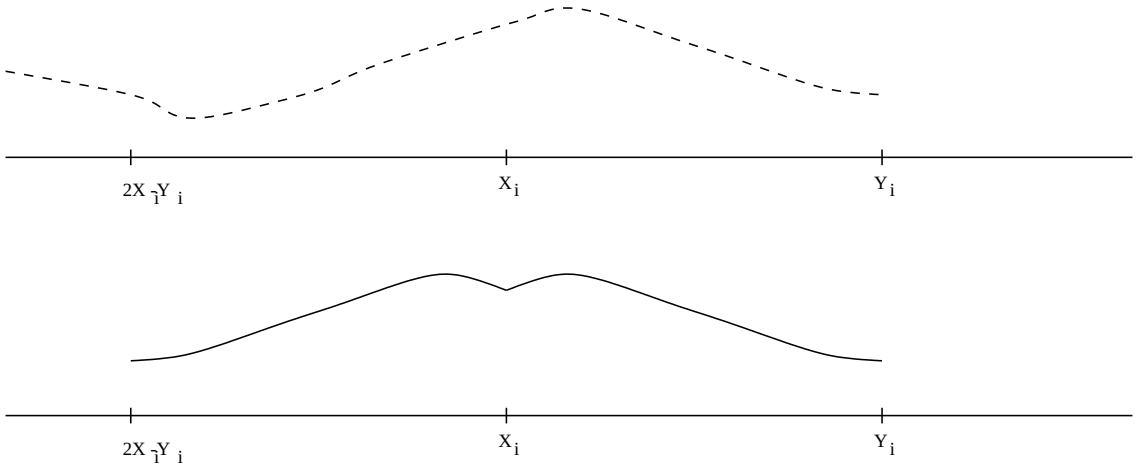

Figure 1: The symmetrisation process described by equations (22) and (23): above, the true density ρ_N, and below, the symmetrised one.

Likewise, $\int_{X_N^N}^{+\infty} (\sqrt{\rho_N}\,')^2 + \rho_N^p + \frac{1}{2}(\phi_N')^2 \geq \frac{1}{2} I_1$. Together with (21), this shows that

$$I_N \geq (N-1) I_{per} + I_1.$$

Dividing this inequality by N and letting N go to infinity, we find (19). $\Diamond$

4 Convergence of the density

This section is devoted to the proof of Theorem 1.2.

We know from [2] that $I_1 > I_{per}$. We also know that, $I_{per,R}$ being defined by (8), $\lim_{R\to\infty} I_{per,R} = I_1$. This implies in particular that there exists an $R_0 > 0$ such that

$$\forall R > R_0, \quad I_{per,R} > \frac{1}{2}(I_{per} + I_1). \tag{25}$$

Remark 4.1 *Inequality (25) also shows that the set of solutions $\overline{R}$ of problem (9) is bounded from above.*

Next, we notice that inequality (24) may be improved, since $\frac{1}{2} E_{per,R}^{TFW}(\rho_i) \geq I_{per,R}$ is an equality only if ρ_i is the solution of $I_{per,R}$, due to the strict convexity of this variational problem [3]. Thus, denoting by A_N the number of indexes i in $\{1, \ldots, N\}$ such that $X_{i+1}^N - X_i^N > R_0$, we have:

$$I_N \geq \frac{A_N}{4}(I_1 + I_{per}) + (N - \frac{A_N}{2} - 1) I_{per} + I_1.$$

We thus have $\frac{I_N}{N} - I_{per} + \frac{I_{per}-I_1}{N} \geq \frac{I_1-I_{per}}{4}\frac{A_N}{N}$, which implies, according to Theorem 1.1 and the fact that $I_1 > I_{per}$, that

$$A_N = o(N), \quad \text{as} \quad N \longrightarrow \infty. \tag{26}$$

Next, denote by B_N the number of indexes $i \in \{1, \ldots, N\}$ such that

$$\liminf_{N\to\infty} \int_{X_i^N}^{X_{i+1}^N} (\sqrt{\rho_N}\,')^2 + \rho_N^p + \frac{1}{2}(\phi_N')^2 > I_{per}.$$

For the same reason, B_N also satisfies (26). Hence, one can find a sequence (i_N) of indexes such that:

(i) $i_N \longrightarrow \infty, \quad N - i_N \longrightarrow \infty,$

(ii) $X_{i_N+1}^N - X_{i_N}^N \leq R_0,$

(iii) $\displaystyle\int_{X_{i_N}^N}^{X_{i_N+1}^N} (\sqrt{\rho_N}\,')^2 + \rho_N^p + \frac{1}{2}(\phi_N')^2 \longrightarrow I_{per}.$

Changing the origin if necessary, we may assume without loss of generality that $X_{i_N}^N = 0$. From (iii) and Corollary 2.3, we deduce that $\sqrt{\rho}_N$ is bounded in $H^1_{loc} \cap L^\infty$. Using (iii) and Proposition 2.4, similar bounds may be obtained for ϕ_N. Hence, we may extract a subsequence so that (ρ_N, ϕ_N) converges to some $(\rho_\infty, \phi_\infty)$ strongly in all L^p_{loc}, and that $X_{i_N+1}^N$ converges to $R \leq R_0$. We may also assume that $Y_{i_N}^N$ converges to some $r \leq R$. Then,

$$\int_0^R (\sqrt{\rho_\infty}\,')^2 + \rho_\infty^p + \frac{1}{2}(\phi_\infty')^2 \leq \liminf_{N\to\infty} \int_0^R (\sqrt{\rho_N}\,')^2 + \rho_N^p + \frac{1}{2}(\phi_N')^2 = I_{per}. \tag{27}$$

Moreover, equation $\phi_N'' = \rho_N$ passes to the limit, together with the fact that $\phi_N'(0) = -\frac{1}{2} = -\phi_N'(X_{i_N+1}^N)$ and $\phi_N'(Y_{i_N}^N) = 0$, so that $\phi_\infty'(0) = -\phi_\infty'(R) = -\frac{1}{2}$, and $\phi_\infty'(r) = 0$. Hence, using the same tricks as in the proof of Theorem 1.1, we have:

$$\int_0^r (\sqrt{\rho_\infty}\,')^2 + \rho_\infty^p + \frac{1}{2}(\phi_\infty')^2 \geq \frac{1}{2} I_{per}, \tag{28}$$

$$\int_r^R (\sqrt{\rho_\infty}\,')^2 + \rho_\infty^p + \frac{1}{2}(\phi_\infty')^2 \geq \frac{1}{2} I_{per}, \tag{29}$$

and equality holds in (28), respectively (29), only if ρ_∞ is the solution $\rho_{per,2r}$ of the periodic problem $I_{per,2r}$, respectively the solution $\rho_{per,2(R-r)}$ of $I_{per,2(R-r)}$. On the other hand, (27) implies that equality does hold in these two equations, showing that $\rho_\infty = \rho_{per,2r}$ on $[0, r]$ and $\rho_\infty = \rho_{per,2(R-r)}$ on $[r, R]$. Hence, setting $u_\infty = \sqrt{\rho_\infty}$, the functions (u_∞, ϕ_∞) are solutions of the system (13) on $]0, R[$, namely

$$\left\{ \begin{array}{l} -u_\infty'' + p u_\infty^{2p-1} - \phi_\infty u_\infty = 0, \\ -\phi_\infty'' = -u_\infty^2. \end{array} \right. \tag{30}$$

Consequently, $\phi_\infty = \phi_{per,2r}$ on $[0,r]$, where $\phi_{per,2r} = G_{2r} - G_{2r} \star \rho_{per,2r}$. Hence, (u_∞, ϕ_∞) and $(\sqrt{\rho_{per,2r}}, \phi_{per,2r})$ share the same values and the same derivatives at 0, and satisfy the same differential equation on $]0,R[$. According to Cauchy-Lipschitz theorem, together with the fact that the function $(u,\phi) \mapsto (pu^{2p-1} - \phi u, -u^2)$ is locally lipschitz continuous from $\mathbf{R}^2$ to $\mathbf{R}^2$, this implies that they are equal on the whole interval $[0,R]$. Since the unique point at which $\phi'_{per,2r}$ reaches $\frac{1}{2}$ is $2r$, this implies that $R = 2r$ is a solution of problem I_{per}, and that $\rho_\infty = \rho_{per,R}$. Next, we point out that (30) is also satisfied on the right of R, so that, still using Cauchy-Lipschitz theorem, $(\rho_\infty, \phi_\infty) = (\rho_{per,R}, \phi_{per,R})$ on the right of R. Hence, the unique point satisfying $\phi'_\infty = \frac{1}{2}$ on the right of R is $2R$, which means that $X^N_{i_N+2} \longrightarrow 2R$ as N goes to infinity. Carrying on this process on both sides of the interval $[0,R]$, we conclude our proof. $\Diamond$

5 Consequences and extensions

We give in this section some side-remarks and extension to the Thomas-Fermi (TF) case. First of all, an adaptation of the above proof shows that:

Corollary 5.1 *(a) Let $\{X_i\}_{i\in\mathbf{Z}}$ be a periodic configuration of nuclei, in the sense that $X_{i+N} = X_i + L$, for some fixed N, L. Then the minimum of energy per nuclei, as defined in (31) below, is reached only for the equidistant configuration ($X_{i+1} = X_i + \frac{L}{N}$).*

(b) Let $(\rho, \{X_i\})$ be a system such that $0 < X_1 \leq X_2 \leq \cdots \leq X_N < L$, and ρ satisfies periodic boundary conditions on $]0,L[$. Assume in addition that this system is a minimizer of the following energy:

$$\overline{E}^{TFW}_L(\rho, \{X_i\}) = \int_0^L (\sqrt{\rho}\,')^2 + \int_0^L \rho^p + \frac{1}{2}\int_0^L (\phi')^2,$$

where ϕ is a solution of $-\phi'' = \sum \delta_{X_i} - \rho$ with periodic boundary conditions. Then $X_{i+1} = X_i + \frac{L}{N}$, for all i.

An illustration of Corollary 5.1 is shown in figure 2. In (a), the periodic TFW energy is defined by (we assume that $X_0 = 0$):

$$\begin{aligned}\tilde{E}^{TFW}(\rho, \{X_i\}) \;=\; & \int_{-\frac{L}{2}}^{\frac{L}{2}} (\sqrt{\rho}\,')^2 + \int_{-\frac{L}{2}}^{\frac{L}{2}} \rho^p - \sum_{|j|<\frac{N}{2}} \int_{-\frac{L}{2}}^{\frac{L}{2}} G_L(x - X_j)\rho(x)dx \\ & + \frac{1}{2}\int_{-\frac{L}{2}}^{\frac{L}{2}}\int_{-\frac{L}{2}}^{\frac{L}{2}} \rho(x)G_L(x-y)\rho(y)dxdy + \frac{1}{2}\sum_{|i|,|j|<\frac{N}{2}} G_L(X_i - X_j),\end{aligned}$$

where G_L is defined by (7), and the electronic ground state is:

$$I^N_{per,L} = \inf\left\{\tilde{E}^{TFW}(\rho, \{X_i\}), \quad \rho \geq 0, \quad \sqrt{\rho} \in H^1_{per}(]0,L[), \quad \int_0^L \rho = N\right\}, \tag{31}$$

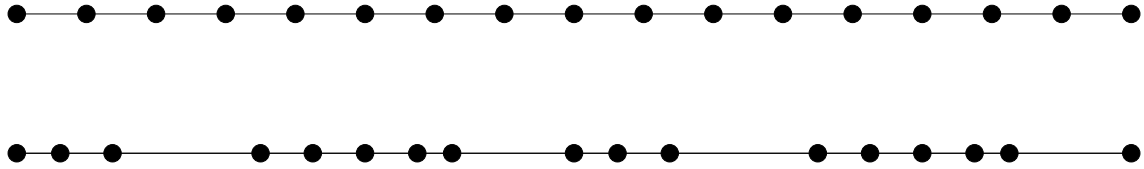

Figure 2: Two periodic distributions of nuclei, with $N = 9$. Corollary 5.1 states that the first one has strictly lower energy than the other.

and the energy per nuclei is equal to $\frac{I^N_{per,L}}{N}$.

Using similar techniques as for the TFW case, one can show that Corollary 5.1 holds in the TF case, where one forgets the term $\int(\sqrt{\rho}\,')^2$ in the energy. On the contrary, Theorem 1.2 does not hold in this case since problem (1) has no solution [9]. More precisely, $I_N = NI_1$ in this case, and this value is reached only in the limit $X_{i+1} - X_i \to \infty$, for all i. The proof is more simple in fact, since (10) is still valid, and (13) reads:

$$\begin{cases} -\phi'' + \left(\frac{1}{p}\right)^{\frac{1}{p-1}} \phi^{\frac{1}{p-1}} = \sum_{i=1}^N \delta_{X_i}, \\ \phi = p\rho^{p-1}. \end{cases}$$

And the analogue of (15) is $-\frac{1}{2}\phi'^2 + (p-1)\left(\frac{1}{p}\phi\right)^{\frac{p}{p-1}} = a$, where a is a constant (not necessarily 0). Hence, thanks to the fact that ϕ'^2 has a fixed value at X_i, so does ϕ, and we may apply Cauchy-Lipschitz theorem to show that the configuration is indeed periodic with one atom per cell.

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Chapitre 5

Énergie et état fondamental de systèmes infinis non périodiques

Ce chapitre, écrit en collaboration avec C. Le Bris et P.-L. Lions [P5], traite du problème de limite thermodynamique dans le cas d'une géométrie de noyaux non périodique. Nous définissons par ce biais une notion d'état fondamental que nous étudions, en lien avec une notion de minimisation *locale* d'énergie. En annexe à ce chapitre, nous présentons un résultat utilisé dans la section 3, consistant à caractériser les fonctions dont le potentiel newtonien est borné [P6].

A definition of the ground state energy for systems composed of infinitely many particles

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Abstract We introduce here one possible definition of the energy of an infinite non-periodic system of particles. We investigate the minimization of it, and the link with standard definitions of local ground state for such systems. The specific models under study are issued from Quantum Mechanics (namely from Density-Functional type theories) but our construction and analysis can be adapted to treat other cases.

1 Introduction

The purpose of this work is to contribute to the difficult problem of defining the energy of a system composed of an infinite number of particles. Our goal is to determine in some sense the *most general set* of infinite systems for which a ground state energy may be defined in a rigorous mathematical way. Of course, by the word *energy* for an infinite system, we mean *energy per unit volume* as it is well known that energy is an extensive quantity, and therefore that if some energy can be defined, it is only by considering it per unit volume (or per unit mass, or per particle). The systems we deal with here consist of an infinite number of nuclei (treated classically in the framework of the Born-Oppenheimer approximation), together with the "same" infinite number of electrons modeled through a Quantum Density Functional theory. Our analysis is however likely to be adapted to treat other infinite systems.

When an infinite system exhibits a specific geometric property of long range order, such as periodicity, or any mild extensions of periodicity (quasi-periodicity, almost periodicity), the question of defining its energy is not that difficult.

To illustrate this fact, let us recall that the simple Thomas-Fermi model defining the ground state energy of a neutral system of N nuclei of unit charge located at $\{X_i\}$ together with N electrons described through their density ρ in the setting of quantum mechanics

$$\begin{aligned} E^{TF}(\rho,\{X_i\}) &= \int_{\mathbf{R}^3}\rho^{5/3}+\frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3}\frac{\rho(x)\rho(y)}{4\pi|x-y|}dxdy-\sum_{i=1}^{N}\int_{\mathbf{R}^3}\frac{\rho(x)dx}{4\pi|x-X_i|} \\ &\quad +\frac{1}{2}\sum_{i\neq j}\frac{1}{4\pi|X_i-X_j|}. \end{aligned} \tag{1}$$

$$I^{TF}(\{X_i\})=\inf\left\{E^{TF}(\rho,\{X_i\}),\quad \rho\in L^1(\mathbf{R}^3)\cap L^{5/3}(\mathbf{R}^3),\quad \rho\geq 0,\quad \int_{\mathbf{R}^3}\rho=N\right\}. \tag{2}$$

can be extended, when $\{X_i\}$ goes to $\mathbf{Z}^3$, to define the ground state energy of an infinite *periodic* system of the same kind in the following manner:

$$E^{TF}_{per}(\rho)=\int_Q\rho^{5/3}+\frac{1}{2}\int_Q\int_Q\rho(x)G(x-y)\rho(y)dxdy-\int_Q G\rho, \tag{3}$$

$$-\Delta G=\sum_{k\in\mathbf{Z}^3}\delta_k-1, \tag{4}$$

$$I^{TF}_{per}=\inf\left\{E^{TF}_{per}(\rho),\quad \rho\geq 0,\quad \rho\in L^{5/3}_{per}(Q),\quad \int_Q\rho=1\right\}. \tag{5}$$

To define the above minimization problem requires essentially one and only one property : we have assumed that the locations $\{X_i\}$ of the nuclei fill in exactly the whole lattice

$\mathbf{Z}^3$, whose unit cell is above denoted by Q. As a consequence, a) the potential ruling the interactions between particles, which is the Coulomb potential in (3) has been transformed into its periodic analogue (4), and b) the integrals over the whole space $\mathbf{R}^3$ in (3) have turned, for periodic functions, into integrals on the unit cell Q in (5). The infinite character of the system is completely enclosed in this transformation.

It may be enlightening, in this expository section, to see that in the case where the nuclei are smeared out, which is just a question of regularization of the measure $\sum_k \delta(\cdot - X_k)$ defining the nuclei (convolute it with some nonnegative normalized $C_0^\infty(\mathbf{R}^3)$ function m), the above transformation going from (1)-(2) to (3)-(4)-(5) may be written

$$I^{TF}(\{X_i\}) = \inf\Big\{ \int_{\mathbf{R}^3} \rho^{5/3} + \frac{1}{2}\int_{\mathbf{R}^3} |\nabla\Phi|^2, \quad \rho \in L^1(\mathbf{R}^3) \cap L^{5/3}(\mathbf{R}^3), \\ \rho \geq 0, \quad \int_{\mathbf{R}^3} \rho = N, \Phi \in H^1(\mathbf{R}^3),\ -\Delta\Phi = m - \rho \Big\}. \quad (6)$$

$$\text{yields} \quad I^{TF}_{per} = \inf\Big\{ \int_Q \rho^{5/3} + \frac{1}{2}\int_Q |\nabla\Phi|^2, \quad \rho \in L^{5/3}_{per}(Q), \quad \rho \geq 0, \quad \int_Q \rho = 1, \\ \Phi \in H^1_{per}(Q),\ -\Delta\Phi = m - \rho \Big\}. \quad (7)$$

The mathematical analysis needed to lay all the above definitions on a sound ground, as well as extensions of it, have been detailed in [5]. The key notion involved there is that of the thermodynamic limit process, a notion to which we shall come back later on in this article (see Section 3.5).

Suppose now that we wish to define the energy of a system of the same kind, again with some simplified model such as the Thomas-Fermi one, in the case when the $\{X_i\}_{i\in\mathbf{N}}$ are a rather general set of points spread in $\mathbf{R}^3$, and not necessarily $\mathbf{Z}^3$. It is clear that it will not be possible for pathological cases of $\{X_i\}_{i\in\mathbf{N}}$ (think of sets with infinitely large holes, for instance), but one may ask the question : what kind of sets $\{X_i\}_{i\in\mathbf{N}}$ allow to define in a rigorous mathematical way such an energy? As the models above feature not only the set of nuclei, but also the electronic density that is a consequence of it, it is clear that this question embodies a preliminary question : what are the properties awaited from the electronic density once the form of the set of nuclei is prescribed?

What we learn from the above periodic example (and from its extensions described in [5]) is that the form of the electronic density is expected to reproduce the form of the set of nuclei. Periodicity of the nuclei implies periodicity of the ground state electronic density, *e.g.*, even if it is not so simple to prove it rigorously (see [5]). Next, we learn that we need to be able to manipulate the density. Typically we need to use powers of the density and we need to convolute it (look at (1)). We also learn we shall need to define averages of functionals of the density. It suggests that we need to define for each convenient set of nuclei $\{X_i\}_{i\in\mathbf{N}}$ an *algebra* (at least !) of electronic densities, and next choose properly the properties of the set $\{X_i\}_{i\in\mathbf{N}}$ so that the whole construction holds.

Typically, in view of (7), what we have in mind is to build some model of the following type

$$I_\infty^{TF} = \inf\left\{ \langle \rho^{5/3} \rangle + \frac{1}{2}\langle |\nabla \Phi|^2 \rangle, \quad \rho \geq 0, \quad \langle \rho \rangle = 1, \quad -\Delta \Phi = m - \rho \right\}, \tag{8}$$

where we have denoted by $\langle \cdot \rangle$ an average that needs to be defined. Then, we shall say that an electronic density minimizes this minimization problem if it belongs to the right functional space where all the averages above are well defined, and if it satisfies the associated Euler-Lagrange equation. It will turn out that this is enough to effectively minimize (8), as will be seen in Section 3.4. Of course, all this is only formal so far, and we shall make it precise in the sequel.

The article is organized as follows. We introduce in Section 2 a list of properties that we require to be true on the set of nuclei $\{X_i\}_{i\in\mathbf{N}}$, and then define an algebra of functions, which is to be the set of functions where electronic densities are defined. Our definitions are illustrated by simple examples of sets and algebra that are covered by our general framework. In Section 3, we apply our construction to the Thomas-Fermi type theories. The simple Thomas-Fermi case is first dealt with. We next turn to the Thomas-Fermi-von Weizsäcker model. In both cases, our strategy is to choose a set of nuclei which obeys to the properties pointed out in Section 2, then show that the electronic density that is a solution the Euler-Lagrange equation associated to the energy functional (in which the locations $\{X_i\}_{i\in\mathbf{N}}$ appear as parameters) indeed belongs to the algebra defined in Section 2. All the properties needed to define the energy are therefore fulfilled. We also exhibit the connections between our notion of energy minimizer with another one, more familiar to the community of physicists, namely that of *local minimizer*.

2 Definition of the functional spaces

2.1 The natural space: its necessary properties

We investigate in this subsection the necessary properties, given an infinite set of nuclei $\{X_i\}_{i\in\mathbf{N}}$, of the function space which we expect the corresponding electronic density to belong to. We indicate here only formal arguments, the rigorous ones being given in the following subsections.

The first natural property is the fact that the density should reflect the geometry of the nuclei. Typically, this is the case for any function ρ of the form:

$$\rho(x) = \sum_{i\in\mathbf{N}} \varphi(x - X_i),$$

with $\varphi \in \mathcal{D}(\mathbf{R}^3)$.

The next natural condition is, since we deal with nonlinear PDEs, that the space should be stable under product. Hence, we enlarge the preceding space by taking all functions of

the form:

$$\rho(x) = \sum_{i_0 \in \mathbf{N}} \cdots \sum_{i_n \in \mathbf{N}} \varphi_n(x - X_{i_0}, x - X_{i_1}, \ldots x - X_{i_n}), \tag{9}$$

with $\varphi_n \in \mathcal{D}(\mathbf{R}^{3n})$ and $n \in \mathbf{N}$.

The set of functions which may be written in this way being not a vector space, we need to consider the vector space generated by all such functions. For any such function, we need to be able to compute its average over the space:

Definition 2.1 *Given $\rho \in L^1_{\text{unif}}(\mathbf{R}^3)$, we shall say that it has an average if the following limit exists:*

$$\langle \rho \rangle = \lim_{R \to \infty} \frac{1}{|B_R|} \int_{B_R} \rho(x) dx.$$

The scalar $\langle \rho \rangle$ will then be called the average of ρ.

Saying that ρ of the form (9) has an average amounts to assuming that the set $\{X_i\}_{i \in \mathbf{N}}$ satisfies the following kind of properties: for any $n \in \mathbf{N}$, any $(h_1, h_2, \ldots h_n) \in \mathbf{R}^{3n}$, the following limit should exist:

$$l^n(h_1, h_2, \ldots h_n) = \lim_{R \to \infty} \frac{1}{|B_R|} \#\{X_{i_0}, \ldots X_{i_n} \in B_R / \quad X_{i_0} - X_{i_k} = h_k, 1 \leq k \leq n\}.$$

Here, $\#A$ denotes the cardinal of the set A. In such a case, the average of ρ given by (9) is

$$\langle \rho \rangle = \int_{\mathbf{R}^{3n}} \varphi(x, x - h_1, x - h_2, \ldots x - h_n) l^n(h_1, \ldots h_n) dh_1 \ldots dh_n dx.$$

In fact, the preceding two formulas are *not exactly true*, and need to be in some sense regularized, as we shall see below in Definition 2.3. But the essential ideas are present here: we need some kind of n-body correlation for the set of nuclei.

This vector space being constructed, there only remains to close it for a suitable norm (which should be uniform, at least in order to preserve the average property). The next subsection presents a rigorous version of this construction.

Remark 2.2 *Let us point out that although the above construction seems to depend on the center (which is 0 here), it* does not. *Another way of stating it is that the properties exposed above are indeed invariant under translation.*

2.2 Construction of the functional space

We start by stating the properties we expect the set of nuclei to satisfy in order to construct the adequate functional spaces.

Definition 2.3 *We shall say that a set of points $\{X_i\}_{i \in \mathbf{N}}$ is admissible if it satisfies the following:*

(H1) $\sup_{x\in\mathbf{R}^3} \#\{i\in\mathbf{N} \quad / \quad |x-X_i|<1\} < +\infty$

(H2) $\lim_{R\to\infty} \frac{1}{R} \inf_{x\in\mathbf{R}^3} \#\{i\in\mathbf{N} \quad / \quad |x-X_i|<R\} = +\infty$

(H3) for any $n\in\mathbf{N}$, any $(h_1,h_2,\dots h_n)\in\mathbf{R}^{3n}$ and any positive δ sufficiently small, the following limit exists:

$$l^n(h_1,h_2,\dots h_n,\delta) = \lim_{R\to\infty} \frac{1}{|B_R||B_\delta|^n} \#\{X_{i_0},\dots X_{i_n}\in B_R / X_{i_0}-X_{i_k}\in B_\delta(h_k), 1\le k\le n\}.$$

We have used here the convention that if $n=0$, l^0 is the constant function equal to

$$l^0 = \lim_{R\to\infty} \frac{1}{|B_R|} \#\{i\in\mathbf{N} \quad / \quad X_i\in B_R\}. \tag{10}$$

The properties of the above definition deserve some comments.

First, the properties (H1)-(H2) are exactly the hypotheses of the existence and uniqueness theorem of the TFW electronic density [5], and therefore certainly are necessary conditions. Nevertheless, we shall see in the sequel that they also play a role in the definition of the functional spaces $\mathcal{A}^{k,p}$.

Next, let us point out that (H1), (H2) and (H3) are not logically linked, as will be proved in section 2.3.

Another point is that hypothesis (H3) may be seen as a n-body correlation function, and therefore is rather natural in view of the existence of averages. However, in particular cases there might be no need of higher order correlations, as for instance in the case where the energy is defined by a two-body potential: in such a case, only (H3) for $n=1$ is needed (if one computes the energy per unit volume. For the energy per particle, one needs in addition (H3) for $n=0$.) In the cases we address below, namely quantum models, nonlinearities imply the need of (H3) for all $n\in\mathbf{N}$.

In order to be able to define these averages, what is really relevant is the limit of l^n as δ goes to 0:

Proposition 2.4 *Let $\{X_i\}_{i\in\mathbf{N}}$ be a set of points satisfying (H1) and (H3). Then for any $n\in\mathbf{N}$, there exists a non-negative uniformly locally bounded measure, that we denote by dl^n, such that for all $\varphi\in C_c(\mathbf{R}^{3n})$,*

$$\lim_{\delta\to 0}\int_{\mathbf{R}^{3n}} \varphi(h_1,h_2,\dots h_n) l^n(h_1,h_2,\dots h_n,\delta)dh = \int_{\mathbf{R}^{3n}} \varphi(h_1,h_2,\dots h_n) dl^n(h_1,h_2,\dots h_n). \tag{11}$$

Here $C_c(\mathbf{R}^{3n})$ denotes the set of continuous functions on $\mathbf{R}^{3n}$ having compact support.

Proof: Let $\varphi \in C_c(\mathbf{R}^{3n})$. We first show that

$$\int_{\mathbf{R}^{3n}} \varphi(h_1, h_2, \dots h_n) l^n(h_1, h_2, \dots h_n, \delta) dh$$

is a Cauchy sequence (with respect to δ). Indeed, noticing that

$$l^n(h_1, h_2, \dots h_n, \delta) = \lim_{R\to\infty} \frac{1}{|B_R|} \sum_{X_{i_0} \in B_R} \cdots \sum_{X_{i_n} \in B_R} \frac{1}{|B_\delta|^n} \mathbf{1}_{B_\delta(X_{i_0}-X_{i_1})\times\cdots\times B_\delta(X_{i_0}-X_{i_n})}(h_1, \dots h_n),$$

and noticing that for δ fixed, the function $\varphi(h_1, \dots h_n) l^n(h_1, \dots h_n, \delta)$ satisfies the hypotheses of the dominated convergence theorem, we deduce that

$$\int_{\mathbf{R}^{3n}} \varphi(h) l^n(h, \delta) dh = \lim_{R\to\infty} \frac{1}{|B_R|} \sum_{X_{i_0} \in B_R} \cdots \sum_{X_{i_n} \in B_R} \frac{1}{|B_\delta|^n} \int_{\prod_{k=1}^n B_\delta(X_{i_0}-X_{i_k})} \varphi(h) dh.$$

Next, we denote by A the radius of some ball containing the support of φ, and point out that the above sums, except for the first one, reduce to sums over points belonging to $B_R \cap B_{A+\delta}(X_{i_0})$, which is a finite sum, the number of term being bounded independently of R, thanks to (H1). Thus, our claim reduces to prove that

$$\frac{1}{|B_\delta|^n} \int_{\prod_{k=1}^n B_\delta(X_{i_0}-X_{i_k})} \varphi(h) dh$$

is a Cauchy sequence. Since, φ being uniformly continuous, it converges to $\varphi(X_{i_0} - X_{i_1}, \dots, X_{i_0} - X_{i_n})$, uniformly with respect to the X_{i_k}'s, this is trivially true. This proves our claim. In order to conclude our proof, we point out that if we replace φ by the function $\mathbf{1}_{B_1(h_0)}$, for some fixed $h_0 \in \mathbf{R}^{3n}$, an argument similar to the above one shows that

$$\|l^n(\cdot, \delta)\|_{L^1_{\text{unif}}(\mathbf{R}^{3n})} \leq C,$$

with C independent of δ. This shows that up to a subsequence, $l^n(h, \delta)$ converges to some non-negative uniformly locally bounded measure in the sense of (11). Now, in view of the Cauchy property of the sequence, the whole sequence converges. $\Diamond$

Remark 2.5 *The above proof also shows that, under hypotheses (H1) and (H3), the following limit exists*

$$\lim_{R\to\infty} \frac{1}{|B_R|} \sum_{X_{i_0} \in B_R} \cdots \sum_{X_{i_n} \in B_R} \delta_{(X_{i_0}-X_{i_1}, \dots X_{i_0}-X_{i_n})}(h_1, \dots, h_n) = l^n(h_1, \dots, h_n),$$

and is a non-negative uniformly locally bounded measure. This is an alternative definition of l^n.

Remark 2.6 *Let us also point out that in the periodic case, that is if $\{X_i\}_{i\in\mathbf{N}}$ is a periodic lattice ℓ, then the hypotheses (H1), (H2), (H3) are satisfied, and the measure l^n is simply the corresponding sum of Dirac masses:*

$$l^n(h_1,\dots,h_n) = \frac{1}{V}\sum_{h_1\in\ell}\cdots\sum_{h_n\in\ell}\delta_{(h_1,h_2,\dots,h_n)},$$

where V is the volume of the primitive cell of the lattice ℓ.

Proposition 2.4 allows us to directly define averages of functions of the type (9):

Proposition 2.7 *Let $\{X_i\}_{i\in\mathbf{N}}$ be a set of points satisfying (H1) and (H3). Then for any $\varphi\in\mathcal{D}(\mathbf{R}^{3n})$, the function*

$$f(x) = \sum_{i_1\in\mathbf{N}}\cdots\sum_{i_n\in\mathbf{N}}\varphi(x-X_{i_1},\dots x-X_{i_n})$$

admits an average which satisfies:

$$\langle f\rangle = \int_{\mathbf{R}^3}\int_{\mathbf{R}^{3(n-1)}}\varphi(x,x-h_1,\dots,x-h_{n-1})dl^{n-1}(h_1,\dots h_{n-1})dx. \tag{12}$$

Proof: The point here is to write

$$\begin{aligned}\frac{1}{|B_R|}\int_{B_R}f(x)dx &= \frac{1}{|B_R|}\sum_{i_1\in\mathbf{N}}\cdots\sum_{i_n\in\mathbf{N}}\int_{B_R}\varphi(x-X_{i_1},\dots,x-X_{i_n})dx\\ &= \frac{1}{|B_R|}\sum_{i_1\in\mathbf{N}}\cdots\sum_{i_n\in\mathbf{N}}\int_{B_R-X_{i_1}}\varphi(x,x-(X_{i_2}-X_{i_1}),\dots\\ &\quad \dots,x-(X_{i_n}-X_{i_1}))dx\end{aligned}$$

Note that since φ has compact support, there exists some $A>0$ such that for any $(y_1,\dots y_n)\in(\mathbf{R}^3)^n$, $\max|y_j|\geq A\Rightarrow\varphi(y_1,\dots y_n)=0$. Hence, the only indexes i_1 that have a non-zero contribution to the sum are those for which X_{i_1} belongs to B_{R+A}. A similar remark holds for the sums over i_2, i_3, etc... Therefore,

$$\begin{aligned}&\frac{1}{|B_R|}\int_{B_R}f(x)dx =\\ &\frac{1}{|B_R|}\sum_{X_{i_1}\in B_{R+A}}\cdots\sum_{X_{i_n}\in B_{R+A}}\int_{B_R-X_{i_1}\cap B_A}\varphi(x,x-(X_{i_2}-X_{i_1})\dots,x-(X_{i_n}-X_{i_1}))dx.\end{aligned}$$

Here, we point out that, according to (H1), the number of indexes i_1 such that $X_{i_1}\in B_{R+A}$ and $B_R-X_{i_1}$ does not contain the ball B_A is asymptotically negligible compared to the total number of points X_{i_1} in B_R. Hence, the integral is, at leading order, equal to the

integral over B_A, that is to say over $\mathbf{R}^3$. We thus have

$$\begin{aligned}\frac{1}{|B_R|}\int_{B_R} f(x)dx &= \frac{1}{|B_R|}\sum_{X_{i_1}\in B_{R+A}}\cdots\sum_{X_{i_n}\in B_{R+A}}\int \varphi(x, x-(X_{i_2}-X_{i_1}),\dots \\ &\quad \dots, x-(X_{i_n}-X_{i_1}))dx + o(1) \\ &= \int \langle \varphi(x, x-h_1,\dots,x-h_{n-1}), m_{R+A}(h_1,\dots,h_{n-1})\rangle dx + o(1),\end{aligned}$$

where the measure m_{R+A} is:

$$m_{R+A}(h_1,\dots h_{n-1}) = \frac{1}{|B_R|}\sum_{X_{i_1}\in B_{R+A}}\cdots\sum_{X_{i_n}\in B_{R+A}}\delta_{(X_{i_1}-X_{i_2},\dots,X_{i_1}-X_{i_n})}(h_1,\dots,h_{n-1}).$$

In order to conclude, one may alternatively use Remark 2.5, or approximate the measure m_{R+A} by replacing the Dirac masses by the functions $\frac{1}{|B_\delta|}\mathbf{1}_{B_\delta(X_{i_1}-X_{i_k})}$ and use Proposition 2.4. $\Diamond$

We are now in position to define the functional spaces we are going to use:

Definition 2.8 *Let $\{X_i\}_{i\in\mathbf{N}}$ be an admissible set, and denote by $\mathcal{A}(\{X_i\})$ the vector space generated by the functions of the form*

$$f(x) = \sum_{i_1\in\mathbf{N}}\sum_{i_2\in\mathbf{N}}\cdots\sum_{i_n\in\mathbf{N}}\varphi(x-X_{i_1}, x-X_{i_2},\dots,x-X_{i_n}), \tag{13}$$

with $\varphi\in\mathcal{D}(\mathbf{R}^{3n})$. Then, for any $k\in\mathbf{N}$ and any $p\in[1,+\infty)$, we denote by $\mathcal{A}^{k,p}(\{X_i\})$, or simply $\mathcal{A}^{k,p}$ when there is no ambiguity, the closure of $\mathcal{A}(\{X_i\})$ for the norm $\|\cdot\|_{W^{k,p}_{\rm unif}}$, where

$$\|f\|_{W^{k,p}_{\rm unif}} = \sup_{x\in\mathbf{R}^3}\|f\|_{W^{k,p}(B_1+x)}.$$

When $k=0$, we use the notation $\mathcal{A}^p$ for $\mathcal{A}^{0,p}$.

The closure of $\mathcal{A}$ for the norm $\|\cdot\|_{L^\infty(\mathbf{R}^3)}$ being a set of continuous functions, we will denote it by $\mathcal{A}_c$.

Finally, we call $\mathcal{A}^\infty$ the closure for the $L^\infty(\mathbf{R}^3)$ norm of the space of functions of the form (13), with $\varphi\in L^\infty(\mathbf{R}^3)$ having compact support.

Remark 2.9 *Let us point out that our construction of the spaces $\mathcal{A}^{k,p}(\{X_i\}_{i\in\mathbf{N}})$ is the closure for the corresponding norm of the algebra generated by the functions of the form*

$$f(x) = \sum_{i\in\mathbf{N}}\varphi(x-X_i), \quad \varphi\in\mathcal{D}(\mathbf{R}^3), \tag{14}$$

since any function of the form (13) may be approximated by functions of the form (14).

2.3 Examples and extensions

We now give a few examples of the set $\mathcal{A}^{k,p}$ in some simple cases.

The periodic case. Assume that the set $\{X_i\}_{i\in\mathbf{N}}$ is a periodic lattice, for instance $\mathbf{Z}^3$. Then the space $\mathcal{A}^{k,p}$ is the space of $W^{k,p}$ periodic functions. In particular,

$$\mathcal{A}^p = L^p_{\rm per}(\mathbf{Z}^3) = \{f \in L^p_{\rm loc}(\mathbf{R}^3), \quad \forall k \in \mathbf{Z}^3, \quad f(\cdot + k) - f(\cdot) = 0 \quad a.e\}$$

when $1 \leq p \leq +\infty$, and

$$\mathcal{A}_c = C^0_{\rm per}(\mathbf{Z}^3) = \{f \in C^0(\mathbf{R}^3), \quad \forall k \in \mathbf{Z}^3, \quad f(\cdot + k) - f(\cdot) = 0.\}$$

The almost periodic case. If the set $\{X_i\}_{i\in\mathbf{N}}$ is almost periodic (see [12]), then the sets $\mathcal{A}^{k,p}$ contain only almost periodic functions. And in some sense, the functions in $\mathcal{A}^{k,p}$ share the almost periodicity of the set of nuclei: indeed, any almost-period of such a function is an almost-period of the measure of the nuclei, and vice versa (see [12] or [3] for the corresponding definitions).

The case of a compactly perturbed periodic system. We consider now the case where $\{X_i\}_{i\in\mathbf{N}}$ is a periodic set, except for a finite number of points. For instance, $\mathbf{Z}^3 \setminus \{0\}$, or $\mathbf{Z}^3 \cup \{(0,0,\frac{1}{2})\}$ satisfy this condition. Then it is possible to show that we have:

$$\mathcal{A}^p(\{X_i\}) = L^p_{\rm per}(\mathbf{Z}^3) + L^p_0(\mathbf{R}^3), \tag{15}$$

where $L^p_0(\mathbf{R}^3) = \{f \in L^p_{\rm loc}(\mathbf{R}^3), \quad \lim_{|x|\to\infty} \|f\|_{L^p(B+x)} = 0\}$. Let us give the ideas of the proof for the example $\mathbf{Z}^3 \setminus \{0\}$: consider the function $\varphi(x) = \sin(\pi x_1)\sin(\pi x_2)\sin(\pi x_3)\mathbf{1}_{[0,2]^3}(x)$, and define $f(x) = \sum_{k\in\mathbf{Z}^3\setminus\{0\}} \varphi(x-k)$. Clearly $f \in \mathcal{A}^1$, and in fact $f = -\varphi$. Now, as shown in the next subsection (Proposition 2.11), this implies that for any $\alpha > 0$, $|f|^\alpha \in \mathcal{A}^1$. Let α go to zero, this implies that $\mathbf{1}_{[0,1]^3} \in \mathcal{A}^1$. Since $\mathcal{A}^1$ is stable under translations and is a vector space, this implies that any compactly supported function of $L^1_{\rm loc}(\mathbf{R}^3)$ belongs to $\mathcal{A}^1$. The closure with respect to the $L^1_{\rm unif}(\mathbf{R}^3)$ norm allows to conclude that $L^1_0(\mathbf{R}^3) \subset \mathcal{A}^1$. Next, using this fact, the same computations allow to show that $L^1_{\rm per}(\mathbf{Z}^3) \subset \mathcal{A}^1$. Since the sum of these sets is closed for $\|\cdot\|_{L^1_{\rm unif}(\mathbf{R}^3)}$, this shows (15).

In other words, in this case, the spaces $\mathcal{A}^{k,p}$ consist of periodic functions up to local perturbations, clearly reflecting the geometry of the set of points $\{X_i\}$. On the other hand, the presence of these local perturbations implies the presence in $\mathcal{A}^{k,p}$ of compactly supported functions, thereby preventing for instance the function $\langle|\cdot|\rangle$ from being a norm on this space (whereas it is a norm in the previous case). Note indeed that $\forall f \in L^p_0(\mathbf{R}^3), \quad \langle|f|\rangle = 0$. We shall come back to this difficulty later on.

The case of two semi-crystals glued together. Another example is the case when the set $\{X_i\}_{i\in\mathbf{N}}$ is equal to some lattice ℓ_1 on a half space, and to some other lattice ℓ_2 on the other half space: $\{X_i\}_{i\in\mathbf{N}} = (\ell_1 \cap H^+) \cup (\ell_2 \cap H^-)$, where $H^+ = \{x \in \mathbf{R}^3, x \cdot a \geq 0\}$ and $H^- = \{x \in \mathbf{R}^3, x \cdot a < 0\}$, for some vector $a \neq 0$. Such a set clearly satisfies (H1), (H2), (H3) of Definition 2.3. More generally, separating $\mathbf{R}^3$ into n intersections of half-spaces

of the form H^+, and defining $\{X_i\}$ to be equal to some lattice on each of them gives an admissible set.

As announced in Subsection 2.2, we now prove that hypotheses (H1), (H2), and (H3) are not logically linked to one another: consider first the set $\{X_i\}_{i\in\mathbf{N}}$ defined by

$$\begin{cases} \{X_i\}_{i\in\mathbf{N}} \cap (2Q) = \mathbf{Z}^3 \cap (2Q), \\ \{X_i\}_{i\in\mathbf{N}} \cap (2^{2p+1}Q \setminus 2^{2p}Q) = \mathbf{Z}^3 \cap (2^{2p+1}Q \setminus 2^{2p}Q) \quad \text{if} \quad p \geq 1 \\ \{X_i\}_{i\in\mathbf{N}} \cap (2^{2p}Q \setminus 2^{2p-1}Q) = 2\mathbf{Z}^3 \cap (2^{2p}Q \setminus 2^{2p-1}Q) \quad \text{if} \quad p \geq 1, \end{cases}$$

where $Q = [-\frac{1}{2}, \frac{1}{2}[$ is the unit cube of $\mathbf{R}^3$. This set of points clearly satisfies $2\mathbf{Z}^3 \subset \{X_i\}_{i\in\mathbf{N}} \subset \mathbf{Z}^3$, so that (H1) and (H2) are satisfied. On the contrary, the sequence $\frac{1}{2^{3n}}\#\{i/X_i \in 2^nQ\}$ may be shown to oscillate between two different values, corresponding to the evenly indexed and oddly indexed subsequences. This prevents (H3) from being satisfied.

Consider now the set $\{X_i\}_{i\in\mathbf{N}}$ composed of all the points of $\mathbf{Z}^3$ except those in the set $nQ + 2^n e_1$, where n is any integer, Q the unit cube of $\mathbf{R}^3$, and e_1 the first vector of the canonical basis of $\mathbf{R}^3$. Such a set satisfies (H1) and (H3), but (H2) is not fulfilled (note that $\{X_i\}_{i\in\mathbf{N}} = \emptyset$ is also a counter-example to this case).

The preceding counter-example gives the idea to construct the last one: consider the set $\{X_i\}_{i\in\mathbf{N}}$ defined by

$$\{X_i\}_{i\in\mathbf{N}} = \bigcup_{n\in\mathbf{N}} \left((2^n e_1 + Q) \cap \frac{1}{n}\mathbf{Z}^3 \right).$$

This set satisfies (H2) and (H3), but $\sup_{x\in\mathbf{R}^3} \#\{i/X_i \in B_1 + x\} = \infty$.

A third point is, one may ask whether the hypotheses we have chosen, in particular (H3), are necessary in order to ensure the existence of mean values for elements of the spaces $\mathcal{A}^{k,p}$. We answer this question in the following lemma:

Lemma 2.10 *Let $\{X_i\}_{i\in\mathbf{N}}$ be a set of points in $\mathbf{R}^3$, satisfying (H1). Then (H3) of Definition 2.3 is satisfied if and only if any element of $\mathcal{A}(\{X_i\}_{i\in\mathbf{N}})$ has an average.*

Proof: The fact that (H1) and (H3) implies that any $f \in \mathcal{A}(\{X_i\}_{i\in\mathbf{N}})$ has an average is contained in the proof of Proposition 2.7. The reverse implication is shown as follows: let $\varphi \in \mathcal{D}(\mathbf{R}^3)$ having compact support, and such that $\int \varphi = 1$. The function $f(x) = \sum \varphi(x - X_i)$ belongs to $\mathcal{A}$, and we have, using (H1),

$$\int_{B_R} f = \sum_{i\in\mathbf{N}} \int_{B_R + X_i} \varphi = \#\{i \in \mathbf{N}, X_i \in B_R\} + O(R^2).$$

Hence, if f has an average, (H3) is satisfied for $n = 0$. Next, consider the function $f = f_1 f_2$, with f_1 and f_2 defined by

$$f_j(x) = \sum_{i\in\mathbf{N}} \varphi_j(x - X_i),$$

with $\varphi_j \geq 0$ enjoying the same properties as φ above. Then, we have

$$\begin{aligned}\frac{1}{|B_R|}\int_{B_R} f &= \frac{1}{|B_R|}\sum_{i\in\mathbf{N}}\sum_{j\in\mathbf{N}}\int_{B_R}\varphi_1(x-X_i)\varphi_2(x-X_j)dx \\ &= \frac{1}{|B_R|}\sum_{X_i\in B_R}\sum_{X_j\in B_R}\int_{\mathbf{R}^3}\varphi_1(x-X_i)\varphi_2(x-X_j)dx + \frac{1}{|B_R|}O(R^2) \\ &= \sum_{X_i\in B_R}\sum_{X_j\in B_R}\psi(X_j-X_i)+O(\frac{1}{R}),\end{aligned}$$

with $\psi = (\varphi_1(-x)) * \varphi_2$. Since the above quantity converges to the average of f, we thus see that the measure $\frac{1}{|B_R|}\sum_{X_i\in B_R}\sum_{X_j\in B_R}\delta_{X_i-X_j}$ converges to some measure l^1, defined on all functions in $C_c(\mathbf{R}^3)$ which are convolution products of two functions in L^1. There only remains to point out that this set is dense in $C_c(\mathbf{R}^3)$ to conclude that (H3) holds with $n=1$. Finally, we repeat the preceding argument with a product of n functions, and show that (H3) holds for any $n \in \mathbf{N}$. $\Diamond$

What we have been looking for so far is a way of ensuring that a function f has an average, in the sense of Definition 2.1. We now briefly investigate other similar conditions that ensure that, some $f \in L^\infty$ being given:

(1) f has an average, i.e $\lim_{R\to\infty}\frac{1}{|B_R|}\int_{B_R} f$ exists;

(2) $\frac{1}{|B_R|}\int_{B_R+x_0} f$ converges, uniformly with respect to x_0;

(3) for any open bounded set A, $\lim_{R\to\infty}\frac{1}{|RA|}\int_{RA} f$ exists;

(4) for any open bounded set A, $\lim_{R\to\infty}\frac{1}{|RA|}\int_{RA} f$ exists and is independent of A.

We then have the following implications:

$$\begin{array}{ccc}(2) & \Rightarrow & (4) \\ \Downarrow & & \Downarrow \\ (1) & \Leftarrow & (3),\end{array}$$

any other implication being false. Indeed, it is clear that (1) cannot imply (3). Think of the example (in dimension 1) $f(x) = \sin(\log(1+x)) + \cos(\log(1+x)) - 1$ when $x > 0$, with $f(-x) = -f(x)$. This function clearly has an average, which is 0. However, a primitive of f is $F(x) = (1+x)\sin(\log(1+x))$ on $(0,+\infty)$, so that

$$\frac{1}{R}\int_0^R f(t)dt = \frac{1+R}{R}\sin(\log(1+R)),$$

which has no limit as R goes to infinity. Thus, (1) does not imply (3), so that it can neither imply (2) nor (4).

The fact that (3) does not imply (4) is shown by the example of the Heaviside function $f = \mathbf{1}_{(0,+\infty)} - \mathbf{1}_{(-\infty,0)}$.

Finally, in order to show that (4) does not imply (2), we use the function $f(x) = \cos(\sqrt{|t|}) + \frac{\sin(\sqrt{|t|})}{\sqrt{|t|}}$, for which $\frac{1}{R}\int_{Ra}^{Rb} f(t)dt$ converges to 0 for any $a, b \in \mathbf{R}$, whereas $\frac{1}{R}\int_{R^2-R}^{R^2+R} f(t)dt$ has no limit.

Of course, one may require these properties (2), (3), (4) for the set $\mathcal{A}^{k,p}$. The preceding analysis (and the subsequent one) apply to these cases, provides one changes accordingly the hypothesis (H3) (for instance, (2) would require (H3) to be true *uniformly* with respect to the center of the ball.)

The last remark of this section is that the construction of the space $\mathcal{A}^{k,p}$ does not depend on the dimension. Hence, one may consider the following construction:

Let $\{\overline{X}_i\}_{i\in\mathbf{N}} = \{(X_i^1, X_i^2, \dots X_i^m\}$ be set of m-uplets of points in $\mathbf{R}^3$. Consider the hypothesis (H3) made on the set $\{\overline{X}_i\}_{i\in\mathbf{N}}$ in $(\mathbf{R}^3)^m$, that is,

$$l^n(\overline{h}_1, \overline{h}_2, \dots, \overline{h}_n, \delta) = \lim_{R\to\infty} \frac{1}{|B_R||B_\delta|^n} \#\{\overline{X}_{i_0}, \dots \overline{X}_{i_n} \in (B_R)^k / \overline{X}_{i_0} - \overline{X}_{i_k} \in B_\delta(\overline{h}_k), 1 \le k \le n\} \quad (16)$$

exists for any $n \in \mathbf{N}$, any $(\overline{h}_1, \overline{h}_2, \dots \overline{h}_n) \in \big((\mathbf{R}^3)^m\big)^n$. Here, the ball B_δ is a ball in $(\mathbf{R}^3)^m$. Under this hypothesis, one may construct, using the same technics as above, the algebra generated by functions of the form:

$$f(x) = \sum_{i\in\mathbf{N}} \varphi(\overline{x} - \overline{X}_i), \quad (17)$$

where $\varphi \in \mathcal{D}\big((\mathbf{R}^3)^m\big)$, and $\overline{x} = (x, x, \dots x)$. (see remark 2.9.) Denoting by $\mathcal{B}_m(\{X_i\}_{i\in\mathbf{N}})$ the corresponding algebra (of course, $\mathcal{B}_1$ is the algebra $\mathcal{A}$ of the preceding section), one easily checks using (16) that any $f \in \mathcal{B}_m$ has an average. The corresponding spaces $\mathcal{B}_m^{k,p}$ are constructed in the same way. This extension allows to construct, when $\{X_i\}_{i\in\mathbf{N}}$ and $\{Y_i\}_{i\in\mathbf{N}}$ are given satisfying (H3), an algebra of functions containing the set of product of functions of $\mathcal{A}(\{X_i\}_{i\in\mathbf{N}})$ by functions of $\mathcal{A}(\{Y_i\}_{i\in\mathbf{N}})$, namely $\mathcal{B}_2(\{Z_i\}_{i\in\mathbf{N}})$, with $\{Z_i\}_{i\in\mathbf{N}} = \{(X_i, Y_i)\}_{i\in\mathbf{N}}$. Note however that this space is in general larger than the set $\mathcal{A}(\{X_i\}_{i\in\mathbf{N}} \cup \{Y_i\}_{i\in\mathbf{N}})$ when it exists, i.e when the set $\{X_i\}_{i\in\mathbf{N}} \cup \{Y_i\}_{i\in\mathbf{N}}$ satisfies (H3). This is shown by the example of $\{X_i\}_{i\in\mathbf{N}} = 2\mathbf{Z}$, $\{Y_i\}_{i\in\mathbf{N}} = 2\mathbf{Z} + 1$. Since $\{X_i\}_{i\in\mathbf{N}} \cup \{Y_i\}_{i\in\mathbf{N}} = \mathbf{Z}$, the space $\mathcal{A}(\{X_i\}_{i\in\mathbf{N}} \cup \{Y_i\}_{i\in\mathbf{N}})$ is a set of 1-periodic functions, whereas a function of the form (17) is not necessarily 1-periodic.

2.4 Properties of the spaces $\mathcal{A}^{k,p}$

Note that $\mathcal{A}$ is stable under products, hence so is $\mathcal{A}^{k,\infty}$, for any $k \in \mathbf{N}$. Moreover, since, in view of Proposition 2.7, any function belonging to $\mathcal{A}$ admits an average satisfying (12), and since the norms $\|\cdot\|_{L^p_{\text{unif}}}$ preserve this property, any function belonging to $\mathcal{A}^{k,p}$ has an average. We collect these results in the following:

Proposition 2.11 *For any admissible set $\{X_i\}_{i\in\mathbf{N}}$ in the sense of Definition 2.3, the functional spaces $\mathcal{A}^{k,p}(\{X_i\})$ satisfy the following:*

(i) For any $\rho \in \mathcal{A}^{k,p}$ and $\eta \in \mathcal{A}^{k,p'}$, with $\frac{1}{p}+\frac{1}{p'}=\frac{1}{r}$, $\rho\eta \in \mathcal{A}^{k,r}$ $(p,p',r\in[1,\infty].)$

(ii) For any $\rho \in \mathcal{A}^1$, $\langle\rho\rangle = \lim_{R\to\infty} \frac{1}{|B_R|}\int_{B_R}\rho(x)dx$ exists.

(iii) If $f \in C^0(\mathbf{R})$, then for all $\rho\in\mathcal{A}^\infty$, $f(\rho)\in\mathcal{A}^\infty$. Moreover, if f satisfies, for any $t,s\in\mathbf{R}$, $|f(t)-f(s)|\le C(|t-s|+|t-s|^p)$, for some constant C, then for any $\rho\in\mathcal{A}^p$, $f(\rho)\in\mathcal{A}^1$.

Proof: We skip the easy proofs of (i) and (ii), and we focus on (iii). We first point out that according to (i), (iii) is true if f is a polynomial which cancels at 0. In order to show that it is true for any polynomial, we show that $1\in\mathcal{A}^\infty$. For this purpose, we point out that $\eta(x)=\sum_{i\in\mathbf{N}} e^{-|x-X_i|^2}$ belongs to $\mathcal{A}^\infty$. There exists $\alpha>0$ such that $\eta\ge\alpha$, in view of (H2). Now, let $a>0$, and let g be the function defined on $\mathbf{R}^+$ by $g(t)=t^a$. Such a function may be uniformly approximated on $[0,\|\eta\|_{L^\infty(\mathbf{R}^3)}]$ by a sequence g_n of polynomials canceling at 0. Thus, $g_n(\eta)\in\mathcal{A}^\infty$. Letting n go to infinity, this implies that $\eta^a\in\mathcal{A}^\infty$. This being valid for any $a>0$, we may let a go to zero, and the fact that $\eta\ge\alpha>0$ implies that η^a uniformly converges to 1 as a goes to 0. Hence, $1\in\mathcal{A}^\infty$, and thus for any polynomial f, $\rho\in\mathcal{A}^\infty$ implies $f(\rho)\in\mathcal{A}^\infty$. In order to conclude that this is valid for any continuous f, we only need to point out that on $[-\|\rho\|_{L^\infty(\mathbf{R}^3)},\|\rho\|_{L^\infty(\mathbf{R}^3)}]$, f may be uniformly approximated by a polynomial. This proves the first part of (iii). The second part of (iii) is easily proven using Hölder inequality. $\Diamond$

We have shown in the course of the above proof the following corollary:

Corollary 2.12 *Let $\{X_i\}_{i\in\mathbf{N}}$ be an admissible set. Then $1\in\mathcal{A}^\infty$.*

An easy adaptation of Proposition 2.11 also shows the following:

Proposition 2.13 *Let $\{X_i\}_{i\in\mathbf{N}}$ be an admissible set, let $k\in\mathbf{N}$ and $p\ge1$. Let $f\in C^k(\mathbf{R})$ such that*

$$\forall j\le k,\quad \exists C_j\ge 0 \quad / \quad |f^{(j)}(t)-f^{(j)}(s)|\le C_j(|t-s|+|t-s|^p).$$

Then for any $\eta\in\mathcal{A}^{k,p}$, $f(\eta)\in\mathcal{A}^{k,1}$.

The spaces $\mathcal{A}^{k,p}$ are thus stable under any regular enough local transformation. Now, they are also stable under some non-local transformations, and in particular convolutions:

Proposition 2.14 *Let $\{X_i\}_{i\in\mathbf{N}}$ be an admissible set, and let $W\in L^q_{\rm loc}(\mathbf{R}^3)$ be a potential satisfying $|W(x)|\le\frac{C}{|x|^{3+\gamma}}$ outside a ball, for some $\gamma>0$. Then, setting $p=\frac{q}{q-1}$ the conjugate exponent of q, we have*

$$\forall\eta\in\mathcal{A}^{k,p},\quad \eta*W\in\mathcal{A}^{k,\infty},$$

where $\big(\eta*W\big)(x)=\int_{\mathbf{R}^3}\eta(x-y)W(y)dy$.

Proof: We prove the statement in the case $k = 0$, the generalization to k positive being easy. We first point out that the convolution product does exist, and satisfies, for some constant C depending only on W:

$$\|W * \eta\|_{L^\infty(\mathbf{R}^3)} \leq C\|\eta\|_{L^p_{\text{unif}}(\mathbf{R}^3)}. \tag{18}$$

Indeed,

$$\big|(\eta * W)(x)\big| \leq \sum_{k\in\alpha\mathbf{Z}^3} \int_{B_1+k} |\eta(x-y)||W(y)|dy \leq \sum_{k\in\alpha\mathbf{Z}^3} \|W\|_{L^q(B_1+k)}\|\eta\|_{L^p_{\text{unif}}(\mathbf{R}^3)},$$

the constant $\alpha > 0$ being chosen so that $\mathbf{R}^3 = \bigcup_{k\in\alpha\mathbf{Z}^3} B_1 + k$. ($\alpha = \frac{\sqrt{3}}{2\sqrt{2}}$ fulfills this condition.) Now, assuming that $|W(x)| \leq \frac{C}{|x|^{3+\gamma}}$ for $|x| > R$, we have

$$\sum_{k\in\alpha\mathbf{Z}^3} \|W\|_{L^q(B_1+k)} \leq \sum_{k\in\alpha\mathbf{Z}^3\cap B_R} \|W\|_{L^q(B_1+k)} + \sum_{k\in\alpha\mathbf{Z}^3\cap B_R^C} \frac{C}{|k|^{3+\alpha}} \leq C', \tag{19}$$

which proves our claim. Let then η_n be an L^p_{unif} approximation of η belonging to $\mathcal{A}$, and let W_n be an L^q approximation of W in $\mathcal{D}(\mathbf{R}^3)$. Then clearly $W_n * \eta_n \in \mathcal{A}$, and (18) shows that $W_n * \eta_n$ converges to $W * \eta$ in $L^\infty(\mathbf{R}^3)$. $\Diamond$

Remark 2.15 *Note that in the special case $p = \infty$, the condition $W \in L^1(\mathbf{R}^3)$ is sufficient for the above result to hold. However, we will need it in some other cases (typically $p = \frac{5}{3}$). In addition, it is not sufficient when $p \neq \infty$: even if $W \in L^1 \cap L^\infty$, this hypothesis does not allow to show that the left-hand side of (19) is a converging series, which is necessary for (18) to hold.*

The previous Proposition asserts that the belonging to $\mathcal{A}^{k,p}(\{x_i\}_{i\in\mathbf{N}})$ is stable under convolution products. In the same spirit, we have the following:

Proposition 2.16 *For any $k \in \mathbf{N}$ and any $p \geq 1$, we have:*

$$\mathcal{A}^1(\{X_i\}_{i\in\mathbf{N}}) \cap W^{k,p}_{\text{unif}}(\mathbf{R}^3) = \mathcal{A}^{k,p}(\{X_i\}_{i\in\mathbf{N}}).$$

Proof: The fact that $\mathcal{A}^{k,p}(\{X_i\}_{i\in\mathbf{N}})$ is included in $\mathcal{A}^1(\{X_i\}_{i\in\mathbf{N}})$ and $W^{k,p}_{\text{unif}}(\mathbf{R}^3)$ is clear. The reverse inclusion is easily seen using a regularization procedure: assuming that f belongs to $\mathcal{A}^1$, we know that there exists a sequence $(f_n)_{n\in\mathbf{N}}$ belonging to $\mathcal{A}$, converging to f in $L^1_{\text{unif}}(\mathbf{R}^3)$. ω being a non-negative function in $\mathcal{D}(\mathbf{R}^3)$, we have $f_n * \omega \in \mathcal{A}$, for all $n \in \mathbf{N}$, and

$$f_n * \omega \longrightarrow f * \omega \quad \text{in} \quad W^{k,p}_{\text{unif}}(\mathbf{R}^3).$$

Hence, $f * \omega \in \mathcal{A}^{k,p}$, for any $\omega \in \mathcal{D}(\mathbf{R}^3)$. Next, we use for ω an approximation of δ_0, for instance $\omega_\varepsilon(x) = \varepsilon^{-3}\omega_0(\frac{x}{\varepsilon})$, with $\omega_0 \geq 0$, $\omega_0 \in \mathcal{D}(\mathbf{R}^3)$ and $\int \omega_0 = 1$. The convolution product $f * \omega_\varepsilon$ then converges to f in $W^{k,p}_{\text{unif}}(\mathbf{R}^3)$, showing that $f \in \mathcal{A}^{k,p}$. $\Diamond$

3 Application to Thomas-Fermi type theories

In this section, we apply the above results to the case of Thomas-Fermi theory (see [10] for instance).

3.1 Thomas-Fermi energy: the molecular and periodic cases

We recall here that the Thomas-Fermi (TF) model is defined by (1) and (2) when dealing with a finite system, and that in the case of an infinite periodic system, it may be shown to converge in some sense to the model defined by (3)-(5)-(4), of which we give here a generalization in the case of any lattice ℓ:

$$E^{TF}(\rho,\ell) = \int_{Q(\ell)} \rho^{5/3} + \frac{1}{2}\int_{Q(\ell)}\int_{Q(\ell)} \rho(x)G_\ell(x-y)\rho(y)dxdy - \int_{Q(\ell)} G_\ell\rho,$$

where $Q(\ell)$ is a unit cell of the periodic lattice ℓ, and G_ℓ is defined up to an additive constant by

$$-\Delta G_\ell = \sum_{k\in\ell}\delta_k - \frac{1}{|Q(\ell)|}$$

on $Q(\ell)$, with periodic boundary conditions. Hence, the electronic density ρ is the solution of

$$I^{TF}(\ell) = \inf\left\{E^{TF}(\rho,\ell), \quad \rho\geq 0, \quad \rho\in L^{5/3}_{per}(Q(\ell)), \quad \int_{Q(\ell)}\rho = 1\right\}.$$

Here, $L^p_{per}(Q(\ell))$ is the set of functions belonging to $L^p_{loc}(\mathbf{R}^3)$ which are ℓ-periodic. We also recall the Euler-Lagrange equation of this problem: setting $\phi = \frac{5}{3}\rho^{2/3}$, we have

$$-\Delta\phi + \big(\frac{3}{5}\phi\big)^{3/2} = \sum_{k\in\ell}\delta_k. \tag{20}$$

The periodic energy (3) may be defined as the average energy of the system, i.e

$$E^{TF}(\ell,\rho) = \langle\rho^{5/3}\rangle + \frac{1}{2}\langle\rho\big(G_\ell *_{Q(\ell)}\rho\big)\rangle - \langle\rho G_\ell\rangle, \tag{21}$$

where $*_{Q(\ell)}$ is the convolution product over the periodic cell $Q(\ell)$, that is: $(f *_{Q(\ell)} g)(x)\int_{Q(\ell)} f(y)g(x-y)dy$. The quantity $G_\ell *_{Q(\ell)}\rho$ may be interpreted as the Coulomb potential ϕ generated by the density ρ, defined by

$$-\Delta\phi = \rho - \frac{1}{|Q(\ell)|},$$

ϕ satisfying periodic boundary conditions on $Q(\ell)$.

All the above statements carry through if one replaces Coulomb interactions by Yukawa potential, which means replacing $\frac{1}{4\pi|x-y|}$ by $W_a(x-y) = \frac{e^{-a|x-y|}}{4\pi|x-y|}$, for some $a>0$ in the

molecular model (1), and $G_\ell(x)$ by $W_a^\infty(x) = \sum_{k\in\ell} \frac{e^{-a|x-k|}}{4\pi|x-k|}$. In such a case, equation (20) should be replaced by

$$-\Delta\phi + a^2\phi + \left(\frac{3}{5}\phi\right)^{3/2} = \sum_{k\in\ell} \delta_k. \tag{22}$$

3.2 The non-periodic case

We give in this subsection a study of a possible generalization of the preceding results to non-periodic geometries enjoying the properties exposed in section 2. The set of nuclei $\{X_i\}$ is thus here an admissible set in the sense of Definition 2.3. The electronic density ρ will be assumed to belong to $\mathcal{A}^{5/3}(\{X_i\})$. For such a density, we need to define the average TF energy. The kinetic part is easily defined as

$$K(\rho) = \langle \rho^{5/3} \rangle,$$

which exists by virtue of Proposition 2.11. On the contrary, the electrostatic terms are not so easy to define. We start with the Yukawa case, which is rather straightforward, and next tackle the case of Coulomb interaction.

3.2.1 The Yukawa case

If the interaction potential is $W_a(x) = \frac{e^{-a|x|}}{4\pi|x|}$, for some positive a, then it is easily seen that $\sum_{i\in\mathbf{N}} W_a(x - X_i)$ belongs to $\mathcal{A}^p$ for any $p < 3$. Moreover, according to Proposition 2.14, $\rho * W_a \in \mathcal{A}^\infty$. As a consequence, one can define the following Thomas-Fermi energy:

$$E_{\mathrm{Y}}^{TF}(\rho, \{X_i\}) = \langle \rho^{5/3} \rangle + \frac{1}{2}\langle \rho(\rho * W_a) \rangle - \langle \rho W_a^\infty \rangle + M_a(\{X_i\}_{i\in\mathbf{N}}), \tag{23}$$

where the convolution product is taken on $\mathbf{R}^3$, and W_a^∞ is defined similarly to the periodic case by

$$W_a^\infty(x) = \sum_{i\in\mathbf{N}} W_a(x - X_i) = W_a * \left(\sum_{i\in\mathbf{N}} \delta_{X_i}\right).$$

The constant $M_a(\{X_i\}_{i\in\mathbf{N}})$ is the interaction of the nuclei, that is, $M_a = \int W_a(x) d(l^1 - \delta_0)(x)$, or equivalently $\lim_{R\to\infty} \frac{1}{|B_R|} \sum_{i\neq j} W_a(x_i - X_j)$, where we sum over indexes i and j such that $X_i \in B_R$ and $X_j \in B_R$.

3.2.2 The Coulomb case

Trying to reproduce the preceding analysis in the Coulomb case, one is faced with the fact that the Coulomb potential generated by a density ρ is not so easy to define. Not only may it not be computed through a convolution product, but compatibility conditions are needed for the potential to exist. The example of the periodic case is interesting and lightening: if ρ is $\mathbf{Z}^3$-periodic, the existence of a solution to

$$-\Delta\phi = \rho$$

implies that $\int_Q \rho = 0$, where Q is the unit cube or $\mathbf{R}^3$.

We derive here this kind of compatibility conditions for non-periodic densities ρ, and then give a way of defining the TF energy: let f be a function belonging to $\mathcal{A}^\infty$. What condition should we impose on f so that the problem

$$-\Delta\phi = f$$

has a solution in $\mathcal{A}^\infty$, or at least in L^∞? A possible answer is given in Theorem 1 of [2], which we reproduce here for the sake of consistency:

Lemma 3.1 ([2]) *Let $f \in L^p_{\rm unif}(\mathbf{R}^3)$, for some $p > \frac{3}{2}$. Then the following two properties are equivalent:*

(i) There exists $\phi \in L^\infty(\mathbf{R}^3)$ such that $-\Delta\phi = f$,

(ii) There exists a constant $C > 0$ such that for any $x_0 \in \mathbf{R}^3$, and for any $R > 0$,

$$\left| \int_{B_R(x_0)} \left(\frac{1}{|x - x_0|} - \frac{1}{R}\right) f(x)dx \right| \leq C.$$

Moreover, such a ϕ is unique up to an additive constant, and if $f \in \mathcal{A}^p(\{X_i\}_{i\in\mathbf{N}})$, for some admissible set $\{X_i\}_{i\in\mathbf{N}}$, then $\phi \in \mathcal{A}^\infty(\{X_i\}_{i\in\mathbf{N}})$.

Remark 3.2 *As noticed in [2], a necessary condition for f to satisfy (i) or equivalently (ii) is that $\langle f \rangle = 0$. This condition is sufficient if f is periodic, but is not in the general case when $f \in \mathcal{A}^1(\{X_i\}_{i\in\mathbf{N}})$, as the following example shows: $\{X_i\}_{i\in\mathbf{N}} = 2\mathbf{N} \cup \mathbf{Z}^*_-$, and $f = \mathbf{1}_{(-\infty,0)} - \mathbf{1}_{(0,+\infty)}$.*

Remark 3.3 *Note that the above Lemma is valid independently of the dimension, replacing the Newtonian potential $\frac{1}{|x|} - \frac{1}{R}$ in (i) by the corresponding one, that is, $|x|^{2-d} - R^{2-d}$ if $d \neq 2$, and $\log|x| - \log R$ if $d = 2$. Other possible generalizations are presented in [2].*

We are now in position to properly define a non-periodic TF energy in the Coulomb case. The first point is to define the electrostatic potential generated by the nuclei. We first consider the case of smeared out nuclei, that is, when the measure which define them is not a sum of Dirac masses, but a regular measure $\mu = \sum_{i\in\mathbf{N}} m_0(\cdot + X_i)$, with $m_0 \in \mathcal{D}(\mathbf{R}^3)$, $m_0 \geq 0$, $\int m_0 = 1$. In such a case, for $\rho \in \mathcal{A}^{5/3}(\{X_i\}_{i\in\mathbf{N}})$ such that $\mu - \rho$ satisfy (ii) of Lemma 3.1, we may define the TF energy by

$$E^{\rm TF}(\rho, \{X_i\}) = \langle \rho^{5/3} \rangle + \frac{1}{2}\langle |\nabla\phi|^2 \rangle, \quad -\Delta\phi = \mu - \rho, \quad \phi \in L^\infty(\mathbf{R}^3), \tag{24}$$

and ask the question of the well-posedness of the problem

$$I^{\rm TF}(\{X_i\}) = \inf\left\{ E^{\rm TF}(\rho, \{X_i\}), \quad \rho \in \mathcal{A}^{5/3}_{\rm Cb}(\{X_i\}_{i\in\mathbf{N}}) \right\}, \tag{25}$$

where the set $\mathcal{A}^{5/3}_{\mathrm{Cb}}(\{X_i\}_{i\in\mathbf{N}})$ is the set of functions belonging to $\mathcal{A}^{5/3}(\{X_i\}_{i\in\mathbf{N}})$ and satisfying (ii) of Lemma 3.1.

We are now going to define in the same way the TF energy in the case of point nuclei. In order to do so, one needs to screen the nucleic charge (in the periodic case, it is screened by a uniform charge, but it might not be possible to do so here.) Let m_0 be a smooth non-negative function with compact support, which is radially symmetric, and such that $\int m_0 = 1$. Define

$$\mu = \sum_{i\in\mathbf{N}} m_0(\cdot - X_i).$$

Considering $\phi_0 = \frac{1}{4\pi|x|} - m_0 * \frac{1}{4\pi|x|}$ the Coulomb potential generated by $\delta_0 - m_0$, one notices that it has no quadrupole moment, and thus decays faster than $\frac{1}{|x|^4}$ at infinity, so that

$$W(x) = \sum_{i\in\mathbf{N}} \phi_0(x - X_i)$$

exists and is the Coulomb potential generated by $\sum(\delta_{X_i} - m_0(\cdot - X_i))$. Moreover, it belongs to $\mathcal{A}^p(\{X_i\}_{i\in\mathbf{N}})$ for any $p < 3$, so that the average of ρW exists. Next, consider $\rho - \mu$, and assume it satisfies (ii) of Lemma 3.1. Then, one can define the potential ϕ generated by $\mu - \rho$, and $\phi \in \mathcal{A}^\infty(\{X_i\}_{i\in\mathbf{N}})$, so that here again $\langle\rho\phi\rangle$ exists.

This allows us to define a mean TF energy, on a subset of $\mathcal{A}^{5/3}(\{X_i\}_{i\in\mathbf{N}})$, which we define in the following definition:

Definition 3.4 *The set $\{X_i\}_{i\in\mathbf{N}}$ being admissible, let m_0 be a smooth compactly-supported radially symmetric function such that $\int m_0 = 1$. Denote by m the function $\mu(x) = \sum_{i\in\mathbf{N}} m_0(x - X_i)$. We will say that ρ is an admissible test function for the Coulomb TF energy, and we will note $\rho \in \mathcal{A}^{5/3}_{\mathrm{Cb}}(\{X_i\}_{i\in\mathbf{N}})$ if $f = \mu - \rho$ satisfies (ii) of Lemma 3.1. For such a non-negative function ρ, we define the Thomas-Fermi energy by*

$$E^{TF}(\rho, \{X_i\}) = \langle\rho^{5/3}\rangle - \langle W\rho\rangle + \frac{1}{2}\langle\phi(\mu - \rho)\rangle, \tag{26}$$

Where $W, \phi \in L^1_{\mathrm{unif}}(\mathbf{R}^3)$ are defined by

$$\begin{cases} -\Delta W = \sum_{i\in\mathbf{N}}(\delta_{X_i} - m_0(\cdot - X_i)) = \sum_{i\in\mathbf{N}}\delta_{X_i} - \mu, & \langle W\rangle = 0, \\ -\Delta\phi = \sum_{i\in\mathbf{N}} m_0(\cdot - X_i) - \rho = \mu - \rho, & \langle\phi\rangle = 0. \end{cases}$$

The first point is that E^{TF} is well defined in this way, for a fixed m, since all the functions here belong to $\mathcal{A}^1(\{X_i\}_{i\in\mathbf{N}})$, so that their averages exist. Next, one also needs to show that this definition does not depend on μ.

Proposition 3.5 *For any admissible set $\{X_i\}_{i\in\mathbf{N}}$, the set $\mathcal{A}^{5/3}_{\mathrm{Cb}}(\{X_i\}_{i\in\mathbf{N}})$ is independent of m_0. Moreover, given two smooth radially symmetric compactly supported functions m_0*

and m_0', the difference of the TF energy functions are equal up to a constant, i.e there exists C depending only on μ and μ' such that for any non-negative ρ in $\mathcal{A}^{5/3}_{\rm Cb}(\{X_i\}_{i\in\mathbf{N}})$,

$$\langle\rho^{5/3}\rangle - \langle W\rho\rangle + \frac{1}{2}\langle\phi(\mu-\rho)\rangle = \langle\rho^{5/3}\rangle - \langle W'\rho\rangle + \frac{1}{2}\langle\phi'(\mu'-\rho)\rangle + C, \tag{27}$$

where the $'$ indicates that the function is defined using m_0' instead of m_0.

Proof: In order to see that $\mathcal{A}^{5/3}_{\rm Cb}(\{X_i\}_{i\in\mathbf{N}})$ is independent of μ, we take two functions m_0 and m_0' satisfying the hypotheses of Definition 3.4, and point out that $-\Delta V = \mu' - \mu$ has at least one solution in $L^\infty(\mathbf{R}^3)$, that is, $W - W'$. Hence, if $-\Delta\phi = \mu - \rho$ has a solution $\phi \in L^\infty(\mathbf{R}^3)$, then $\phi' = \phi + V \in L^\infty(\mathbf{R}^3)$ is a solution of $-\Delta\phi' = \mu' - \rho$.

We next prove (27). One easily shows using the fact that $\langle\rho-\mu\rangle = 0$ that the difference between the two energies is

$$\begin{aligned}\langle\rho^{5/3}\rangle - \langle W\rho\rangle + \frac{1}{2}\langle\phi(\rho-\mu)\rangle - \langle\rho^{5/3}\rangle + \langle W'\rho\rangle - \frac{1}{2}\langle\phi'(\rho-\mu')\rangle& \\ = -\frac{1}{2}\langle\mu(W-W')\rangle - \frac{1}{2}\langle\rho(W-W')\rangle + \frac{1}{2}\langle\phi'(\mu-\mu')\rangle.&\end{aligned}$$

Now, going back to the definition of the average, one easily shows by integrating by part and estimating boundary terms through standard elliptic regularity results that $\langle\phi'(\mu'-\mu)\rangle = \langle(\rho-\mu')(W-W')\rangle$, finding (27) with $C = \frac{1}{2}\langle(W'-W)(\mu+\mu')\rangle$, which concludes the proof. $\Diamond$

Now that we have defined an energy, which is well defined in the sense that it depends on μ only through an additive constant, and thus that its possible minimizers *do not* depend on μ, we are going to investigate the existence and uniqueness of these minimizers.

3.3 Minimizing the energy

3.3.1 The (almost)-periodic case

We recall here some results of [5] and [10], where the periodic and almost-periodic cases were tackled.

Theorem 3.6 (Existence and uniqueness of the electronic ground state, [5]) *Assume that the set $\{X_i\}_{i\in\mathbf{N}}$ of nuclei is periodic. Then the sets $\mathcal{A}^p(\{X_i\}_{i\in\mathbf{N}})$ are the corresponding set of periodic functions. Moreover, the minimization problem*

$$I^{TF}(\{\{X_i\}_{i\in\mathbf{N}}) = \inf\left\{E^{TF}(\rho,\{X_i\}_{i\in\mathbf{N}}),\quad \rho\geq 0,\quad \rho\in\mathcal{A}^{5/3}_{\rm Cb}(\{X_i\}_{i\in\mathbf{N}})\right\}$$

has a unique solution.

Of course, such a result also holds in the Yukawa case as well as in the almost periodic case. Note that the set $\mathcal{A}^{5/3}_{\rm Cb}(\{X_i\}_{i\in\mathbf{N}})$ is equal to the set of function belonging to $\mathcal{A}^{5/3}(\{X_i\}_{i\in\mathbf{N}})$ which average is equal to 1.

3.3.2 A non-uniqueness case

We now deal with a case where there is no uniqueness of the ground state: consider a set $\{X_i\}_{i\in\mathbf{N}}$ composed of a compactly perturbed lattice ℓ, i.e such that there exists $R>0$ satisfying $\{X_i\}_{i\in\mathbf{N}}\cap B_R^C = \ell\cap B_R^C$. Although the following results are valid in this general case, we shall take $\{X_i\}_{i\in\mathbf{N}}=\mathbf{Z}^3\setminus\{0\}$ to fix the ideas. Then, as pointed out in Section 2.2, we have

$$\mathcal{A}^p(\mathbf{Z}^3\setminus\{0\}) = L^p_{\rm per}(Q)+L^p_0(\mathbf{R}^3),$$

where $L^p_{\rm per}(Q)$ is the set of $L^p_{\rm loc}$ functions satisfying periodic boundary conditions in Q, and

$$L^p_0(\mathbf{R}^3)=\{f\in L^p_{\rm loc}(\mathbf{R}^3),\quad \lim_{|x|\to\infty}\|f\|_{L^p(B_1+x)}=0\}.$$

We then have the following:

Proposition 3.7 *Let $\{X_i\}_{i\in\mathbf{N}}=\mathbf{Z}^3\setminus\{0\}$, or any compactly perturbed lattice. Then, for any $\rho\in\mathcal{A}^{5/3}_{\rm Cb}(\{X_i\}_{i\in\mathbf{N}})$, there exists $\eta\in\mathcal{A}^{5/3}_{\rm Cb}(\{X_i\}_{i\in\mathbf{N}})$ such that $\eta\neq\rho$ and $E^{TF}(\rho)=E^{TF}(\eta)$.*

Proof: According to the above remark, any $\xi\in\mathcal{D}(\mathbf{R}^3)$ belongs to $\mathcal{A}^{5/3}(\{X_i\}_{i\in\mathbf{N}})$. Moreover, it is easily seen, since $\xi*\frac{1}{|x|}$ is well defined, that for such a ξ, $\rho\in\mathcal{A}^{5/3}_{\rm Cb}(\{X_i\}_{i\in\mathbf{N}})$ implies $\xi+\rho\in\mathcal{A}^{5/3}_{\rm Cb}(\{X_i\}_{i\in\mathbf{N}})$. Now, the average of a function is not changed by an addition of a function in $L^p_0(\mathbf{R}^3)$. Thus, $E^{TF}(\rho+\xi)=E^{TF}(\rho)$. $\Diamond$

Note that the same result holds in the Yukawa case. The above result clearly prevents any solution the minimization problem I^{TF} from being unique. In fact, the presence of compactly-supported functions in the variational space also raises difficulties concerning the existence of solutions.

We thus investigate a more local notion of ground state in the following section. Note that it also provides a solution of $I^{\rm TF}$.

3.4 A notion of local ground state

Since, according to the preceding section, a minimization of the average energy with respect to the electronic density does not give a well-defined density ρ in general, we show here that minimizing *locally* the corresponding energy gives a unique density ρ, and show that it may be characterized by a Thomas-Fermi type PDE such as (20). This will give a particular solution of $I^{\rm TF}$, namely

$$I^{\rm TF}_{\rm Y}=\inf\left\{E^{\rm TF}_{\rm Y}(\rho,\{X_i\}),\quad \rho\in\mathcal{A}^{5/3}(\{X_i\}_{i\in\mathbf{N}}),\quad \rho\geq 0,\quad \langle\rho\rangle=l^0\right\} \tag{28}$$

in the Yukawa case, where l^0 is defined by (10), and $E^{TF}_{\rm Y}$ by (23), and

$$I^{\rm TF}_{\rm Cb}=\inf\left\{E^{\rm TF}_{\rm Cb}(\rho,\{X_i\}),\quad \rho\in\mathcal{A}^{5/3}_{\rm Cb}(\{X_i\}_{i\in\mathbf{N}}),\quad \rho\geq 0,\right\} \tag{29}$$

in the Coulomb case, with $E^{\rm TF}_{\rm Cb}$ defined by (26). Note that in order to avoid complications raised by the presence of Dirac masses (and thus singularities of the potential), one may also deal with the smeared nuclei case (24)-(25).

3.4.1 The Yukawa case

Following [13], we define now a notion of local ground state:

Definition 3.8 *Let a be a positive constant, and let $\{X_i\}_{i\in\mathbf{N}}$ be an admissible set. We will say that $\rho \in L^{5/3}_{\rm unif}(\mathbf{R}^3)$ is a local ground state of the system if $\rho \geq 0$ and:*

$$\forall \varphi \in \mathcal{D}(\mathbf{R}^3) \quad / \quad \rho+\varphi \geq 0 \quad \text{and} \quad \int_{\mathbf{R}^3} \varphi = 0,$$
$$\int_{\mathbf{R}^3} \big((\rho+\varphi)^{5/3} - \rho^{5/3}\big) - \int_{\mathbf{R}^3} \varphi W_a^\infty + \int_{\mathbf{R}^3}\int_{\mathbf{R}^3} \varphi(x) W_a(x-y)\rho(y)dxdy$$
$$+ \frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3} \varphi(x) W_a(x-y)\varphi(y)dxdy \geq 0.$$

Here, $W_a(x) = \frac{e^{-a|x|}}{4\pi|x|}$ is the Yukawa potential, and $W_a^\infty(x) = \sum_{i\in\mathbf{N}} W_a(x-X_i)$. In addition, we say that ρ is a neutral local ground state if $\langle\rho\rangle$ exists and is equal to 1.

Note that since we deal here with a notion of *local* minimization of the energy, we also need to deal with local neutrality, imposing $\int \varphi = 0$ so that the total mass of ρ is preserved locally. Otherwise one would end up with the overall local minimizer, and not only the one with prescribed mass.

We now have the following proposition:

Proposition 3.9 *Let $\{X_i\}_{i\in\mathbf{N}}$ be an admissible set of points in $\mathbf{R}^3$. Then, $\rho \geq 0$ is a local ground state in the sense of Definition 3.8 if and only if there exists $\theta \in \mathbf{R}$ such that, setting $\phi = W_a^\infty - \rho * W_a$, we have*

$$-\Delta\phi + a^2\phi + \big(\frac{3}{5}(\phi-\theta)_+\big)^{3/2} = \sum_{i\in\mathbf{N}} \delta_{X_i}. \tag{30}$$

Proof: We first prove that a local ground state satisfies (30). In order to do so, consider a test function φ which support is included in the set $\{\rho > 0\}$. Then, Definition 3.8 implies that for any $t \in \mathbf{R}$,

$$\int_{\mathbf{R}^3} \frac{5}{3}\rho^{2/3}\varphi - \int_{\mathbf{R}^3} W_a^\infty \varphi + \int_{\mathbf{R}^3} \big(\rho * W_a\big)\varphi + O(t) \geq 0.$$

This clearly implies that on the set $\{\rho > 0\}$, $\frac{5}{3}\rho^{2/3} - W_a^\infty + \rho * W_a = -\theta$, for some constant θ. Hence, $\phi - \theta \geq 0$ and $\rho = \big(\frac{3}{5}(\phi-\theta)\big)^{3/2}$ on this set, and consequently (30) holds on $\{\rho > 0\}$. Next, considering a φ such that $\varphi > 0$ on the set $\{\rho = 0\}$, one has, with the same kind of computation, and using the preceding result,

$$-\int_{\{\rho=0\}} W_a^\infty \varphi + \int_{\{\rho=0\}} \rho * W_a \varphi + \int_{\{\rho=0\}} \theta\varphi + O(t) \geq 0.$$

As a consequence, on the set $\{\rho = 0\}$, $-W_a^\infty + \rho * W_a + \theta \geq 0$, so that here again, $\left(\frac{3}{5}(\phi-\theta)_+\right)^{3/2} = 0 = \rho$. This achieves the proof of (30). Consider now a non-negative function ρ such that $\phi = W_a^\infty - \rho * W_a$ satisfies (30). Then, using the convexity of the function $t \mapsto t^{5/3}$ on $\mathbf{R}^+$, we have, for any $\varphi \in \mathcal{D}(\mathbf{R}^3)$ such that $\int \varphi = 0$ and $\rho + \varphi \geq 0$,

$$\int_{\mathbf{R}^3} \left((\rho+\varphi)^{5/3} - \rho^{5/3}\right) \geq \int_{\mathbf{R}^3} \frac{5}{3}\rho^{2/3}\varphi.$$

This, setting

$$A = \int_{\mathbf{R}^3} \left((\rho+\varphi)^{5/3} - \rho^{5/3}\right) - \int_{\mathbf{R}^3} \varphi W_a^\infty + \int_{\mathbf{R}^3}\int_{\mathbf{R}^3} \varphi(x) W_a(x-y)\rho(y)dxdy + \frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3} \varphi(x) W_a(x-y)\varphi(y)dxdy,$$

that

$$A \geq \int_{\mathbf{R}^3} \varphi\left(\frac{5}{3}\rho^{2/3} - W_a^\infty + \rho * W_a\right) + \int_{\mathbf{R}^3}\int_{\mathbf{R}^3} \varphi(x) W_a(x-y)\varphi(y)dxdy = \int_{\mathbf{R}^3}\int_{\mathbf{R}^3} \varphi(x) W_a(x-y)\varphi(y)dxdy,$$

since in view of (30), $\frac{5}{3}\rho^{2/3} - W_a^\infty + \rho * W_a = 0$. The remaining term being a positive bilinear form with respect to φ, we have $A \geq 0$. And in fact $A > 0$ unless $\varphi = 0$. $\Diamond$

The existence, for each $\theta \in \mathbf{R}$, of a solution of (30), is easily shown using techniques similar to that of [4]. As stated in the following theorem, the solution of (30) is unique for each θ. However, we have not assumed so far in this section that the functions we deal with belong to some $\mathcal{A}^p(\{X_i\}_{i\in\mathbf{N}})$, which is not ensured by this uniqueness (except of course in the particular case where the X_i's are periodic). We are now going to show indeed that any solution of (30) belongs to $\mathcal{A}^{5/2}(\{X_i\}_{i\in\mathbf{N}})$.

Theorem 3.10 *Let $\{X_i\}_{i\in\mathbf{N}}$ be an admissible set of points, and let θ be a constant. Then, the unique solution in $L^{3/2}_{\text{unif}}(\mathbf{R}^3)$ of*

$$-\Delta\phi + a^2\phi + \left(\frac{3}{5}(\phi-\theta)_+\right)^{3/2} = \sum_{i\in\mathbf{N}} \delta_{X_i}$$

belongs to $\mathcal{A}^{5/2}(\{X_i\}_{i\in\mathbf{N}})$.

Proof: We prove the uniqueness of the solution through supersolution methods: ϕ_1 and ϕ_2 being two solutions, we set $\psi = \phi_1 - \phi_2$, so that:

$$-\Delta\psi + a^2\psi = \left(\frac{3}{5}(\phi_2-\theta)_+\right)^{3/2} - \left(\frac{3}{5}(\phi_1-\theta)_+\right)^{3/2}.$$

Hence, standard elliptic regularity results show that $\psi \in L^\infty(\mathbf{R}^3)$. Define now $\Omega = \{\psi < 0\}$. On this set, we have $-\Delta\psi + a^2\psi > 0$. Using $f(x) = -\dfrac{AR}{\sinh(aR)}\dfrac{\sinh(a|x|)}{|x|}$, with $A =$

$\|\psi\|_{L^\infty(\mathbf{R}^3)}$, one easily sees that f is satisfies $-\Delta f + a^2 f = 0$, and $f \leq \psi$ on $\partial(\Omega \cap B_R)$. As a consequence, $\psi \geq f$ on $\Omega \cap B_R$, so that, letting R go to infinity, we reach a contradiction. Hence, $\Omega = \emptyset$, and $\psi \geq 0$. Since the role of ϕ_1 and ϕ_2 are symmetric, this also shows that $\psi \leq 0$, so that $\psi = 0$.

The proof of the fact that $\phi \in \mathcal{A}^{5/2}(\{X_i\}_{i\in\mathbf{N}})$ is an easy adaptation of the more involved proof of Theorem 3.15 below. $\Diamond$

Remark 3.11 *Looking closely at the above proof, it is easily seen that we have in fact shown the following: if $\theta_1 \geq \theta_2$, then, ϕ_1 and ϕ_2 being the corresponding solutions of (30), we have $\phi_1 \leq \phi_2$ a.e in $\mathbf{R}^3$, this inequality being strict if $\theta_1 \neq \theta_2$. More precisely, we have in this case:*

$$\phi_1 - \phi_2 \geq \frac{\theta_1 - \theta_2}{a^2} \mathbf{1}_{\{\phi_1 > \theta_1, \phi_2 > \theta_2\}},$$

which implies in particular $\langle \phi_1 \rangle > \langle \phi_2 \rangle$ when $\theta_1 > \theta_2$.

Corollary 3.12 *Let $\{X_i\}_{i\in\mathbf{N}}$ be an admissible set of points, and let λ be a non-negative constant. Then there exists a unique local ground state of mass λ, i.e satisfying $\langle \rho \rangle = \lambda$, and this ground state belongs to $\mathcal{A}^{5/3}(\{X_i\}_{i\in\mathbf{N}})$. It is therefore a solution of $I_{\mathrm{Y}}^{\mathrm{TF}}$ (28).*

Proof: The first point is that for any $\theta \in \mathbf{R}$, a solution ϕ of (30) exists and is unique. What we need to show here is that the function which to θ associates $\langle \left(\frac{3}{5}(\phi - \theta)_+\right)^{3/2} \rangle$ is bijective. Remark 3.11 easily shows that it is injective. We now show that it is surjective.

Equation (30) implies that

$$-\Delta\phi + a^2\phi \leq \sum_{i\in\mathbf{N}} \delta_{X_i},$$

which shows that $\phi - \theta \leq W_a^\infty - \theta$. Hence, $\langle \left((\phi - \theta)_+\right)^{3/2} \rangle \leq \langle \left((W_a^\infty - \theta)_+\right)^{3/2} \rangle$, which goes to zero as θ goes to infinity. Hence:

$$\lim_{\theta\to\infty} \langle \left((\phi - \theta)_+\right)^{3/2} \rangle = 0.$$

Consider now the case where θ goes to $-\infty$. Assuming $\theta < 0$, on the set where ϕ is positive, we have $-\Delta\phi + a^2\phi \leq \sum_{i\in\mathbf{N}} \delta_{X_i} - (-\frac{3}{5}\theta)^{3/2}$. Convoluting this inequality with W_a and then taking the average of each size, one gets $\langle \phi \rangle \leq \frac{M}{4\pi a^2} - \frac{(-\frac{3}{5}\theta)^{3/2}}{4\pi a^2}$, where M is the average of $\sum_{i\in\mathbf{N}} \delta_{X_i}$, i.e l^0 of Definition 2.3. Going back to (30), and taking the average of this equation, this shows that $\langle \left(\frac{3}{5}(\phi - \theta)_+\right)^{3/2} \rangle \geq M - \frac{M}{4\pi} + \frac{(-\frac{3}{5}\theta)^{3/2}}{4\pi}$, and thus:

$$\lim_{\theta\to-\infty} \langle \left((\phi - \theta)_+\right)^{3/2} \rangle = +\infty.$$

Since $\rho = \left(\frac{3}{5}(\phi - \theta)_+\right)^{3/2}$, and since its average is a continuous function of θ, this shows that any non-negative λ is reached by $\langle \rho \rangle$, thereby proving the existence of a local ground state of any prescribed average λ.

The fact that $\rho \in \mathcal{A}^{5/3}(\{X_i\}_{i\in\mathbf{N}})$ is ensured by the fact that $\phi \in \mathcal{A}^{5/2}(\{X_i\}_{i\in\mathbf{N}})$ and Proposition 2.11. $\Diamond$.

3.4.2 The Coulomb case

We generalize in this subsection the results of the Yukawa case to the Coulomb case. Let us start by the equivalent of Definition 3.8:

Definition 3.13 *Let $\{X_i\}_{i\in\mathbf{N}}$ be an admissible set, and let $\rho \in \mathcal{A}^{5/3}_{\mathrm{Cb}}(\{X_i\}_{i\in\mathbf{N}})$. We will say that ρ is a local ground state of the TF Coulomb model if*

$$\forall \varphi \in \mathcal{D}(\mathbf{R}^3) \quad / \quad \rho+\varphi \geq 0 \quad \text{and} \quad \int_{\mathbf{R}^3} \varphi = 0,$$
$$\int_{\mathbf{R}^3} \left((\rho+\varphi)^{5/3} - \rho^{5/3}\right) + \int_{\mathbf{R}^3} \phi\varphi + \frac{1}{2}\int_{\mathbf{R}^3} \varphi(\varphi * \frac{1}{|x|}) \geq 0, \quad (31)$$

where $*$ denotes the convolution product over $\mathbf{R}^3$, and ϕ is the effective potential, namely a solution in $L^1_{\mathrm{unif}}(\mathbf{R}^3)$ of

$$-\Delta\phi = \sum_{i\in\mathbf{N}} \delta_{X_i} - \rho.$$

Note that the hypotheses imposed on the test functions φ allow to define the difference (31). Indeed, even though ϕ is only defined up to an additive constant, since $\int \varphi = 0$, the left-hand side of (31) is not changed by the addition of such a constant. Also, as in the Yukawa case, this constraint may be seen as a local conservation of charge.

Let us now show that a density ρ is a local ground state if and only if it satisfies the equivalent of equation (30):

Proposition 3.14 *Let $\{X_i\}_{i\in\mathbf{N}}$ be an admissible set of points, and let $\rho \in \mathcal{A}^{5/3}(\{X_i\}_{i\in\mathbf{N}})$. Then ρ is a local ground state in the sense of Definition 3.13 if and only if there exists $\phi \in L^{5/2}_{\mathrm{loc}}(\mathbf{R}^3)$ such that $\phi = \frac{5}{3}\rho^{2/3}$ and*

$$-\Delta\phi + \left(\frac{3}{5}\phi\right)^{3/2} = \sum_{i\in\mathbf{N}} \delta_{X_i}. \quad (32)$$

Proof: Let $\rho \geq 0$ be a local ground state. Then, following the computations of Proposition 3.9, and replacing $W_a^\infty - W_a * \rho$ by ψ, which is any solution of $-\Delta\psi = \sum_{i\in\mathbf{N}} \delta_{X_i} - \rho$ in $L^1_{unif}(\mathbf{R}^3)$, one finds that there exists a constant θ such that

$$\frac{5}{3}\rho^{2/3} = (\psi-\theta)_+.$$

Setting $\phi = \psi - \theta$, this implies

$$\phi_+ = \frac{5}{3}\rho^{2/3}, \quad \text{and} \quad -\Delta\phi + \left(\frac{3}{5}\phi_+\right)^{3/2} = \sum_{i\in\mathbf{N}} \delta_{X_i}.$$

We are now going to show that this implies in fact that $\phi \geq 0$, thereby concluding the proof. Assume that this is not true. Then $a = \inf\phi < 0$, and there exists a sequence

$(y_n)_{n\in\mathbf{N}}$ such that $\phi(y_n) \longrightarrow a$ as n goes to infinity. We then denote by ϕ_n the function $\phi(\cdot + y_n)$, getting:

$$-\Delta\phi_n + \big(\frac{3}{5}\phi_n^+\big)^{3/2} = \sum_{i\in\mathbf{N}} \delta_{X_i - y_n} = m(\cdot + y_n) = m_n,$$

where m is the measure $\sum_{i\in\mathbf{N}} \delta_{X_i}$. Now, fixing $R > 0$, the set $K_n(R) = \{X_i - y_n\}_{i\in\mathbf{N}} \cap B_R$, is finite according to (H1) of Definition 2.3. Hence, extracting a subsequence if necessary, we may assume that each of these $X_i - y_n$ converges to some $Y_i \in B_R$ as n goes to infinity. Repeating this operation and using diagonal extraction, one easily sees that m_n locally converges to some measure m_∞, which a sum of Dirac masses of points $(Y_i)_{i\in\mathbf{N}}$ satisfying (H1) and (H2) of Definition 2.3. Next, ϕ_n being bounded in $L^{5/2}_{\mathrm{unif}}(\mathbf{R}^3)$, its Laplacian is a uniformly locally bounded measure, so that ϕ_n is bounded in $L^p_{\mathrm{unif}}(\mathbf{R}^3)$ and $\nabla\phi_n$ is bounded in $L^{p/2}_{\mathrm{unif}}(\mathbf{R}^3)$ for any $p < 3$. Extracting a subsequence again, one may assume that it converges strongly in $L^{3/2}_{\mathrm{loc}}(\mathbf{R}^3)$ to some ϕ_∞, which will be a solution of

$$-\Delta\phi_\infty + \big(\frac{3}{5}\phi_\infty^+\big)^{3/2} = \sum_{i\in\mathbf{N}} \delta_{Y_i},$$

and satisfying $\phi_\infty \geq \phi_\infty(0) = a$. Now, on the set $\Omega = \{\phi_\infty < 0\}$, to which no Y_i belongs, since at Y_i, ϕ_∞ behaves like $\frac{b_i}{|x-Y_i|}$ with $b_i > 0$ (Y_i may coincide with several Y_j's, so b_i may be greater than 1, but not less), ϕ_∞ is harmonic, implying that either ϕ_∞ is constant, or $0 \in \partial\Omega$. Both cases are excluded, so that we may conclude that $\phi \geq 0$.

We next follow exactly the computations of the proof of Proposition 3.9 to show the reverse implication. $\Diamond$

Theorem 3.15 *Let $\{X_i\}_{i\in\mathbf{N}}$ be an admissible set of points, and let ϕ be the unique positive $L^{3/2}_{\mathrm{loc}}$ solution of*

$$-\Delta\phi + \big(\frac{3}{5}\phi\big)^{3/2} = \sum_{i\in\mathbf{N}} \delta_{X_i}. \tag{33}$$

Then $\phi \in \mathcal{A}^{5/2}(\{X_i\}_{i\in\mathbf{N}})$. Moreover, setting $\rho = \big(\frac{3}{5}\phi\big)^{3/2}$, ρ is a local ground state in the sense of Definition 3.13. It is therefore a minimizer of $I^{\mathrm{TF}}_{\mathrm{Cb}}$ defined in (29). Conversely, for any local ground state ρ, $\phi = \frac{5}{3}\rho^{2/3}$ is a solution of (33).

Proof: The fact that the solution ϕ is unique is shown in [4]. We are now going to approximate this ϕ by a sequence belonging to $\mathcal{A}^{5/2}(\{X_i\}_{i\in\mathbf{N}})$, and show that this convergence occurs in $L^{5/2}_{\mathrm{unif}}(\mathbf{R}^3)$. The first step is to prove that, if one replaces the measure $\sum\delta_{X_i}$ by a smooth function $m = \sum m_0(\cdot - X_i)$, where m_0 is a non-negative function in $\mathcal{D}(\mathbf{R}^3)$, then $\phi \in \mathcal{A}^\infty(\{X_i\}_{i\in\mathbf{N}})$. Considering ϕ the corresponding solution, that is,

$$-\Delta\phi + \big(\frac{3}{5}\phi\big)^{3/2} = m,$$

then $\phi \in L^\infty(\mathbf{R}^3)$, as shown in [4]. Let $M > 0$ be a constant such that

$$M \geq \frac{3}{2}\left(\frac{3}{5}\right)^{3/2} \sqrt{\|\phi\|_{L^\infty(\mathbf{R}^3)}}. \tag{34}$$

We now define the sequence $(\phi_n)_{n\in\mathbf{N}}$ by:

$$\begin{cases} \phi_0 = 0, \\ -\Delta\phi_{n+1} + M\phi_{n+1} = m - \left(\frac{3}{5}\phi_n\right)^{3/2} + M\phi_n, \quad \phi_{n+1} \in L^1_{\text{unif}}(\mathbf{R}^3). \end{cases}$$

For any $n \in \mathbf{N}$, if $\phi_n \in \mathcal{A}^\infty(\{X_i\}_{i\in\mathbf{N}})$, then $m - \left(\frac{3}{5}\phi_n\right)^{3/2} + M\phi_n \in \mathcal{A}^\infty(\{X_i\}_{i\in\mathbf{N}})$, so that $\phi_{n+1} \in \mathcal{A}^\infty(\{X_i\}_{i\in\mathbf{N}})$, thanks to Proposition 2.14, since it is the convolution of the Yukawa potential $W_{\sqrt{M}}$ with $m - \left(\frac{3}{5}\phi_n\right)^{3/2} + M\phi_n$. We are now going to show by induction that for any $n \in \mathbf{N}$, we have:

$$0 \leq \phi_n \leq \phi, \tag{35}$$

$$\phi_n \leq \phi_{n+1}. \tag{36}$$

The first point is clearly true for $n = 0$, and computing ϕ_1, one finds $\phi_1 = m * W_{\sqrt{M}}$, where $W_{\sqrt{M}}$ is the Yukawa potential of parameter $\sqrt{M}$,which is positive, so that $\phi_1 \geq 0$, implying (36) for $n = 0$. Next, we point out that on the interval $[0, \|\phi\|_{L^\infty(\mathbf{R}^3)}]$, the function $t \mapsto Mt - \left(\frac{3}{5}t\right)^{3/2}$ is increasing, thanks to (34). Hence, assuming that (35) holds, one gets $0 \leq -\Delta\phi_{n+1} + M\phi_{n+1} \leq m - \left(\frac{3}{5}\phi\right)^{3/2} + M\phi = -\Delta\phi + M\phi$. Convoluting this equation with $W_{\sqrt{M}}$, this implies $0 \leq \phi_{n+1} \leq \phi$, concluding the proof of (35). Next, the proof of (36) follows exactly the same pattern: computing $-\Delta(\phi_{n+2} - \phi_{n+1}) + M(\phi_{n+2} - \phi_{n+1})$, one finds that assuming $\phi_{n+1} \geq \phi_n$, this quantity is non-negative, thereby showing (36).

This proves that $(\phi_n)_{n\in\mathbf{N}}$ converges almost everywhere, to some limit ψ. But passing to the limit in the relation between ϕ_n and ϕ_{n+1}, one shows that $\psi = \phi$. We next show that the limit is in fact uniform: we have, for $n \geq 1$:

$$-\Delta(\phi - \phi_{n+1}) + M(\phi - \phi_{n+1}) = M(\phi - \phi_n) - \left(\frac{3}{5}\right)^{3/2}(\phi^{3/2} - \phi_n^{3/2}),$$

and $\phi^{3/2} - \phi_n^{3/2} \geq \frac{3}{2}\phi_n^{1/2}(\phi - \phi_n) \geq \frac{3}{2}\phi_1^{1/2}(\phi - \phi_n) \geq \alpha(\phi - \phi_n)$, where $\alpha = \inf\phi_1 > 0$, a property which follows from the definition of ϕ_1 and the fact that $\{X_i\}_{i\in\mathbf{N}}$ is admissible. Thus,

$$-\Delta(\phi - \phi_{n+1}) + M(\phi - \phi_{n+1}) \leq (M - \beta)(\phi - \phi_n),$$

where $\beta > 0$. Convoluting with $W_{\sqrt{M}}$ and applying Young's inequality, this implies, using the fact that $\int W_{\sqrt{M}} = \frac{1}{M}$,

$$\|\phi - \phi_{n+1}\|_{L^\infty(\mathbf{R}^3)} \leq \frac{M - \beta}{M}\|\phi - \phi_n\|_{L^\infty(\mathbf{R}^3)}.$$

This clearly shows that the convergence occurs in $L^\infty(\mathbf{R}^3)$, and therefore that ϕ belongs to the space $\mathcal{A}^\infty(\{X_i\}_{i\in\mathbf{N}})$.

We next show that as m_0 converges to δ_0 in the sense of measures, the corresponding ϕ's converge to the solution of $-\Delta\phi + \left(\frac{3}{5}\phi\right)^{3/2} = \sum \delta_{X_i}$. We thus consider a sequence m_0^k of smooth functions converging to δ_0 (for instance $m_0^k(x) = k^3 m_0(kx)$, with $m_0 \geq 0$, belonging to $\mathcal{D}(\mathbf{R}^3)$ and of total mass 1), and denote by ϕ_k the corresponding sequence, i.e the solutions of

$$-\Delta\phi_k + \left(\frac{3}{5}\phi_k\right)^{3/2} = m^k := \sum_{i\in\mathbf{N}} m_0^k(\cdot - X_i).$$

The first point is to show the desired convergence in the linear case: let W^∞ and W_k^∞ be the corresponding Yukawa potential, i.e the solutions of

$$\begin{cases} -\Delta W^\infty + W^\infty = \sum_{i\in\mathbf{N}} \delta_{X_i}, \\ -\Delta W_k^\infty + W_k^\infty = m^k. \end{cases}$$

Then, since in fact $W_k^\infty = m_0^k * W^\infty$, standard functional analysis results show that W_k^∞ converges to W^∞ in $L^p_{\text{unif}}(\mathbf{R}^3)$ for any $p < 3$ as k goes to infinity. Since these functions carry the singularity of ϕ_k, we are now going to use their convergence in order to show that ϕ_k does converge: setting $\psi_k = \phi_k - W_k^\infty$ and $\psi = \phi - W^\infty$, we have:

$$\begin{cases} -\Delta\psi_k + \left(\frac{3}{5}(\psi_k + W_k^\infty)\right)^{3/2} = W_k^\infty, \\ -\Delta\psi + \left(\frac{3}{5}(\psi + W^\infty)\right)^{3/2} = W^\infty. \end{cases}$$

We next substract these two equations, multiply by $\xi^2(\psi - \psi_k)$, where $\xi \in \mathcal{D}(\mathbf{R}^3)$, getting

$$\int_{\mathbf{R}^3} |\nabla\big((\psi - \psi_k)\xi\big)|^2 + \left(\frac{3}{5}\right)^{3/2} \int_{\mathbf{R}^3} \big((\psi + W^\infty)^{3/2} - (\psi_k + W_k^\infty)^{3/2}\big)\xi^2(\psi - \psi_k)$$
$$= \int_{\mathbf{R}^3} (W^\infty - W_k^\infty)(\psi - \psi_k)\xi^2 + \int_{\mathbf{R}^3} (\psi - \psi_k)^2 |\nabla\xi|^2.$$

We deal with the nonlinear term through the following inequality:

$$\big((\psi + W^\infty)^{3/2} - (\psi_k + W_k^\infty)^{3/2}\big)(\psi - \psi_k) \geq a(\psi - \psi_k)^2 - b\big(W^\infty\big)^{3/2} |W^\infty - W_k^\infty|, \quad (37)$$

for some constants a and b independent of k. This inequality is easily shown using the following one

$$\big((\psi + W^\infty)^{3/2} - (\psi_k + W_k^\infty)^{3/2}\big)(\psi + W^\infty - \psi_k - W_k^\infty) \geq \alpha(\psi + W^\infty - \psi_k - W_k^\infty)^2,$$

for some constant $\alpha > 0$ independent of k. This latter inequality is a direct consequence of the convexity of the function $t \mapsto t^{3/2}$ and the fact that, thanks to Harnack inequality [9], $\psi + W^\infty$ as well as $\psi_k + W_k^\infty$ are bounded from below by a positive constant not depending on k. Using (37), we thus have:

$$\frac{a}{2} \int_{\mathbf{R}^3} (\psi - \psi_k)\xi^2 \leq C \int_{\mathbf{R}^3} \big(W^\infty\big)^{3/2} \xi^2 |W^\infty - W_k^\infty| + \int_{\mathbf{R}^3} (\psi - \psi_k)^2 |\nabla\xi|^2.$$

We now choose $\xi(x) = \exp(-\sqrt{\frac{a}{4}}|x - x_0|)$, so that $|\nabla\xi|^2 = \frac{a}{4}\xi^2$, hence

$$\frac{a}{4}\exp(-\sqrt{\frac{a}{4}})\int_{B+x_0}(\psi-\psi_k)^2 \leq \frac{a}{4}\int_{\mathbf{R}^3}(\psi-\psi_k)^2\xi^2 \leq C\int_{\mathbf{R}^3}\left(W^\infty\right)^{3/2}\xi^2|W^\infty - W_k^\infty|.$$

Next, using the convergence result we have on W_k^∞, one easily shows that the right-hand side goes to zero as k goes to infinity, uniformly with respect to x_0. This proves that ψ_k converges to ψ as k goes to infinity, in $L^2_{\rm unif}(\mathbf{R}^3)$. Consequently, $\psi \in \mathcal{A}^2(\{X_i\}_{i\in\mathbf{N}})$, so that $\phi \in \mathcal{A}^2(\{X_i\}_{i\in\mathbf{N}})$. Next, we point out that in fact $\phi \in L^{5/2}_{\rm unif}(\mathbf{R}^3)$, so that $\phi \in \mathcal{A}^{5/2}(\{X_i\}_{i\in\mathbf{N}})$. $\Diamond$

Remark 3.16 *The general scheme developed in the preceding proof is clearly adaptable to the Yukawa case, therefore proving Theorem 3.10. The point is that the function* $t \mapsto Mt - \left(\frac{3}{5}t\right)^{3/2} - a^2t$ *is non-decreasing on a compact subset of* $\mathbf{R}^+$ *for* M *large enough.*

3.5 Thermodynamic limit

We give in this Section a few remarks on the notion of thermodynamic limit, and on the link between this scheme and the present work.

The thermodynamic limit is a way of deriving a solid-state model from a molecular one through a limit process. We refer to [5] for a detailed presentation of this topic. Roughly speaking, the thermodynamic limit problem is the following: wanting to derive a model with an infinite number of atoms, one approximates it by a finite system, then lets the number of particles go to infinity in a suitable way and passes to the limit. Here, we have an infinite number of nuclei denoted by $\{X_i\}_{i\in\mathbf{N}}$, and we will approximate it by $\Lambda_R = \{X_i\}_{i\in\mathbf{N}} \cap B_R$. In the Thomas-Fermi setting, we thus need to study the following problem:

$$I_R^{\rm TF} = \inf\left\{E^{\rm TF}(\rho,\Lambda_R), \quad \rho \geq 0, \quad \int_{\mathbf{R}^3}\rho = |\Lambda_R|\right\},$$

where $|\Lambda_R|$ denotes the cardinal of the set Λ_R, and where $E^{\rm TF}(\rho,\Lambda_R)$ is the Thomas-Fermi energy (1), or the corresponding one in the Yukawa case. Denoting by ρ_R the unique minimizer of the above problem, we address the following questions:

(L1) Does the energy per unit volume $\frac{I_R^{\rm TF}}{|B_R|}$ *converge as* R *goes to infinity?*

(L2) Does the density ρ_R *converge to a limit* ρ_∞ *as* R *goes to infinity?*

(L3) Does the limit ρ_∞ *share the symmetries of the set of nuclei* $\{X_i\}_{i\in\mathbf{N}}$*, in other words, do we have* $\rho_\infty \in \mathcal{A}^p(\{X_i\}_{i\in\mathbf{N}})$ *for some* $p \geq 1$*?*

In the special case of a periodic set $\{X_i\}_{i\in\mathbf{N}}$, these questions are exactly those addressed in [5]. Now, the methods developed to deal with such a problem are the following:

- First, derive bounds on the density ρ_R;
- next, using these bounds, pass to the limit in the Euler-Lagrange equation of $I_R^{\rm TF}$;

- show a uniqueness theorem on the limit equation, and show that the corresponding unique solution belongs to the desired space (i.e, here, $\mathcal{A}^p(\{X_i\}_{i\in\mathbf{N}})$.

Now, looking at the proofs given in [5], it is clear that the first point makes no use of the periodicity, but is rather based on hypotheses (H1) and (H2) of Definition 2.3. They are therefore applicable to the present case. The next step is also clearly straightforward, and the last step has been dealt with in Subsections 3.3 and 3.4, answering positively to the questions (L1), (L2), (L3).

3.6 Thomas-Fermi-von Weizsäcker theory: a non-local model

We now turn to the case of Thomas-Fermi-von Weizsäcker (TFW) theory, which consists in adding to the kinetic energy term $\int \rho^{5/3}$ the term $\int |\nabla\sqrt{\rho}|^2$, so that formula (1) translates into:

$$\begin{aligned} E^{TFW}(\rho,\{X_i\}) &= \int_{\mathbf{R}^3} |\nabla\sqrt{\rho}|^2 + \int_{\mathbf{R}^3} \rho^{5/3} + \frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3} \frac{\rho(x)\rho(y)}{4\pi|x-y|}dxdy \\ &\quad - \sum_{i=1}^{N} \int_{\mathbf{R}^3} \frac{\rho(x)dx}{4\pi|x-X_i|} + \frac{1}{2}\sum_{i\neq j} \frac{1}{4\pi|X_i-X_j|}, \end{aligned} \tag{38}$$

and similarly for subsequent formulas. All the preceding results apply to this case, including thermodynamic limit properties (see [5] for the periodic case), except for Theorem 3.15. Indeed, the Euler-Lagrange equation may not be, as was the case in the TF model, recast into a local PDE. It becomes a nonlocal one, reading (here, $u=\sqrt{\rho}$):

$$-\Delta u + \frac{5}{3}u^{7/3} - \Big(\sum \frac{1}{|x-X_j|} - u^2 * \frac{1}{|x|} + \theta\Big)u = 0,$$

whenever these terms (in particular the sum and the convolution product) make sense. One may also write it as a system of PDEs:

$$\begin{cases} -\Delta u + \frac{5}{3}u^{7/3} - \phi u = 0, \\ -\Delta\phi = m - u^2, \\ u \geq 0, \end{cases} \tag{39}$$

where m denotes the measure defining the nuclei, namely $\sum \delta_{X_i}$, and ϕ is the effective potential of the system. Since, as pointed out above, up to questions which have been already dealt with in [5], the thermodynamic limit problem may be reduced to the question of uniqueness of the solution of (39) and of its belonging to $\mathcal{A}^p(\{X_i\}_{i\in\mathbf{N}})$ for some $p\geq 1$, we give here only the proof of this fact. Note that the uniqueness for system (39) has been shown, under hypotheses (H1) and (H2), in [5].

Aiming at showing that if $\{X_i\}_{i\in\mathbf{N}}$ is admissible, then the unique solution (u,ϕ) of (39) belongs to $\mathcal{A}^\infty(\{X_i\}_{i\in\mathbf{N}}) \times \mathcal{A}^1(\{X_i\}_{i\in\mathbf{N}})$, we start by replacing the Coulomb potential by the Yukawa potential, yielding

$$-\Delta u + \frac{5}{3}u^{7/3} - Vu + (W * u^2)u = 0,$$

where $V(x) = \theta - \sum W(x - X_i)$, and W is the Yukawa potential $\frac{e^{-a|x|}}{|x|}$, with $a > 0$; We now introduce a coupling parameter λ in order to deal with the nonlocal term, studying the set of equations:

$$-\Delta u + \frac{5}{3}u^{7/3} - Vu + \lambda(W * u^2)u = 0. \tag{40}$$

We are going to treat these equations through an implicit function theorem approach. The first point is, when $\lambda = 0$, the technics used in the proof of Theorem 3.15 apply (for now on, we drop the irrelevant factor $\frac{5}{3}$ in the equations):

Proposition 3.17 (TFW theory: the non-interacting case) *Let $\{X_i\}_{i\in\mathbf{N}}$ be an admissible set of points in $\mathbf{R}^3$. Consider $V \in \mathcal{A}^p(\{X_i\}_{i\in\mathbf{N}})$ for some $p > \frac{21}{8}$, and satisfying the following*

$$\exists R_0 > 0, \quad \forall x \in \mathbf{R}^3, \quad \lambda_1(-\Delta - V, B_{R_0} + x) < 0.$$

Then, any solution of the problem

$$\begin{cases} -\Delta u + u^{7/3} - Vu = 0, \\ u \geq 0, \quad u \neq 0. \end{cases} \tag{41}$$

belongs to $\mathcal{A}^\infty(\{X_i\}_{i\in\mathbf{N}})$. Moreover, such a solution is unique and is bounded from below by some positive constant.

Here, $\lambda_1(H, \Omega)$ denotes the first eigenvalue of the operator H on Ω with homogeneous Dirichlet boundary conditions.

Proof: The question of uniqueness is easily dealt with by the same arguments of [5] (Lemma 4.17).

The fact that any solution of (41) is bounded from below by a positive constant is an easy adaptation of the proof of Lemma 4.17 of [5].

We now focus on the proof of the fact that $u \in \mathcal{A}^\infty$. We will give here only a proof in the regular case, that is, when we assume that $V \in \mathcal{A}^\infty(\{X_i\}_{i\in\mathbf{N}})$, the generalization to the non-regular case being only a technical matter that we skip here. In such a case, we use the same algorithm as the one used in the proof of Theorem 3.15, except that here, 0 is a fixed point of the algorithm, so that we will need to start from a supersolution of the equation and then decrease towards u. The constant $A = \|V^+\|_{L^\infty}^{3/4}$ is easily shown to satisfy these conditions. Next, we denote by M the constant

$$M = \|V^-\|_{L^\infty(\mathbf{R}^3)} + \frac{7}{3}A^{4/3},$$

which ensures that the function $t \mapsto Mt + Vt - t^{7/3}$ is non decreasing with respect to t on $[0, A]$, a.e in x. We define the following sequence of functions

$$\begin{cases} u_0 = A, \\ -\Delta u_{n+1} + Mu_{n+1} = Mu_n - u_n^{7/3} + Vu_n. \end{cases}$$

It is then easy to show, using the same arguments as in the proof of Theorem 3.15, that $\forall x \in \mathbf{R}^3, \quad u(x) \leq u_{n+1}(x) \leq u_n(x) \leq A$. It thus converges point-wise. In order to show that the convergence is in fact uniform, we set $v_n = u_n - u \geq 0$, we have, using the convexity of $t \mapsto t^{7/3}$ on $\mathbf{R}^+$, $(-\Delta + M)v_{n+1} = (M+V)v_n - (u_n^{7/3} - u^{7/3}) \leq (M+V)v_n - \frac{7}{3}u^{4/3}v_n$. Hence,

$$\frac{4}{3}u^{4/3}v_n + (-\Delta + M)v_{n+1} + (-\Delta + u^{4/3} - V)v_n \leq (-\Delta + M)v_n. \tag{42}$$

Now, $(-\Delta + M)v_{n+1} = (-\Delta + M)u_{n+1} - (-\Delta + M)u = Mu_n + Vu_n - u_n^{7/3} - (Mu + Vu - u^{7/3}) \geq 0$, so that $\big((-\Delta + M)v_{n+1}\big)v_n \geq \big((-\Delta + M)v_n\big)v_n$. Hence, multiplying (42) by $\varphi^2 v_n$, where φ is a smooth compactly-supported function, and integrating over $\mathbf{R}^3$, we have

$$\frac{4}{3}\alpha \int \varphi^2 v_n^2 + \int \big((-\Delta + M)v_{n+1}\big)\varphi^2 v_{n+1} + \int \big((-\Delta + u^{4/3} - V)v_n\big)\varphi^2 v_n \leq \int \big((-\Delta + M)v_n\big)\varphi^2 v_n, \tag{43}$$

where $\alpha = \inf u^{4/3} > 0$. We next remark that since $u \geq 0$ and $-\Delta u + u^{7/3} - Vu = 0$, $\lambda_1(-\Delta + u^{4/3} - V) \geq 0$, so that, integrating by parts the third term of (43), we find

$$\int (\frac{4}{3}\alpha\varphi^2 - |\nabla\varphi|^2)v_n^2 \leq \int \big((-\Delta + M)v_n\big)\varphi^2 v_n - \int \big((-\Delta + M)v_{n+1}\big)\varphi^2 v_{n+1}.$$

Summing these inequalities for $0 \leq n \leq N$ we deduce

$$\begin{aligned} \sum_{n=0}^{N} \int (\frac{4}{3}\alpha\varphi^2 - |\nabla\varphi|^2)v_n^2 &\leq \int (-\Delta + M)v_0\varphi^2 v_0 - \int (-\Delta + M)v_{N+1}\varphi^2 v_{N+1} \\ &\leq \int (-\Delta + M)v_0\varphi^2 v_0. \end{aligned}$$

We now point out that this being valid for any $\varphi \in \mathcal{D}(\mathbf{R}^3)$, we can take $\varphi(x) = e^{-\sqrt{\frac{2\alpha}{3}}|x|}$, so that $|\nabla\varphi|^2 = \frac{2\alpha}{3}\varphi^2$, and thus, using the monotonicity of u_n (i.e of v_n), we have

$$\frac{2\alpha}{3}e^{-\sqrt{\frac{2\alpha}{3}}}(n+1)\int_{B_1} v_n^2 \leq \int |\nabla(\varphi v_0)|^2 + M\varphi^2 v_0^2.$$

This shows that $\|v_n\|_{L^2(B_1)} \leq \frac{C}{\sqrt{n}}$, for some constant C depending only on u and V. Now, the same argument may be repeated with $\varphi(x - x_0)$ instead of $\varphi(x)$ with no change, so that we have:

$$\|v_n\|_{L^2_{\text{unif}}(\mathbf{R}^3)} \leq \frac{C}{\sqrt{n}},$$

which shows the convergence in $L^2_{\text{unif}}(\mathbf{R}^3)$. We then show that it is in fact a convergence in L^∞ by pointing out that the scheme we use is regularizing. $\Diamond$

Remark 3.18 *Note that the condition imposed on the first eigenvalue of $-\Delta+V$ is in fact a necessary condition for the existence of a solution of (41) isolated from 0, i.e bounded from below by some positive constant. Moreover, such a condition is easily shown to be satisfied for instance by $V = m * W_a - \theta$, where $m = \sum \delta_{X_i}$ and W_a is the Yukawa potential of parameter $a > 0$, for $\theta \in \mathbf{R}$ small enough.*

We then treat the case $\lambda > 0$:

Proposition 3.19 *Let $\{X_i\}_{i\in\mathbf{N}}$ be an admissible set of points in $\mathbf{R}^3$, and let $\lambda \geq 0$. Consider $V \in \mathcal{A}^p(\{X_i\}_{i\in\mathbf{N}})$ for some $p > \frac{21}{8}$, such that*

$$\exists R_0 > 0, \quad \forall x \in \mathbf{R}^3, \quad \lambda_1(-\Delta - V, B_{R_0} + x) < 0.$$

Then, any solution of the problem

$$\left\{ \begin{array}{l} -\Delta u + u^{7/3} - Vu + \lambda(W * u^2)u = 0, \\ u \geq 0, \quad u \neq 0. \end{array} \right. \tag{44}$$

belongs to $\mathcal{A}^\infty(\{X_i\}_{i\in\mathbf{N}})$. In addition, this solution is unique and bounded away from 0.

Proof: The bound from below and the uniqueness are ensured by the results and technics of [5]. The case $\lambda = 0$ is contained in Proposition 3.17. We therefore concentrate on the case $\lambda > 0$. Moreover, and as in the proof of Proposition 3.17, we may very well assume that V is, say, in $\mathcal{A}^\infty$, the generalization to less regular potentials being easy.

We consider the function $\mathcal{F}$ from $H^2_{\text{unif}} \times \mathbf{R}$ to L^2_{unif}, defined by

$$\mathcal{F}(u, \lambda) = -\Delta u + |u|^{4/3}u - Vu + \lambda(W * u^2)u.$$

Remark that if $u \in \mathcal{A}^{2,2}(\{X_i\}_{i\in\mathbf{N}})$, then $\mathcal{F}(u, \lambda) \in \mathcal{A}^2(\{X_i\}_{i\in\mathbf{N}})$. Next, consider the first derivative of $\mathcal{F}$, which is a bounded operator from H^2_{unif} to L^2_{unif}:

$$Gh := \frac{\partial \mathcal{F}}{\partial u}(u, \lambda)h = -\Delta h + \frac{7}{3}|u|^{1/3}uh - Vu + \lambda(W * u^2)h + 2\lambda(W * (uh))u.$$

In [5] (section 4.3.4), this operator is shown to be bijective from H^2_{unif} to L^2_{unif} for any (u, λ) satisfying (44) such that u is bounded away from 0 . We now claim it is bijective from $\mathcal{A}^{2,2}$ to $\mathcal{A}^2$. We only need to show that it is surjective: given $\varphi \in \mathcal{A}^2$, we need to show that $G^{-1}\varphi \in \mathcal{A}^{2,2}$. For this purpose, define ψ the solution to

$$\left\{ \begin{array}{l} \frac{\partial \psi}{\partial t} + G\psi = \varphi, \\ \psi(t = 0, \cdot) = 0. \end{array} \right.$$

We claim that:

$$\forall t \geq 0, \quad \psi(t, \cdot) \in \mathcal{A}^2, \tag{45}$$

and

$$\lim_{t\to+\infty} \psi = G^{-1}\varphi \quad \text{in} \quad L^2_{\text{unif}}(\mathbf{R}^3). \tag{46}$$

In order to show (45), we write $G = G_1 + G_2 + G_3$, with $G_1 = -\Delta$, $G_2 = \frac{7}{3}|u|^{1/3}u - V + \lambda W * u^2$, and $G_3 h = 2\lambda(W*(uh))u$, and apply Trotter's formula [8]. It is indeed easily seen that these operators satisfy the hypotheses of [8, chap XVII, Part. B, 6, Corollary 4], so that we have

$$\lim_{N\to\infty}\Big(e^{-\frac{t}{N}G_1}e^{-\frac{t}{N}G_2}e^{-\frac{t}{N}G_3}\Big)^N\varphi = e^{-tG}\varphi, \quad \text{in} \quad L^2_{\text{unif}}(\mathbf{R}^3).$$

Now, $e^{-tG_1}\varphi$ is the solution of the heat equation with initial condition φ, that is, a convolution of φ with the heat kernel. Consequently, $e^{-tG_1}\varphi \in \mathcal{A}^{2,2}$ for any $t \geq 0$. Next, $e^{-tG_2} = e^{-t(\frac{7}{3}|u|^{1/3}u - V + \lambda W * u^2)}$, so that $e^{-tG_2}\varphi \in \mathcal{A}^2$. Finally, G_3 is a bounded operator mapping $\mathcal{A}^2$ onto $\mathcal{A}^2$, so that e^{-tG_3} may be defined by its series expansion $\sum \frac{(-tG_3)^n}{n!}$, which ensures that $e^{-tG_3}\varphi \in \mathcal{A}^2$. Consequently, we have:

$$\forall t \geq 0, \quad e^{-tG}\varphi \in \mathcal{A}^2(\{X_i\}_{i\in\mathbf{N}}).$$

Hence, pointing out that $\psi = \displaystyle\int_0^t e^{-sG}\varphi ds$, this proves (45)

We next show (46). This amounts to prove that $G^{-1}\varphi = \int_0^\infty e^{-sG}\varphi$, which means exactly that $\lim\limits_{t\to\infty} e^{-tG}\varphi = 0$. Although this seems to be a well-known fact, we provide a proof of it for the convenience of the reader. Denote by $\tilde{\psi}$ the function $\tilde{\psi} = \psi - G^{-1}\phi$. Then, we have

$$\partial_t\tilde{\psi} = -G\tilde{\psi}.$$

Fixing $\xi \in \mathcal{D}(\mathbf{R}^3)$, multiplying this equation by $\xi^2\tilde{\psi}$ and integrating over $\mathbf{R}^3$, we have:

$$\begin{aligned}
\frac{1}{2}\frac{d}{dt}\Big(\int_{\mathbf{R}^3}\tilde{\psi}^2\xi^2\Big) = \int_{\mathbf{R}^3}\partial_t\tilde{\psi}\xi^2 &= \int_{\mathbf{R}^3}\Delta\tilde{\psi}\tilde{\psi}\xi^2 - \int_{\mathbf{R}^3}(\frac{7}{3}|u|^{1/3}u - V + \lambda W*u^2)\tilde{\psi}^2\xi^2 \\
&\quad -2\lambda\int_{\mathbf{R}^3}\Big(W*(u\tilde{\psi})\Big)u\tilde{\psi}\xi^2. \\
&= -\Big(\int_{\mathbf{R}^3}|\nabla(\tilde{\psi}\xi)|^2 + (u^{4/3} - V + \lambda W*u^2)\tilde{\psi}^2\xi^2\Big) \\
&\quad -\frac{4}{3}\int_{\mathbf{R}^3}u^{4/3}\tilde{\psi}^2\xi^2 + \int_{\mathbf{R}^3}\tilde{\psi}|\nabla\xi|^2 \\
&\quad -2\lambda\int_{\mathbf{R}^3}\Big(W*(u\tilde{\psi})\Big)u\tilde{\psi}^2\xi^2.
\end{aligned}$$

Now, the first eigenvalue of the operator $-\Delta + u^{4/3} - V + \lambda\big(W*u^2\big)$ with homogeneous Dirichlet boundary condition on Ω is non-negative, on any domain Ω, because u is a positive solution of (44). Using in addition the fact that $u \geq \nu > 0$, we deduce that there exists $\alpha > 0$ such that

$$\frac{1}{2}\frac{d}{dt}\Big(\int_{\mathbf{R}^3}\tilde{\psi}^2\xi^2\Big) \leq -\alpha\int_{\mathbf{R}^3}\tilde{\psi}^2\xi^2 + \int_{\mathbf{R}^3}\tilde{\psi}^2|\nabla\xi|^2 - 2\lambda\int_{\mathbf{R}^3}\Big(W*(u\tilde{\psi})\Big)u\tilde{\psi}\xi^2.$$

Next, define $v = W*(u\tilde{\psi})$: the last term is equal to

$$-2\lambda\int_{\mathbf{R}^3}v\big((-\Delta + a^2)v\big)\xi^2 = -2\lambda a^2\int_{\mathbf{R}^3}v^2\xi^2 - 2\lambda\int_{\mathbf{R}^3}|\nabla(v\xi)|^2 + 2\lambda\int_{\mathbf{R}^3}v^2|\nabla\xi|^2,$$

so that

$$\frac{1}{2}\frac{d}{dt}\left(\int_{\mathbf{R}^3}\tilde{\psi}^2\xi^2\right) \leq -\alpha\int_{\mathbf{R}^3}\tilde{\psi}^2\xi^2 + \int_{\mathbf{R}^3}\tilde{\psi}^2|\nabla\xi|^2 - 2\lambda a^2\int_{\mathbf{R}^3}v^2\xi^2 + 2\lambda\int_{\mathbf{R}^3}v^2|\nabla\xi|^2.$$

We now take for ξ a sequence converging to $e^{-\beta|x|}$, with $0 < \beta^2 \leq \min(\frac{\alpha}{2}, a^2)$, so that

$$\frac{1}{2}\frac{d}{dt}\left(\int_{\mathbf{R}^3}\tilde{\psi}^2\xi^2\right) \leq -\frac{\alpha}{2}\int_{\mathbf{R}^3}\tilde{\psi}^2\xi^2,$$

which proves that $\|\tilde{\psi}\|_{L^2(B_1)} \leq Ce^{-\alpha t}$ converges to 0. Pointing out that the argument may be repeated with $e^{-\beta|x-x_0|}$, involving exactly the same constants, this proves (46).

Consequently, $G^{-1}\varphi \in \mathcal{A}^2$. Since in addition we know that $G^{-1}\varphi \in H^2_{\rm unif}$, we have $G^{-1}\varphi \in \mathcal{A}^{2,2}$, according to Proposition 2.16.

We are now in position to complete the proof of Proposition 3.19: at any point (u,λ) satisfying (44) and $u \in \mathcal{A}^{2,2}$, we may apply the implicit function theorem, which implies that on a neighborhood of λ, any solution of (44) belongs to $\mathcal{A}^{2,2}$. A standard connexity argument allows one to conclude. $\Diamond$

We now finally turn to the Coulomb case:

Theorem 3.20 (TFW theory: the interacting case) *Let $\{X_i\}_{i\in\mathbf{N}}$ be an admissible set, and let (u,ϕ) be the unique solution in $L^\infty(\mathbf{R}^3)\times L^1_{\rm unif}(\mathbf{R}^3)$ of the system*

$$\left\{\begin{array}{l} -\Delta u + u^{7/3} - \phi u = 0, \\ -\Delta\phi = \displaystyle\sum_{i\in\mathbf{N}}\delta_{X_i} - u^2, \\ u \geq 0. \end{array}\right. \tag{47}$$

Then, $u \in \mathcal{A}^{2,2}(\{X_i\}_{i\in\mathbf{N}})$, and $\phi \in \mathcal{A}^p(\{X_i\}_{i\in\mathbf{N}})$ for any $p < 3$.

Proof: Let us consider for $a > 0$ and $\theta > 0$, $V_{a,\theta} = \displaystyle\sum_{i\in\mathbf{N}} W(x-X_i) - \theta$ where $W(x) = \frac{e^{-a|x|}}{|x|}$. There exists some bounds $a_0 > 0$ and $\theta_0 > 0$ such that for any $0 \leq a \leq a_0$ and $0 \leq \theta \leq \theta_0$, we have $\lambda_1(-\Delta - V_{a,\theta}, B_R + x) < 0$ for any $x \in \mathbf{R}^3$. For any such (a,θ), the positive solution u of

$$-\Delta u + u^{7/3} - Vu + (W * u^2)u = 0,$$

belongs to $\mathcal{A}^{2,2}$ by virtue of Proposition 3.19. The multiplier $\theta = \theta_0$ being fixed, we now let a go to zero: u is also a solution of

$$\left\{\begin{array}{l} -\Delta u + u^{7/3} - \phi u = 0, \\ -\Delta\phi + a^2\phi = \displaystyle\sum_{i\in\mathbf{N}}\delta_{X_i} - u^2 + a^2\theta. \end{array}\right.$$

Here, standard elliptic regularity results allow to show (see [5] for the details) that

$$\|u\|_{H^2_{\rm unif}(\mathbf{R}^3)} + \|\phi\|_{L^p_{\rm unif}(\mathbf{R}^3)} \leq C, \quad \forall p < 3,$$

for some constant C independent of a. Therefore, we may assume convergence of u in H^1_{loc}, and weak convergence of ϕ in L^2_{loc}. Passing to the limit in the above system, we see that the limit is a solution of (47). What we need to show then is that the convergence is in fact uniform. In order to do so, we argue by contradiction, exactly as in the proof of Proposition 3.14. $\Diamond$

Caractérisation des fonctions de $\mathbf{R}^3$ à potentiel newtonien borné

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Résumé. Nous présentons dans cette Note une caractérisation des fonctions f définies sur $\mathbf{R}^3$ (ou plus généralement sur $\mathbf{R}^N$) pour lesquelles il existe une fonction $\Phi \in L^\infty$ telle que $-\Delta\Phi = f$.

Characterization of functions on $\mathbf{R}^3$ with bounded newtonian potential

Abstract. *We present in this Note a necessary and sufficient condition for a function f defined on $\mathbf{R}^3$ (or more generally on $\mathbf{R}^N$) to have a bounded Newtonian potential, i.e for the existence of $\Phi \in L^\infty$ such that $-\Delta\Phi = f$.*

Abridged English Version - The aim of this work is to derive a characterization of the functions f defined on $\mathbf{R}^N$ for which there exists some $\Phi \in L^\infty(\mathbf{R}^N)$ such that $-\Delta\Phi = f$. Our interest in this question stems from our work on the definition of the ground state energy for systems composed of infinitely many particles when the positions of these particles are not necessarily periodic, nor almost periodic [1]. A distribution f of charges (respectively of masses, in the language of gravitation) being given, we would like to rigorously define the coulombian (resp. newtonian) potential Φ (resp. $-\Phi$) that it creates. For this purpose, we need to impose some condition on f (that will then be fulfilled using some renormalization procedure). Indeed, when f is periodic, the necessary and sufficient condition for the potential Φ to exist and be bounded is simple, and only states that the mean value of f over its periodic cell vanishes. On the other hand, when f exhibits no periodic feature, the condition is less simple. The purpose of this work is to state and prove such a necessary and sufficient condition. It is contained in the following

Theorem 0.1 *Let $f \in L^p_{\rm unif}(\mathbf{R}^N)$, with $N \geq 3$ and $p > \frac{N}{2}$. Then the following two assertions are equivalent :*

(i) there exists $\Phi \in L^\infty(\mathbf{R}^N)$ such that $-\Delta\Phi = f$

(ii) $$\sup_{x_0 \in \mathbf{R}^N, 0<R<+\infty} \left| \int_{B_R(x_0)} \left(\frac{1}{|x-x_0|^{N-2}} - \frac{1}{R^{N-2}} \right) f(x)dx \right| < +\infty.$$

When such a Φ exists, it is unique up to an additive constant in $L^\infty(\mathbf{R}^N)$, and belongs to the space $W^{2,p}_{\rm unif}(\mathbf{R}^N)$.

The proof of this result follows from two observations. The first one consists in proving that the quantity appearing in (ii) defines a seminorm for Φ that is equivalent to the oscillation norm for bounded functions. Then, we build the solution Φ by regularizing the potential at infinity and passing to the limit. Various extensions of the results are collected in Section 3. In particular, the dimension N may be equal to 1 or 2 using the corresponding fondamental solution, and we may allow f to belong to other functional spaces than the simple $L^p_{\rm unif}$ space. Likewise, other truncations at infinity may be used, and therefore other equivalent conditions in the spirit of (ii) of Theorem 1 may be given.

The result will be used in [1], which is a sequel to the works [5, 6, 7] devoted to the periodic case.

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1 Motivation et Résultat principal

Nous présentons dans cette Note une manière de caractériser les fonctions f définies sur $\mathbf{R}^N$ qui peuvent s'écrire $f = -\Delta\Phi$ avec $\Phi \in L^\infty(\mathbf{R}^N)$. De façon standard, en relation avec la théorie de la gravitation, la fonction $-\Phi$ est appelée le potentiel *newtonien* de f, ou, ce qui revient au même dans le langage de la théorie de l'électrostatique, Φ est le potentiel *coulombien* de f.

Cette question est motivée par nos travaux sur la définition de l'énergie fondamentale d'un ensemble "quelconque " formé d'un nombre infini de particules dans $\mathbf{R}^N$, lesquelles interagissent entre elles par des interactions plus ou moins simples (potentiel à deux corps, interactions de nature quantique, ...). Par "ensemble quelconque" nous entendons que les positions x_i de ces particules forment un ensemble présentant les propriétés les plus naturelles et les plus générales possibles. Quand cet ensemble forme un réseau périodique, il est simple de définir son énergie. D'autres cas, extensions naturelles de la géométrie périodique, peuvent être traités par des techniques similaires. En revanche, si toute hypothèse liée de près ou de loin à de la périodicité est levée, la question de définir l'énergie d'un nombre infini de particules est largement moins simple. Tout ceci est détaillé dans [1], qui fait suite aux études des cas périodiques menées dans [5, 6, 7].

Si la discussion précédente est traduite en termes de l'équation de Laplace, elle prend la forme suivante. Donnons-nous une fonction f définissant la position des particules. Quelle propriété devons-nous exiger sur cette distribution f pour pouvoir définir le potentiel Φ qu'elle crée ?

Le cas où la fonction f est périodique est à cet effet instructif. Il est facile de voir que le résultat suivant est vrai. *Soit $f \in L^p_{loc}(\mathbf{R}^3)$, $p > \dfrac{3}{2}$ (par exemple), f périodique, alors il*

existe une fonction $\Phi \in L^\infty(\mathbf{R}^3)$, unique à constante additive près, périodique, telle que $-\Delta\Phi = f$ si et seulement si la moyenne $\langle f \rangle$ de f sur sa cellule de périodicité est nulle.

Pour passer au cas où la géométrie de l'ensemble des points x_i n'est plus périodique, on doit comprendre la généralisation de ce résultat au cas de fonctions f non périodiques. C'est l'objet du résultat principal de cette Note.

Notons $B_R(x)$ la boule de centre x et de rayon R, et désignons par $L^p_{\rm unif}(\mathbf{R}^3)$ l'ensemble des fonctions $f \in L^p_{\rm loc}(\mathbf{R}^3)$ telles que $\|f\|_{L^p(B_1(x))}$ est bornée indépendamment de x. L'espace $W^{2,p}_{\rm unif}(\mathbf{R}^3)$ se définit de manière analogue. Nous avons :

Théorème 1.1 *Soit $f \in L^p_{\rm unif}(\mathbf{R}^3)$, $p > \dfrac{3}{2}$. Alors les deux propriétés suivantes sont équivalentes :*

(i) il existe une fonction $\Phi \in L^\infty(\mathbf{R}^3)$ telle que $-\Delta\Phi = f$, au sens des distributions (au moins)

(ii) $$\sup_{x_0 \in \mathbf{R}^3,\ 0<R<+\infty} \left| \int_{B_R(x_0)} \left(\frac{1}{4\pi|x-x_0|} - \frac{1}{4\pi R} \right) f(x)\, dx \right| < +\infty$$

Quand elle existe, la fonction Φ est unique à constante additive près dans la classe des fonctions bornées, et appartient à $W^{2,p}_{\rm unif}(\mathbf{R}^3)$.

La Section 2 de cette Note est consacrée à la preuve de ce résultat. Différentes extensions et remarques sont regroupées dans la Section 3. En effet, par souci de clarté, nous avons énoncé notre résultat dans le cas où

- la dimension de l'espace ambiant est $N = 3$,
- la fonction f est choisie dans l'espace fonctionnel $L^p_{\rm unif}(\mathbf{R}^3)$,
- la troncature à l'infini (ce terme sera expliqué plus bas) est $\left(\frac{1}{4\pi|x|} - \frac{1}{4\pi R}\right)_+$

et chacun de ces points peut être généralisé sans peine.

Comme annoncé ci-dessus, l'étude [1] présentera une utilisation de ce résultat.

2 Preuve du théorème 1.1

La preuve du Théorème 1.1 se fait en deux étapes. Il s'agit d'abord de remarquer que le supremum de la formule (ii) définit en fait une semi-norme pour Φ, équivalente à la norme de l'oscillation. La seconde étape consiste alors en la construction de la fonction Φ.

2.1 Première étape : Equivalence de semi-normes

Soit $f \in L^p_{\rm unif}(\mathbf{R}^3)$ avec $p > 3/2$. Supposons que f s'écrive $f = -\Delta\Phi$ avec $\Phi \in L^\infty(\mathbf{R}^3)$, et donc $\Phi \in W^{2,p}_{\rm unif}(\mathbf{R}^3)$. Soient $x_0 \in \mathbf{R}^3$ et $R > 0$. Une simple application de la formule de Green montre que

$$\int_{B_R(x_0)} \left(\frac{1}{4\pi|x-x_0|} - \frac{1}{4\pi R} \right) f(x)\, dx = \Phi(x_0) - \frac{1}{4\pi R^2} \int_{\partial B_R(x_0)} \Phi \qquad (48)$$

Il est clair que le membre de droite reste borné quand x_0 et R varient. Nous pouvons donc définir sur $L^\infty(\mathbf{R}^3)$ la fonction

$$\mathcal{N}(\Phi) = \sup_{x_0\in\mathbf{R}^3,\ 0<R<+\infty} \Big|\Phi(x_0) - \frac{1}{4\pi R^2}\int_{\partial B_R(x_0)} \Phi\Big|. \tag{49}$$

Cette fonction $\mathcal{N}$ coïncide sur les fonctions $\Phi \in W^{2,p}_{\rm unif}(\mathbf{R}^3)$ avec

$$\sup_{x_0\in\mathbf{R}^3,\ 0<R<+\infty} \left|\int_{B_R(x_0)} \left(\frac{1}{4\pi|x-x_0|} - \frac{1}{4\pi R}\right)\Delta\Phi(x)\,dx,\right|. \tag{50}$$

La première étape de la preuve du Théorème 1.1 consiste à étudier cette fonction $\mathcal{N}$.

Lemma 2.2 *La fonction $\mathcal{N}(\Phi)$ introduite en (49) définit sur $L^\infty(\mathbf{R}^3)$ une semi-norme, nulle exactement pour les fonctions Φ constantes, équivalente à la semi-norme de l'oscillation*

$$Osc\,(\Phi) = \sup_{x\in\mathbf{R}^3} \Phi - \inf_{x\in\mathbf{R}^3} \Phi. \tag{51}$$

Preuve du Lemme 2.2

La majoration $\mathcal{N}(\Phi) \le Osc(\Phi)$ étant claire, on se concentre sur la minoration de $\mathcal{N}(\cdot)$ par $Osc(\cdot)$.

On raisonne par contradiction, en supposant qu'on dispose d'une suite Φ_n de fonctions de L^∞ telles que $\mathcal{N}(\Phi_n)$ tend vers zéro quand n tend vers l'infini, alors que $Osc(\Phi_n) \equiv 1$ pour tout n.

Remarquons alors que les deux fonctions $\mathcal{N}(\cdot)$ et $Osc(\cdot)$ sont invariantes sous les trois transformations suivantes : (a) on ajoute une constante à Φ, (b) on translate Φ, i.e. on change Φ en $\Phi(\cdot + a)$ pour $a \in \mathbf{R}^3$ fixé, et (c) on dilate Φ, i.e. on change Φ en $\Phi(\lambda\,\cdot)$ pour $\lambda > 0$ fixé.

Ces trois invariances nous permettent de supposer, sans perte de généralité,

- que la suite Φ_n est uniformément bornée en norme L^∞, et que le suprémum de Φ_n vaut 1, pour tout n,
- que l'infimum de Φ_n (qui vaut 0, pour tout n) est "essentiellement" atteint en zéro, i.e. que $\Phi_n(0) \le \frac{1}{n}$
- que le suprémum de Φ_n est "essentiellement" atteint sur la sphère unité, i.e. que $\Phi_n(x_n) \ge 1 - \frac{1}{n}$ pour un certain x_n tel que $|x_n| = 1$.

De plus, le fait que $\mathcal{N}(\Phi_n)$ tende vers zéro entraîne, en intégrant entre les deux rayons a et $b > a$ que, uniformément en $x_0 \in \mathbf{R}^3$,

$$\Big|\Phi_n(x_0) - \frac{3}{4\pi(b^3-a^3)}\int_{a<|x-x_0|<b} \Phi_n\Big| \overset{n\to+\infty}{\longrightarrow} 0. \tag{52}$$

Quitte à extraire une sous-suite, nous pouvons toujours supposer que la suite Φ_n converge pour la topologie L^∞ faible-$*$ vers un certain Φ. De plus, la suite $\int_{a<|x-x_0|<b}\Phi_n$ est équicontinue en x_0 et converge pour tout x_0 vers $\int_{a<|x-x_0|<b}\Phi$. De (52), on déduit alors

que Φ_n converge vers Φ uniformément sur tout compact, que Φ est continue et égale à ses moyennes sphériques, pour toute sphère. La fonction Φ est donc harmonique. Comme elle est bornée, il s'ensuit qu'elle est constante. Ceci est contradictoire, puisque la convergence uniforme sur la boule unité fermée implique que $\Phi(0) = 0$ et que Φ vaut 1 en un certain point de la sphère unité.

L'équivalence des deux semi-normes est donc démontrée. Le fait qu'elles soient nulles exactement pour les fonctions constantes est donc immédiat, et le lemme est donc prouvé. $\diamondsuit$

Remark 2.3 *Mentionnons ici, en anticipant un peu sur la Section 3, que dans le cas monodimensionnel, l'équivalence des semi-normes est immédiate. En effet, l'analogue monodimensionnel de la formule (49) est*

$$\mathcal{N}(\Phi) = \sup_{x_0 \in \mathbf{R}^3,\ 0<R<+\infty} \Big| \Phi(x_0) - \frac{1}{2}(\Phi(x_0+R) + \Phi(x_0-R)) \Big|. \tag{53}$$

A cause des invariances citées dans la preuve, il est toujours possible de supposer qu'il existe $x_n \longrightarrow 0$ *telle que* $\Phi(x_n) \longrightarrow 1 = \sup \Phi$ *et* $\Phi(x_n + 1) \longrightarrow 0 = \inf \Phi$. *On a alors*

$$\mathcal{N}(\Phi) \geq \frac{1}{2}(\Phi(x_n) - \Phi(x_n - 1)) + \frac{1}{2}(\Phi(x_n) - \Phi(x_n + 1)),$$

et on passe à la limite inférieure pour trouver $\mathcal{N}(\Phi) \geq \frac{1}{2} Osc(\Phi)$ *(cette minoration est optimale ; il suffit pour le voir de considérer la fonction de Heaviside). La majoration* $\mathcal{N}(\Phi) \leq Osc(\Phi)$ *étant toujours immédiate, le résultat est facilement prouvé.*

2.2 Deuxième étape : construction de Φ

La première étape ci-dessus montre facilement que, dans le Théorème 1.1, (i) implique (ii). Nous nous concentrons donc désormais sur l'implication réciproque. Fixons f comme dans le Théorème, vérifiant (ii). Nous allons construire un Φ convenable.

Fixons $\varepsilon > 0$ et définissons

$$\Phi_\varepsilon = f \star \frac{e^{-\varepsilon|x|}}{4\pi|x|}, \tag{54}$$

qui est solution de

$$-\Delta\Phi_\varepsilon + \varepsilon^2 \Phi_\varepsilon = f. \tag{55}$$

La condition (ii) étant vérifiée par f, l'inégalité de Young permet de montrer qu'elle est aussi vérifiée par la fonction

$$\varepsilon^2 \Phi_\varepsilon = f \star \varepsilon^2 \frac{e^{-\varepsilon|x|}}{4\pi|x|} \tag{56}$$

et ce *uniformément en* ε, car la norme L^1 de la fonction $\varepsilon^2 \dfrac{e^{-\varepsilon|x|}}{4\pi|x|}$ est en fait indépendante de ε. Il en résulte, par linéarité, que la fonction $-\Delta\Phi_\varepsilon = f - \varepsilon^2\Phi_\varepsilon$ vérifie aussi la condition

(ii) *uniformément* en ε. D'après la première étape (formule (48) et Lemme 1), on sait donc que la suite Φ_ε est bornée pour la semi-norme de l'oscillation.

Posons alors

$$\psi_\varepsilon = \Phi_\varepsilon - \inf \Phi_\varepsilon. \tag{57}$$

La suite ψ_ε est donc bornée dans L^∞. A extraction d'une sous-suite près, on peut supposer qu'elle converge dans L^∞ faible-$*$, vers ψ.

Pour la suite du raisonnement, on considère d'abord le cas où la fonction f appartient à L^∞. On indiquera ensuite comment procéder dans le cas général.

Par application du principe du maximum sur l'équation (55), on sait

$$|\varepsilon^2 \inf \Phi_\varepsilon| \leq \|f\|_{L^\infty}, \tag{58}$$

et on peut donc supposer, en extrayant si nécessaire une sous-suite, que cette suite de réels converge vers un réel λ.

En passant à la limite $\varepsilon \longrightarrow 0$ dans l'équation vérifiée par ψ_ε

$$-\Delta\psi_\varepsilon + \varepsilon^2\psi_\varepsilon = f - \varepsilon^2 \inf \Phi_\varepsilon, \tag{59}$$

on obtient donc

$$-\Delta\psi = f - \lambda. \tag{60}$$

Comme $\psi \in L^\infty$ et f vérifie (ii), on en déduit par linéarité que la constante λ vérifie aussi la condition (ii). Or ceci ne peut être que si la constante est nulle (laisser tendre R vers l'infini). On en déduit donc $-\Delta\psi = f$, et la fonction ψ est donc la fonction L^∞ cherchée. La preuve du Théorème 1.1 est terminée pour le cas $f \in L^\infty$. Pour un f non borné, on construit d'abord la solution ψ_η de $-\Delta\psi_\eta = f_\eta$ où $f_\eta = f \star \omega_\eta$ est une régularisation L^∞ de f ($\omega_\eta = \eta^3\omega(\eta\,\cdot)$ pour $\eta > 0$ petit et $\omega \in \mathcal{D}(\mathbf{R}^3)$ fixée). D'après la construction précédente, la norme L^∞ de ψ_η ne dépend pas de η mais seulement de la quantité apparaissant dans (ii), laquelle ne dépend que de f. On peut donc supposer que ψ_η converge dans L^∞ faible-$*$, vers un ψ qui vérifie $-\Delta\psi = f$. Ceci conclut la preuve. ♢

3 Remarques et extensions

Comme annoncé, plusieurs points peuvent être généralisés dans ce qui précède.

Il est clair que la dimension de l'espace ne joue pas de rôle particulier. Nous avons énoncé et démontré le Théorème 1.1 dans le cas de $\mathbf{R}^3$, et donc du potentiel $\dfrac{1}{4\pi|x|}$ dans (ii). Le même résultat tient en dimension $N \geq 4$ en remplaçant $\dfrac{1}{4\pi|x|}$ par $\dfrac{1}{a_N|x|^{N-2}}$, où $a_N = N(N-2)\omega_N$, $\omega_N = \dfrac{2\pi^{N/2}}{N\Gamma(\frac{N}{2})}$ étant le volume de la boule unité de $\mathbf{R}^N$. C'est donc $\dfrac{1}{a_N|x-x_0|^{N-2}} - \dfrac{1}{a_N R^{N-2}}$ qui figure alors dans (ii). Pour l'hypothèse $f \in L^p_{\text{unif}}$, la

condition $p > 3/2$ est remplacée par la condition $p > \dfrac{N}{2}$. Cette hypothèse d'intégrabilité L^p ne sert en effet qu'à bien définir

$$\int_{B_R(x_0)} \left(\frac{1}{a_N |x - x_0|^{N-2}} - \frac{1}{a_N R^{N-2}} \right) f(x)\, dx \tag{61}$$

de manière uniforme en x_0. On utilise bien sûr pour cela l'inégalité de Hölder et le fait que $\dfrac{1}{|x|^{N-2}} \in L^q_{loc}(\mathbf{R}^N)$ pour $q < \frac{N}{N-2}$.

Les cas $N = 1$ et $N = 2$ sont comme d'habitude particuliers. Pour $N = 1$, c'est $-\dfrac{|x - x_0|}{2} + \dfrac{R}{2}$ qui figure dans (ii). Pour le cas $N = 2$, c'est $-\dfrac{1}{2\pi} \log |x - x_0| + \dfrac{\log R}{2\pi}$.

On peut aussi étendre l'espace fonctionnel où considérer f en utilisant que, pour $N \geq 3$, $\dfrac{1}{|x|^{N-2}}$ appartient à l'espace de Lorentz $L^{\frac{N}{N-2},\infty}(\mathbf{R}^N)$. Il s'ensuit que l'hypothèse $f \in L^{\frac{N}{2},1}(\mathbf{R}^N)$ convient.

Enfin, on peut étendre le résultat au cas où f est une mesure uniformément localement bornée en remplaçant alors la condition (ii) par une condition régularisée où $f \star \omega$ remplace f dans (ii) pour un noyau de régularisation ω fixé. L'assertion (i) est alors remplacée par *il existe une mesure uniformément localement bornée* Φ *telle que* $-\Delta\Phi = f$ *au sens des distributions.*

Une autre généralisation repose sur l'observation suivante. On peut réécrire (ii) ainsi

$$\sup_{x_0 \in \mathbf{R}^3,\ 0<R<+\infty} \left| \int_{\mathbf{R}^3} \left(\frac{1}{4\pi|x - x_0|} - \frac{1}{4\pi R} \right)_+ f(x)\, dx \right| < +\infty \tag{62}$$

où $t_+ = \max(t, 0)$ désigne la partie positive de t. Il est alors clair que $\left(\dfrac{1}{4\pi|x|} - \dfrac{1}{4\pi R} \right)_+$ joue le rôle d'une troncature à l'infini de la solution élémentaire du Laplacien. Dans nos travaux, c'est précisément de cette troncature dont nous avons besoin. Cependant, n'importe quelle autre troncature conviendrait pour la caractérisation des fonctions à potentiel borné. Ainsi, par exemple, on peut remplacer (ii) par

$$\sup_{x_0 \in \mathbf{R}^3,\ \varepsilon>0} \left| \int_{\mathbf{R}^3} \frac{e^{-\varepsilon|x-x_0|}}{4\pi|x - x_0|} f(x)\, dx \right| < +\infty \tag{63}$$

La preuve de l'équivalence est en fait contenue dans la Section 2 ci-dessus, puisqu'on voit explicitement apparaître la fonction $f \star \Phi_\varepsilon$ et que la condition (63) exprime que les Φ_ε sont uniformément bornées en ε pour la norme L^∞. Une autre formulation est de dire qu'on a en fait prouvé l'équivalence entre les deux assertions suivantes

(i') il existe une solution $L^\infty(\mathbf{R}^3)$ de $-\Delta\Phi = f$

(ii') les Φ_ε solutions de $-\Delta\Phi_\varepsilon + \varepsilon^2 \Phi_\varepsilon = f$ sont bornées dans $L^\infty(\mathbf{R}^3)$ uniformément en ε.

Terminons par une remarque.

On l'a vu, la condition (ii) généralise au cas de fonctions non périodiques la condition de moyenne nulle pour les fonctions périodiques.

Dans le cas non périodique, on pourrait espérer que la condition (ii) soit en fait équivalente à l'extension "naturelle" de la condition de moyenne nulle, à savoir

$$\lim_{R\longrightarrow+\infty} \frac{3}{4\pi R^3} \int_{B_R(x_0)} f(x)\,dx = 0, \tag{64}$$

pour un $x_0 \in \mathbf{R}^3$ et donc pour tous. Cette équivalence n'est pas vraie. Certes (ii) *implique* (64), il suffit pour le voir d'utiliser l'équivalence avec (i) et d'intégrer $-\Delta\Phi = f$ sur la boule $B_R(x_0)$, mais la réciproque est fausse (pour f non périodique). En effet, on le montre (par exemple) en dimension 1 en considérant la fonction de Heaviside $f = \mathbf{1}_{(0,+\infty)} - \mathbf{1}_{(-\infty,0)}$. Les solutions de $-\Phi'' = f$ se comportent comme $-\frac{x^2}{2}$ en $+\infty$, et ne sont donc pas bornées.

Même lorsque l'on impose la condition que la limite dans (64) soit *uniforme* en x_0 (ce qui est aussi nécessaire), on ne peut pas conclure que (ii) est vraie. Cette fois, c'est le cas de la fonction $\Phi(x) = (1+x^2)^{3/4}$ en dimension 1 qui constitue un contre-exemple possible. On a bien $\lim_{R\to+\infty} \frac{1}{2R} \int_{x_0-R}^{x_0+R} \Phi''(x)\,dx = 0$, la limite étant uniforme en x_0, et pourtant Φ n'est pas bornée, à aucune fonction harmonique (i.e. affine) près.

On peut même montrer que renforcer la convergence uniforme vers 0 dans (64) en imposant que, en dimension N, $\frac{1}{R^N} \int_{B_R(x_0)} f(x)\,dx$ tende vers 0 comme un $O(1/R)$ uniforme en $x_0 \in \mathbf{R}^N$ ne suffit pas à entraîner (i). Un contre-exemple est fourni en dimension 1 par $f(x) = \dfrac{1}{x^2+1}$: les solutions de $-\Phi'' = f$ sont alors $\Phi(x) = -x\arctan(x) + \frac{1}{2}\log(1+x^2) + ax + b$, dont aucune n'est bornée.

Dans le même esprit, on peut montrer que la condition (64) n'est même pas suffisante quand on considère des fonctions f presque périodiques. Ainsi, soit $(a_n)_{n\in\mathbf{N}}$ une suite de réels positifs telle que

$$a_0 = 0, \quad \sum_{n\geq 0} a_n < +\infty, \quad \sum_{n\geq 0} n^2 a_n = +\infty,$$

et posons $f(x) = \sum_{n\geq 0} a_n \cos(\frac{x}{n})$. Cette fonction est presque périodique, et vérifie même la propriété $\dfrac{1}{R}\displaystyle\int_{x_0}^{x_0+R} f = O(\frac{1}{R})$ uniformément en x_0. Cependant, les solutions de $-\Delta\Phi = f$ s'écrivent $\Phi(x) = -\sum_{n\geq 0} n^2 a_n \cos(\frac{x}{n}) + ax + b$, dont aucune n'est bornée en 0.

Il semble donc qu'aucune condition de type (64) ne s'avère correcte dans un cadre non périodique, et que le bon point de vue soit celui du Théorème 1.1.

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Chapitre 6

Des modèles moléculaires à la mécanique des milieux continus

Ce chapitre a été écrit en collaboration avec C. Le Bris et P.-L. Lions [P8], et traite du passage de modèles moléculaires (aussi bien à deux corps que Thomas-Fermi) vers des modèles de mécanique des milieux continus. Le préambule consiste en une note aux Comptes-Rendus de l'Académie des Science [P7] qui présente le corps du chapitre.

Convergence de modèles moléculaires vers des modèles de mécanique des milieux continus

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Résumé. Nous présentons dans cette Note un travail visant à faire le lien, pour des matériaux cristallins, entre des théories microscopiques modélisant les interactions atomiques et une description macroscopique de leurs propriétés mécaniques. Ce lien apparaît comme une asymptotique en la distance inter-atomique du cristal considéré. Des modèles macroscopiques existant sont justifiés, des modèles (apparemment) nouveaux sont introduits et étudiés.

From molecular models to continuum mechanics

Abstract. *The work we present here is focused on the justification of continuum mechanics as a natural asymptotic of molecular theories when the interatomic distance goes to zero. We give a sound theoretical ground to existing models, and derive and next study (apparently) new ones.*

Abridged English Version - We present in this Note a rigorous mathematical derivation of various formulas commonly used in the literature of mathematical continuum mechanics [3, 17, 24, 53] to model the behaviour of cristalline hyperelastic materials through their macroscopic stored energy. In addition, taking into account higher order terms, our mathematical argument allows us to derivate (apparently new) energy functionals which give rise to interesting mathematical phenomena that seem to reproduce some realistic mechanical behaviours.

Our starting point is a microscopic model for the energy of a crystal, either defined by a two-body interaction (formulas (3) and (4)), or by a more general model issued from quantum mechanics (formulas (7) and (8)). By letting both the characteristic length of

the lattice ε and the characteristic range of the potential δ go to zero, following different regimes depending on the fact that $\varepsilon \sim \delta$, $\varepsilon \ll \delta$ or $\delta \ll \varepsilon$, we obtain a precise Taylor expansion of the macroscopic energy of the material experiencing a deformation u from a reference configuration state Ω. Note that although we deal here with simple lattices, the same analysis carries through the case of multilattices.

These expansions are detailed in Theorem 2.1 (at order 0 for two-body potential), Theorem 2.2 (at order 0 for quantum models), and Theorem 2.3 (at higher orders in the two-body potential case). These theorems are valid under relatively weak technical hypotheses that allow us to treat a large variety of interaction at the microscopic level.

Each associated variational problem will be studied in [10] : existing studies will be completed, new models will be analyzed. Even in the one-dimensional case (see formula (14)), interesting phenomena like convexification of the non-convex 0-order energy occur.

All the results announced here will be proved and completed in [10].

---

1 Introduction

L'étude des propriétés mécaniques des matériaux cristallins introduit des formes d'énergies internes liées à la géométrie du cristal considéré, comme dans [3, 17, 24, 53], et en particulier à sa structure microscopique. Voir également [19, 39] pour les applications de ces théories. Cependant, le lien entre de telles théories macroscopiques et l'échelle atomique sous-jacente semble incomplètement connu (voir cependant [4, 5, 13, 40]). Cette Note présente une contribution sur ce sujet.

Dans le cadre de ces modèles macroscopiques, l'énergie interne du solide (dite hyperélastique [18, 33]) est en générale supposée de la forme suivante :

$$\mathcal{E}(u) = \int_\Omega E(\nabla u(x))dx, \tag{1}$$

où u est la déformation et Ω le domaine occupé par le solide dans l'état de référence. La fonctionnelle E est supposée refléter les symétries du cristal à l'échelle microscopique placé au point x macroscopique, donc satisfaire aux propriétés suivantes, où G est le groupe d'invariance du réseau cristallin :

$$\forall M \in GL_3^+(\mathbf{R}), \quad \forall Q \in G, \quad \forall R \in SO_3(\mathbf{R}), \quad E(RMQ) = E(M). \tag{2}$$

$GL_3^+(\mathbf{R})$ désigne ici l'ensemble des matrices carrées inversibles de taille 3 dont le déterminant est positif, sur lequel E est définie. Beaucoup de propriétés mécaniques (et en fait de difficultés mathématiques) sont liés à cette invariance [24, 53], appelée règle de Cauchy-Born.

Pour simplifier cet exposé introductif, partons du modèle atomique le plus simple possible : l'interaction à deux corps par un potentiel W. Dans ce cas, l'énergie de N atomes aux positions X_i est définie par

$$E(\{X_i\}) = \frac{1}{2}\sum_{i \neq j} W(X_i - X_j). \tag{3}$$

Nous cherchons à comprendre quel est le lien exact entre W et l'énergie E de (1). La même question se pose lorsque l'énergie à deux corps est remplacée par une expression plus compliquée, comme par exemple des énergies de type Thomas-Fermi pour les électrons [14].

Dans la configuration de référence, les atomes du cristal sont placés sur un réseau ℓ, que l'on prend égal à $\varepsilon\mathbf{Z}^3$ pour fixer les idées, bien qu'il puisse être quelconque, voire multiple (cas où chaque maille élémentaire ne contient pas un atome, mais plusieurs). Deux paramètres vont jouer un rôle : le paramètre ε représente la distance inter-atomique du cristal, et est destiné à tendre vers 0 dans la limite macroscopique. Sous la déformation u, les positions des atomes deviennent égales à $X_i = u(\varepsilon k_i)$, avec $k_i \in \mathbf{Z}^3$ et $\varepsilon k_i \in \Omega$. Outre ε, le second paramètre important est la portée caractéristique du potentiel d'interaction W, que nous noterons δ, de sorte que $W(x) = W_0(\frac{x}{\delta})$, où W_0 est de portée 1. Cette distance tendra elle aussi vers 0. Ainsi, on obtient pour l'énergie par particule du cristal

$$\mathcal{E}_{\varepsilon,\delta}(u) = \frac{1}{2N} \sum_{j \neq k} W_0\left(\frac{u(\varepsilon k) - u(\varepsilon j)}{\delta}\right), \tag{4}$$

où la somme porte sur tous les points de $\mathbf{Z}^3$ qui sont dans $\frac{1}{\varepsilon}\Omega$, et N est le nombre d'atomes présents dans l'échantillon. Asymptotiquement, $N \sim |\Omega|\varepsilon^{-3}$. L'énergie "homogénéisée" $\mathcal{E}$ du cristal est la limite de $\mathcal{E}_{\varepsilon,\delta}$ quand ε (et δ) tend(ent) vers 0.

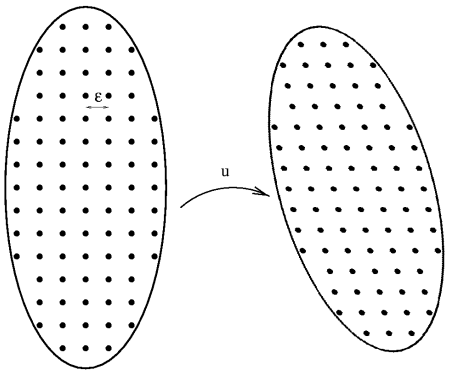

FIG. 1 – La configuration de référence et la configuration déformée.

Suivant le scaling de δ par rapport à ε, on obtient différents régimes asymptotiques :

(i) Si $\varepsilon \sim \delta$, alors $\mathcal{E}_{\varepsilon,\delta}$ converge vers une énergie du type (1), où $E(F) = \sum_{j \in \mathbf{Z}^3 \setminus \{0\}} W_0(Fj)$. (L'échelle macroscopique garde mémoire de la structure cristalline ; on constate que les invariances (2) sont vérifiées.) Notons que ce cas est physiquement plus acceptable que les autres : il est normal que l'espacement atomique de la configuration de référence soit comparable à la portée du potentiel.

(ii) Si $\varepsilon \ll \delta$, alors, en renormalisant multiplicativement de façon appropriée, l'énergie converge vers une énergie du type (1), avec $E(F) = \frac{1}{|\det(F)|}$: la structure microscopique a disparu. Ce phénomène est dû au fait qu'on a ici une limite "haute densité".

Cependant, cette énergie limite est reconnue [44] comme une énergie décrivant un fluide, ce qui peut sembler étrange.

(iii) Si $\delta \ll \varepsilon$ et que W_0 est à décroissance rapide à l'infini, alors l'énergie converge vers 0 plus vite que toute puissance de $\frac{\delta}{\varepsilon}$. L'énergie dégénère car la distance inter-atomique devient infiniment plus grande que la portée du potentiel d'interaction.

Dans le cas mentionné plus haut d'une interaction plus complexe entre les atomes, comme un modèle de type Thomas-Fermi, il est en général possible de faire apparaître une longueur caractéristique du modèle, et l'analyse précédente reste valable.

Les considérations ci-dessus donnent la limite de l'énergie, c'est-à-dire l'ordre 0 d'un développement en puissances de ε. Il est possible de calculer les ordres supérieurs de ce développement. En particulier, le terme d'ordre 1 ne possède qu'un terme de bord qui peut, dans certains cas lever en partie les dégénerescences associées à (2) mises en évidence dans [24]. Le terme d'ordre 2 fait apparaître des termes de volume et peut régulariser en un certain sens l'énergie. La suite de cette Note présente quelques résultats significatifs, qui seront justifiés, détaillés et complétés dans [10].

2 Du modèle atomique au continuum

2.1 À l'ordre 0

2.1.2 Cas du potentiel à deux corps

Nous montrons dans [10] le théorème suivant :

Théorème 2.1 *Soit W_0 un potentiel lipschitzien sur $\{x \in \mathbf{R}^d, \quad |x| > R\}$, pour tout $R > 0$, tel que pour tout réseau ℓ de $\mathbf{R}^d$, $\sum_{j \in \ell \setminus \{0\}} |W_0(j)| < \infty$. Soient Ω un ouvert régulier de $\mathbf{R}^d$ de volume 1 et u un C^∞-difféomorphisme de Ω dans $\mathbf{R}^d$. On considère $\mathcal{E}_{\varepsilon,\delta}(u)$ défini par (4), où la somme porte sur tous les couples de $\mathbf{Z}^d \cap \frac{1}{\varepsilon}\Omega$. Alors*

(i) Si $\varepsilon = \delta$, on trouve à la limite une énergie du type (1) :

$$\lim_{\varepsilon \to 0} \mathcal{E}_{\varepsilon,\delta}(u) = \frac{1}{2} \int_\Omega \sum_{j \in \mathbf{Z}^d \setminus \{0\}} W_0(\nabla u(x) j) dx. \tag{5}$$

(ii) Si $\varepsilon \ll \delta$, et si $W_0 \in L^1(\mathbf{R}^d)$,

$$\lim_{\varepsilon \to 0} \left(\left(\frac{\varepsilon}{\delta}\right)^d \mathcal{E}_{\varepsilon,\delta}(u) \right) = \frac{1}{2} \left(\int_{\mathbf{R}^d} W_0 \right) \int_\Omega \frac{1}{|\det(\nabla u(x))|} dx. \tag{6}$$

(iii) Si $\delta \ll \varepsilon$ et si pour tout $p > 0$, $|x|^p W_0(x)$ est borné à l'infini, $\lim_{\varepsilon \to 0} \left(\frac{\delta}{\varepsilon}\right)^p \mathcal{E}_{\varepsilon,\delta}(u) = 0$, quel que soit $p > 0$. S'il existe $p > 0$ tel que $|x|^p W_0(x)$, ait une limite a quand $|x|$ tend vers l'infini, alors $\lim_{\varepsilon \to 0} \left(\frac{\delta}{\varepsilon}\right)^p \mathcal{E}_{\varepsilon,\delta}(u) = \int_\Omega \sum_{j \in \mathbf{Z}^d \setminus \{0\}} \frac{a}{2|\nabla u(x) j|^p} dx$.

Notons que le changement d'inconnue $v = u^{-1}$ conduit à une expression de l'énergie (6) de la forme

$$\mathcal{E}(u) = \frac{1}{2}\left(\int_{\mathbf{R^d}} W_0\right) \int_{u(\Omega)} |\det(\nabla v(x))|^2 dx,$$

qui est polyconvexe (donc quasi-convexe), tout comme (6).

Les hypothèses de régularité sur W_0 étant faibles, elles permettent d'appliquer ce qui précède à des potentiels classiques utilisés pour modéliser l'interaction des particules d'un solide : le potentiel de Lennard-Jones, qui décrit de façon satisfaisante les cristaux de gaz nobles [2], satisfait aux hypothèses de (i) et (iii) ; le potentiel de Morse permet d'appliquer (i), (ii) et (iii) ; d'une façon générale, la plupart des potentiels "raisonnables" (Buckingham, Stillinger-Weber, Yukawa, ...) entre dans les hypothèses de (i). Même pour un potentiel de sphères dures, (i) reste valable.

Remarquons également que dans le cas d'un potentiel radial (ce qui est généralement le cas), et sous l'hypothèse (i), il est clair que l'invariance (2) est vérifiée.

D'autre part, dans le cas (ii), le fait que les atomes soient distribués sur un réseau dans la position de référence n'est pas indispensable, et en particulier toute suite équirépartie de points de Ω donnerait le même résultat. Ceci permettrait donc de traiter des cas où les atomes ne sont pas considérés comme fixes, mais aléatoirement répartis, avec une certaine homogénéité, sous l'effet de la température par exemple, ou encore le cas de quasi-cristaux, avec le même résultat.

Enfin, l'interprétation des positions εj comme des positions d'atomes n'est pas rigide, et on peut également se placer à une échelle intermédiaire où les particules du solide sont des "grains" de matière mésoscopique et interagissent suivant le potentiel W_0. Dans ce cas, le potentiel ne sera peut-être plus radial, mais le théorème ci-dessus reste valable.

2.1.2 Le cas d'un modèle quantique

Sauf cas exceptionnel (indiqué dans [10]), la section précédente ne couvre pas la situation où le caractère quantique des électrons est pris en compte : dans ce cas, nous allons supposer que les électrons sont dans leur état fondamental, c'est-à-dire dans une configuration qui minimise une certaine énergie. Un modèle très simple dans ce cadre est le modèle de Thomas-Fermi [14]. Les électrons sont alors définis par leur densité ρ, qui minimise l'énergie de Thomas-Fermi

$$\begin{aligned} E^{TF}(\rho, X_i) \;=\; & \frac{\hbar^2}{m}\int_{\mathbf{R}^3} \rho^{5/3} + \frac{e^2}{4\pi\varepsilon_0}\left(-\sum_j \int_{\mathbf{R}^3} \frac{\rho(x)}{|x - X_i|} dx \right. \\ & \left. + \frac{1}{2}\iint_{\mathbf{R}^6} \frac{\rho(x)\rho(y)}{|x-y|} dxdy + \frac{1}{2}\sum_{i\neq j} \frac{1}{|X_i - X_j|}\right), \end{aligned} \tag{7}$$

sous l'hypothèse que $\rho \in L^{5/3}(\mathbf{R}^3)$, $\rho \geq 0$, et que $\int_{\mathbf{R}^3} \rho = N$, nombre de noyaux. $\hbar$ est la constante de Planck, m la masse de l'électron, e la charge élémentaire et ε_0 la permittivité du vide. Nous supposons ici le cristal constitué d'atomes de numéro atomique

1, la généralisation à un cas plus réaliste étant facile. La distance caractéristique du système est $\delta = \frac{\hbar^2 4\pi\varepsilon_0}{me^2}$. L'analogue de (4) est alors :

$$\mathcal{E}_{\delta,\varepsilon}(u) = \frac{1}{N}\inf\left\{E^{TF}(\rho, \{u(\varepsilon i)\}), \quad \rho \geq 0, \quad \rho \in L^{5/3}(\mathbf{R}^3), \quad \int_{\mathbf{R}^3}\rho = N\right\}. \tag{8}$$

$\{u(\varepsilon i)\}$ désigne ici l'ensemble des $u(\varepsilon i)$, tels que $i \in \mathbf{Z}^3$ et $\varepsilon i \in \Omega$. Une analyse mathématique plus lourde mais reposant sur les mêmes idées permet d'établir la version correspondante du Théorème 2.1 :

Théorème 2.2 *Soit Ω un ouvert régulier de $\mathbf{R}^3$, de volume 1, et soit u un C^∞-difféomorphisme défini sur Ω. On a alors :*

(i) Si $\delta = \varepsilon$, et si $\frac{\hbar^2}{m} = \varepsilon^2$, la limite obtenue est du type (1) :

$$\lim_{\varepsilon\to 0}\mathcal{E}_{\delta,\varepsilon}(u) = \int_\Omega E^{TF}_{per}(\nabla u(x)\mathbf{Z}^3)dx, \tag{9}$$

où $E^{TF}_{per}(\ell)$ désigne, pour un réseau ℓ, l'énergie de Thomas-Fermi du réseau ℓ définie comme dans [14], et rappelée ci-dessous dans (11).

(ii) Si $\varepsilon \ll \delta$, et si $\frac{\hbar^2}{m} = \varepsilon^2$, alors

$$\lim_{\varepsilon\to 0}\mathcal{E}_{\delta,\varepsilon}(u) = \frac{3}{5}\int_\Omega \frac{dx}{|\det(\nabla u(x))|^{2/3}}. \tag{10}$$

(iii) Si $\delta \ll \varepsilon$, et si $\frac{\hbar^2}{m} = \delta^2$, alors $\mathcal{E}_{\delta,\varepsilon}(u)$ converge vers une constante non nulle indépendante de u. Cette constante peut de plus être identifiée comme l'énergie atomique Thomas-Fermi [14].

L'expression de l'énergie de Thomas-Fermi périodique $E^{TF}_{per}(\ell)$, pour un réseau ℓ est :

$$E^{TF}_{per}(\ell) = \inf\left\{E_\ell(\rho), \quad \rho \geq 0, \quad \rho \in L^{5/3}(Q(\ell)), \quad \int_{Q(\ell)}\rho = 1\right\}, \tag{11}$$

où $Q(\ell)$ est une cellule unité du réseau ℓ, et l'énergie $E_\ell(\rho)$ s'écrit :

$$E_\ell(\rho) = \int_{Q(\ell)}\rho^{5/3} - \int_{Q(\ell)}G_\ell\rho + \frac{1}{2}\int_{Q(\ell)}\int_{Q(\ell)}\rho(x)G_\ell(x-y)\rho(y)dxdy.$$

Le potentiel G_ℓ est ici une version ℓ-périodique du potentiel Coulombien.

Aux ordres supérieurs

Nous nous limitons dans cette section au cas de la modélisation par un potentiel à deux corps, et donnons les expressions des termes d'ordre 1 et 2 du développement de $\mathcal{E}_{\delta,\varepsilon}$ en puissance de ε.

Théorème 2.3 *Soit W_0 un potentiel lipschitzien sur $\{x \in \mathbf{R}^d, \quad |x| \geq R\}$, pour tout $R > 0$, et sommable à l'infini (voir théorème 2.1). Soit Ω un ouvert régulier de $\mathbf{R}^d$ de volume 1, et u un C^∞-difféomorphisme défini sur Ω. $\mathcal{E}_{\delta,\varepsilon}(u)$ étant défini par (4), on a :*

(i) Si $\delta = \varepsilon$, alors

$$\begin{aligned}\mathcal{E}_{\delta,\varepsilon}(u) &= \int_\Omega \sum_{j\neq 0} W_0(\nabla u(x)j)dx - \frac{\varepsilon}{2}\int_{\partial\Omega}\sum_{i\geq 1}\sum_{j\in\mathbf{Z}^d\cap\omega(x,i)} W_0(\nabla u(x)j)d\sigma(x)\\ &\quad -\frac{\varepsilon^2}{24}\int_\Omega \sum_{j\neq 0} D^2W_0(\nabla u(x)j)(D^2u(x)(j,j),D^2u(x)(j,j))dx\\ &\quad +\varepsilon^2 F_1(u)+O(\varepsilon^3), \qquad (12)\end{aligned}$$

avec $\omega(x,i) = \{z \in \mathbf{R}^d,\quad zn(x) \geq d(-\nabla u(x)n(x)i, \nabla u(x)\Gamma(x))\}$, $n(x)$ étant la normale extérieure à Ω en x, et $\Gamma(x)$ l'orthogonal de $n(x)$. De plus, le terme $F_1(u)$ ne contient que des termes de bord.

(ii) si $\varepsilon \ll \delta$, et si $W_0 \in L^1(\mathbf{R}^d)$, alors

$$\begin{aligned}\mathcal{E}_{\delta,\varepsilon}(u) &= \frac{\int_{\mathbf{R}^d} W_0}{2}\int_\Omega \frac{dx}{|\det(\nabla u(x))|} - \varepsilon\int_{\partial\Omega}\int_0^\infty\left(\int_{\omega(x,y)} W_0(\nabla u(x)z)dz\right)dyd\sigma(x)\\ &\quad -\frac{\varepsilon^2}{24}\int_\Omega\int_{\mathbf{R}^d} D^2W_0(\nabla u(x)y)(D^2u(x)(y,y),D^2u(x)(y,y))dydx\\ &\quad +\varepsilon^2F_2(u)+O(\varepsilon^3), \qquad (13)\end{aligned}$$

où $\omega(x,y)$ est défini comme au (i), et où F_2 ne contient que des termes de bord.

Il est possible de procéder de la même façon pour des modèles quantiques comme ceux évoqués ci-dessus.

Notons que dans le cas particulier où $n(x)$ est le premier vecteur de la base canonique et $\nabla u(x)$ l'identité, l'ensemble $\omega(x,i)$ devient très simple, et l'intégrande du deuxième terme de (12) s'écrit $\sum_{i\geq 1}\sum_{j\in\mathbf{Z}^d, j_1\geq i} W_0(j)$, qui peut s'interpréter comme une énergie de surface du cristal.

3 Problèmes variationnels associés

Les divers régimes examinés dans la section précédente ont fait apparaître des énergies limites pouvant servir de définitions à des énergies macroscopiques de matériaux cristallins (formules (5), (6), (9), (10), (12), (13)). Soulignons encore une fois que les énergies obtenues "à l'ordre 0" apparaissent explicitement dans la littérature mécanique [53, 44] et les problèmes variationnels qui leur sont associés ont été étudiés mathématiquement [24, 17]. Nous présenterons dans [10] une extension de ces études, et les conséquences des formules explicites (5), (6), (9), (10).

En revanche, il semble que les formules aux ordres supérieurs (12) et (13) soient nouvelles. Il est tentant d'étudier les problèmes variationnels auxquels elles donnent naissance. Même en dimension 1, des phénomènes intéressants apparaissent déjà : apparition d'une couche limite due aux termes de bord, convexification du terme quasi-convexe d'ordre 0, etc...

Donnons ici un seul exemple (qui sera largement complété dans [10]) : en dimension 3, la formule (13) peut se réécrire sous la forme suivante, en posant $v = u^{-1}$ et en négligeant les termes de bord :

$$\mathcal{E}(u) = \frac{1}{2}\left(\int_{\mathbf{R}^3} W_0\right) \int_{u(\Omega)} \det(\nabla v(\xi))^2 d\xi$$
$$- \frac{\varepsilon^2}{24} \int_{u(\Omega)} \int_{\mathbf{R}^3} D^2 W_0(z) \left[\left(\frac{\nabla v(\xi)}{\det(\nabla v(\xi))} \right)^{-1} D^2 v(\xi)(z,z), \left(\frac{\nabla v(\xi)}{\det(\nabla v(\xi))} \right)^{-1} D^2 v(\xi)(z,z) \right] dz d\xi.$$

Si maintenant on suppose que u ne dépend que de x_1, donc que $v(\xi_1, \xi_2, \xi_3) = (w(\xi_1), \xi_2, \xi_3)$, le terme d'ordre 2 de la formule ci-dessus se simplifie en

$$\mathcal{E}_2(u) = -\frac{\varepsilon^2}{24} \int_{\mathbf{R}^3} z_1^4 \partial_{11} W_0(z) dz \int_{u(\Omega)} w''(\xi_1)^2 d\xi = -\frac{\varepsilon^2}{6} \int_{\mathbf{R}^3} |z|^2 W_0(z) dz \int_{u(\Omega)} w''(\xi_1)^2 d\xi. \tag{14}$$

Ainsi, sous la condition $\displaystyle\int_{\mathbf{R}^3} |z|^2 W_0(z) dz < 0$, vérifiée par certains W_0 comme par exemple le potentiel de Morse, ce terme convexifie l'énergie globale, et peut comme le montre S. Müller dans [36] limiter la taille des micro-structures apparaissant naturellement dans les problèmes de minimisation quasi-convexes [3].

4 Remarques et compléments

Plusieurs aspects n'ont pas été pris en compte dans l'approche simpliste présentée ici. Citons-en quatre comme exemples de piste où du travail mathématique reste à faire.

Tout d'abord, un solide réel n'est pas purement périodique, et présente en général des défauts, qui ont souvent un impact important sur les propriétés macroscopiques du solide. La présence de ces défauts est également la base de la théorie des dislocations, qui explique la plasticité des matériaux par l'apparition de défauts sous l'effet d'efforts mécaniques. La prise en compte de ces défauts pourrait se faire soit en les prenant en compte à l'échelle moléculaire, soit en perturbant *a posteriori* les modèles macroscopiques. Également, le travail présenté ici peut probablement être étendu au cas des polycristaux, où en un point macroscopique sont présents plusieurs réseaux et non un seul comme nous l'avons supposé ici.

Un deuxième aspect est l'effet de la présence d'une surface sur la géométrie du cristal. La structure, donc le réseau du cristal, évolue de façon nette en fonction de la distance au bord du cristal, faisant apparaître ainsi une couche limite. Ce phénomène pourrait peut-être être expliqué par une approche de type optimisation de géométrie (voir [7]).

Nous avons aussi supposé ici que la déformation u était la même à l'échelle microscopique qu'à l'échelle macroscopique. Cette hypothèse simplificatrice pourrait être remise en question, et en particulier, dans l'esprit de [25], on pourrait introduire une déformation microscopique u_ε dépendant de ε et qui convergerait (en un certain sens à préciser) vers la déformation macroscopique u.

Enfin, un quatrième aspect important est l'effet de la température, déterminant dans l'étude des propriétés mécaniques des cristaux, et qu'il serait souhaitable de savoir prendre en compte.

From molecular models to continuum mechanics

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Abstract We present here a limiting process allowing us to write some continuum mechanics models as a natural asymptotic of molecular models. The approach is based on the hypothesis that the macroscopic displacement is equal to the microscopic one. We carry out the corresponding calculations in the case of two-body energies, including higher order terms, and also in the case of Thomas-Fermi type models.

1 Introduction

It is commonly admitted in the continuum mechanics literature that the stored energy of an elastic crystal is of the form:

$$\mathcal{E}(u) = \int_\Omega E(\nabla u(x))dx, \tag{15}$$

where $\Omega \subset \mathbf{R}^3$ is the reference configuration of the solid, and u is the deformation to which the solid is subjected. Moreover, the stored energy density E is assumed to reflect the microscopic symmetries of the crystal [3, 17, 24, 53], in addition to the standard frame invariance [18, 33]. In other words, denoting by G the invariance group of the underlying crystalline structure, we have:

$$\forall M \in M_+^{3\times 3}, \quad \forall Q \in G, \quad \forall R \in SO(3), \quad E(RMQ) = E(M), \tag{16}$$

where $M_+^{3\times 3}$ denotes the set of three by three matrices having positive determinant, on which the energy density E is supposed to be defined. This invariance property is at the origin of many important properties of crystalline solids, as well as mathematical difficulties in the use of energies of the form (15). See for instance [17, 24, 53]. However, an exact expression, or even an approximation for E is rarely available. Closely linked with this problem is the question of the associated functional space: to what space A should u belong in order to properly define the minimization problem

$$I_A = \inf\{\mathcal{E}(u), \quad u \in A\}.$$

The definition of A should include, in addition to regularity properties, suitable boundary conditions.

In order to answer these questions, a rigorous derivation of (15) and (16) is needed, starting from the atomic level, since it is the scale at which the crystalline lattice is present. A standard approach to this kind of problem is Γ-convergence [21], which assumes implicitly that at an intermediate level, the *microscopic* (or *mesoscopic*) deformation, which is not necessarily equal to the *macroscopic* deformation u, should locally minimize the energy. Roughly speaking, this approach consists in setting a microscopic version of the minimization problem I_A in term of the microscopic deformation u_ε, depending on the interatomic distance ε. Letting this distance go to zero, this yields a (weak) limit deformation $u = u_0$ together with an energy, possibly of the form (15). However, it is far from clear what should be the microscopic counterpart of I_A: what regularity should the deformation exhibit at this level, and how should the boundary conditions (which are by nature macroscopic) be translated microscopically? This kind of strategy is used in [13, 41] in the case of a two-body finite range energy. In [25], the case of a more complex microscopic model is considered.

Another (and seemingly more naive) approach is the following: the whole point is in fact to link the macroscopic deformation u appearing in (15) with the deformation truely experienced by the atoms of the solid, that is, a sort of microscopic deformation. Since

this link is far from being clear physically, let us assume the simplest link, that is, equality. This is the approach used in [4, 5], and also the one we adopt here.

Let us give the example of a two-body interaction, in order to fix the ideas: the energy $\mathcal{E}(\{X_i\})$ of N identical atoms of positions X_i is then given by

$$\mathcal{E}(\{X_i\}) = \sum_{1 \le i < j \le N} W(X_i - X_j), \tag{17}$$

where W is the interaction potential. Let us now assume that a solid is defined by a domain Ω, and a lattice ℓ, and that the interatomic distance is equal to $\varepsilon > 0$, which *in fine* will tend to zero. Assuming that the solid experiences a deformation u, which is a C^∞-diffeomorphism defined on Ω, then the positions of the atoms of the deformed solid are

$$X_i = u(X_i^0), \quad \{X_i^0\}_{1 \le i \le N} = \varepsilon\ell \cap \Omega,$$

the set of points $\{X_i^0\}$ being the reference state. Consequently, the energy per atom of the deformed configuration is:

$$\mathcal{E}(u(\varepsilon\ell \cap \Omega)) = \frac{1}{2N} \sum_{i \ne j \in \ell \cap \frac{1}{\varepsilon}\Omega} W(u(\varepsilon i) - u(\varepsilon j)). \tag{18}$$

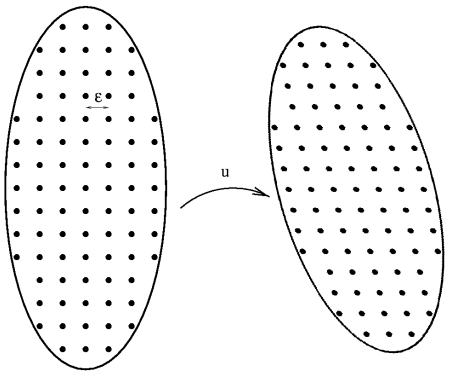

Figure 2: The reference configuration and the deformed one.

Next, considering the potential W, its characteristic length δ should be comparable with ε. In other words, considering the reference configuration, which minimizes the energy (17), its atomic spacing should be proportional to δ. (This is clear since if $\{X_i^0\}$ is a ground state for W, $\{\delta X_i^0\}$ is a ground state for $W(\frac{\cdot}{\delta})$.) We will however also study other cases apart from the $\varepsilon = \delta$ case, that is, cases when $\varepsilon \ll \delta$ and $\delta \ll \varepsilon$, respectively. The total energy of the deformed system is thus equal to:

$$\mathcal{E}_{\varepsilon,\delta}(u) = \frac{1}{2N} \sum_{i \ne j \in \ell \cap \frac{1}{\varepsilon}\Omega} W_0\left(\frac{u(\varepsilon i) - u(\varepsilon j)}{\delta}\right), \tag{19}$$

where $N = \#(\ell \cap \frac{1}{\varepsilon}\Omega)$ is the total number of atoms, and W_0 is the rescaled potential, and does not depend on ε nor on δ. The energy $\mathcal{E}$ appearing in (15) should then be the limit, as ε and δ go to zero, of $\mathcal{E}_{\varepsilon,\delta}$:

$$\mathcal{E}(u) = \lim_{\varepsilon,\delta\to 0} \mathcal{E}_{\varepsilon,\delta}(u). \tag{20}$$

Despite the seemingly crude assumption we make in this strategy (namely, the microscopic deformation being *equal* to the macroscopic one), one can find some advantages in this approach:

First of all, the above limiting process (20) is clearly not linked with the fact that the energy originates from a two-body interaction. Indeed, we will see in Section 3 below that the case of more complex microscopic models, taking (at least partially) the quantum nature of the electrons into account, give rise to the same kind of convergence results. This allows to hope that similar results will hold for more complex microscopic theories.

Another point is that since it is a mere limiting process, involving no Γ-convergence properties, one may very well go further: considering the limit as a zero-order term in the development of the energy with respect to ε, it is possible to compute the next orders. This is what is done in Theorem 2.3.

Finally, let us point out that for numerical purposes, this approach gives a way of computing the sum (18) in the limit $\varepsilon \to 0$, which is the exact expression of the energy, u being the microscopic deformation. Of course, there still remains to know its link with the macroscopic one, but independently of this link, the above limit (20) may be seen as a good approximation in the case where ε is small, hence N large, circumventing any direct computation of (18), which indeed may be out of reach of computer facilites for very large N.

Finally, let us point out that our approach is intimately linked with the concept of thermodynamic limit [30, 14], as explained in Section 3, which *is* a Γ-limit process, although standardly not presented as such.

The article is organized as follows: Section 2 gives the computation of the limit (20), together with the corresponding development, up to order two with respect to ε (Theorem 2.3). Section 3 then studies the limit (20) in the case of Thomas-Fermi type theories, which are quantum models. We give a few possible extensions of the present work in Section 4, while the last section is devoted to the derivation of a few simple properties of the computed elastic energies, these aspects being more completely studied in a forthcoming work [11].

Most of the results detailed here have been announced in [9].

2 The simplest case: two-body potentials

We present here the homogenization scheme described in Section 1 in the simplest case, that is, when the microscopic energy is defined by a two-body potential. In other words,

we study the limit (20), with the energy $\mathcal{E}_{\varepsilon,\delta}$ being given by (19), that is:

$$\mathcal{E}_{\varepsilon,\delta}(u) = \frac{1}{2N} \sum_{i \neq j \in \ell \cap \frac{1}{\varepsilon}\Omega} W_0\left(\frac{u(\varepsilon i) - u(\varepsilon j)}{\delta}\right).$$

We recall that, assuming that the reference configuration is an equilibrium state, i.e that an infinite system with minimal energy is periodic, it is physically reasonable to assume that δ and ε have comparable size, i.e that in the limit process $\varepsilon \to 0$, we should take $\delta = \varepsilon$. We will nevertheless study the other possible cases, that is, when $\varepsilon \ll \delta$ and $\delta \ll \varepsilon$, respectively. Note also that the fact that the equilibrium configuration is periodic is *not* proven, so far as we know, except in one dimension [8, 27, 50, 37, 38, 45, 47], or in very simple cases in two dimensions [46].

2.1 Zero-order term

Hereafter, we denote by ε a sequence of positive real converging to zero, and $\delta = \delta(\varepsilon)$ also going to zero. The property $\varepsilon \ll \delta$ means that $\lim_{\varepsilon \to 0} \frac{\varepsilon}{\delta(\varepsilon)} = 0$, and $\delta \ll \varepsilon$ means that $\lim_{\varepsilon \to 0} \frac{\delta(\varepsilon)}{\varepsilon} = 0$, these limits being taken along the corresponding sequence.

Theorem 2.1 *Let W_0 be a function defined on $\mathbf{R}^d \setminus \{0\}$, which is Lipschitz on the exterior of any ball B_R, with $R > 0$, and such that there exists $C \geq 0$ and $a > 0$ such that $|W_0(x)| \leq \frac{C}{|x|^{d+a}}$. Let Ω be a bounded Lipschitz open subset of $\mathbf{R}^d$, and let u be a C^∞-diffeomorphism defined on Ω, with values in $\mathbf{R}^d$. Consider $\mathcal{E}_{\varepsilon,\delta}$ the energy defined by (19). Then we have:*

(i) If $\varepsilon = \delta$, then

$$\lim_{\varepsilon \to 0} \mathcal{E}_{\varepsilon,\delta}(u) = \frac{1}{2|\Omega|} \int_\Omega \sum_{j \in \ell \setminus \{0\}} W_0(\nabla u(x) j) dx. \tag{21}$$

(ii) If $\varepsilon \ll \delta$, and if $W_0 \in L^1(\mathbf{R}^3)$, then

$$\lim_{\varepsilon \to 0} \left(\frac{\varepsilon}{\delta}\right)^d \mathcal{E}_{\varepsilon,\delta}(u) = \frac{1}{2|\Omega|} \left(\int_{\mathbf{R}^3} W_0\right) \int_\Omega \frac{dx}{|\det(\nabla u(x))|}. \tag{22}$$

(iii) If $\delta \ll \varepsilon$, and if for some $p \in \mathbf{R}$, $\lim_{|x| \to \infty} |x|^p W_0(x) = a$, then

$$\lim_{\varepsilon \to 0} \left(\frac{\varepsilon}{\delta}\right)^p \mathcal{E}_{\varepsilon,\delta}(u) = \frac{1}{2|\Omega|} \int_\Omega \sum_{j \in \ell \setminus \{0\}} \frac{a}{|\nabla u(x) j|^p} dx. \tag{23}$$

Proof: We first prove (i). Note that this result seems to be well-known, but since we found no rigorous proof of it in the literature, we provide the reader with one. Consider equation (19), with $\varepsilon = \delta$, that is:

$$\mathcal{E}_{\varepsilon,\delta}(u) = \frac{1}{2N} \sum_{i \neq j \in \ell \cap \frac{1}{\varepsilon}\Omega} W_0\Big(\frac{u(\varepsilon i) - u(\varepsilon j)}{\varepsilon}\Big).$$

We first split this sum into two sums, using a cut-off radius $A > 0$, which *in fine* will go to infinity:

$$\mathcal{E}_{\varepsilon,\delta}(u) = \frac{1}{2N} \sum_{|i-j| \leq A} W_0\Big(\frac{u(\varepsilon i) - u(\varepsilon j)}{\varepsilon}\Big) + \frac{1}{2N} \sum_{|i-j| > A} W_0\Big(\frac{u(\varepsilon i) - u(\varepsilon j)}{\varepsilon}\Big), \tag{24}$$

both sums being reduced to couples (i,j) in $\big(\frac{1}{\varepsilon}\Omega \cap \ell\big)^2$ such that $i \neq j$. The deformation u being a C^∞-diffeomorphism, we have $\alpha|i-j| \leq \frac{|u(\varepsilon i)-u(\varepsilon j)|}{\varepsilon} \leq \beta|i-j|$, for some constants α and β depending only on u. Consequently, the second sum in (24) is easily seen to vanish as A goes to infinity, uniformly with respect to ε. Turning to the first term, we use a Taylor expansion to write:

$$\Big|\frac{u(\varepsilon i) - u(\varepsilon j)}{\varepsilon} - \nabla u(\varepsilon i)(j-i)\Big| \leq CA^2\varepsilon,$$

where C depends only on u. Then, using the fact that W_0 is Lipschitz on the exterior of any ball, and that $\alpha d(\ell) \leq \alpha|i-j| \leq \frac{|u(\varepsilon i)-u(\varepsilon j)|}{\varepsilon}$ for any i and j appearing in the sum, where $d(\ell)$ is the minimal distance between two points of the lattice ℓ, we may write:

$$\Big|W_0\big(\frac{u(\varepsilon i) - u(\varepsilon j)}{\varepsilon}\big) - W_0\big(\nabla u(\varepsilon i)(j-i)\big)\Big| \leq C_{d(\alpha)}A^2\varepsilon.$$

Using this inequality in (24), we thus have:

$$\Big|\mathcal{E}_{\varepsilon,\delta}(u) - \frac{1}{2N} \sum_{i \in \ell \cap \frac{1}{\varepsilon}\Omega} \sum_{0<|i-j|\leq A} W_0\big(\nabla u(\varepsilon i)(j-i)\big)\Big| \leq C_{d(\alpha)}A^{2+d}\varepsilon + R(A), \tag{25}$$

where $R(A)$ corresponds to an upper bound of the second term of (24), and may thus be chosen equal to $R(A) = \frac{1}{2N}\sum_{|i-j|>A} \frac{C}{|i-j|^{d+a}} \leq \frac{C}{A^a}$, where C are various constants independent of ε. Next, the sum in (25) may be written as

$$\frac{1}{2N} \sum_{i \in \ell \cap \frac{1}{\varepsilon}\Omega} \sum_{0<|j|\leq A} W_0\big(\nabla u(\varepsilon i) j\big),$$

where the sum over j is restricted to $j \in \ell$ (as well as in (25)). Next, using the regularity of u, we may write $|\nabla u(\varepsilon i) j| \geq \alpha|j|$, where α does not depend on ε and i. Consequently, the sum over j is, up to a term going to zero as A goes to infinity, uniformly with respect to ε, the sum over the whole lattice:

$$\Big|\mathcal{E}_{\varepsilon,\delta}(u) - \frac{1}{2N} \sum_{i \in \ell \cap \frac{1}{\varepsilon}\Omega} \sum_{j \in \ell \setminus \{0\}} W_0\big(\nabla u(\varepsilon i) j\big)\Big| \leq C_{d(\alpha)}A^{2+d}\varepsilon + \frac{C}{A^a}.$$

The last step is to point out that since $N = \#\varepsilon\ell \cap \Omega$, the sum over i is a Riemann sum, converging to the desired integral since the function $x \mapsto \sum_{j\neq 0} W_0(\nabla u(x)j)$ is Lipschitz on Ω. Choosing $A = \varepsilon^{-\frac{d}{2}-1}$, and then letting ε go to zero, we prove (i).

Let us now prove (ii). For the sake of simplicity, we restrict ourselves to the case of a finite-range potential, the generalization to the present case being only a technical matter, similar to the cut-off trick in the proof of (i). We then have, for $i, j \in \ell \cap \frac{1}{\varepsilon}\Omega$,

$$\frac{|u(\varepsilon i) - u(\varepsilon j)|}{\delta} \geq \alpha \frac{\varepsilon}{\delta}|i-j|,$$

for some constant α depending only on u. Consequently, given $i \in \ell \cap \frac{1}{\varepsilon}\Omega$, the number of terms in the sum over j contributing to the energy is of order $\frac{\delta^d}{\varepsilon^d}$, in view of the inequality $|i-j| \leq C\frac{\delta}{\varepsilon}$. Consequently, one easily shows, using the fact that W_0 and u are Lipschitz, that:

$$\left|\varepsilon^{2d} \sum_{i\neq j \in \ell\cap\frac{1}{\varepsilon}\Omega} W_0\big(\frac{u(\varepsilon i) - u(\varepsilon j)}{\delta}\big) - \int_\Omega \int_\Omega W_0\big(\frac{u(x)-u(y)}{\delta}\big)dxdy\right| \leq C(\frac{\varepsilon}{\delta} + \varepsilon)\delta^d,$$

where C depends only on W_0, u and Ω. Now, changing variables in the integral, we have:

$$\int_\Omega \int_\Omega W_0\big(\frac{u(x)-u(y)}{\delta}\big)dxdy = \int_{u(\Omega)} \int_{u(\Omega)} \frac{W_0\big(\frac{\xi-\eta}{\delta}\big)}{|\det(\nabla u(u^{-1}(\xi)))\det(\nabla u(u^{-1}(\eta)))|}d\xi d\eta.$$

Next, we use the fact that as δ goes to infinity, $\frac{1}{\delta^d \int_{\mathbf{R}^d} W_0} W_0(\frac{\cdot}{\delta})$ converges to a Dirac mass at zero, so that

$$\lim_{\delta\to 0} \frac{1}{\delta^d} \int_{u(\Omega)} \int_{u(\Omega)} \frac{W_0\big(\frac{\xi-\eta}{\delta}\big)}{|\det(\nabla u(u^{-1}(\xi)))\det(\nabla u(u^{-1}(\eta)))|}d\xi d\eta$$
$$= \left(\int_{\mathbf{R}^d} W_0\right) \int_{u(\Omega)} \frac{d\xi}{|\det(\nabla u(u^{-1}(\xi)))|^2} = \left(\int_{\mathbf{R}^d} W_0\right) \int_\Omega \frac{dx}{|\det(\nabla u(x))|}.$$

Putting all this together, we thus have:

$$\lim_{\varepsilon \ll \delta \to 0} \frac{N\varepsilon^{2d}}{\delta^d} \mathcal{E}_{\varepsilon,\delta}(u) = \frac{1}{2}\left(\int_{\mathbf{R}^d} W_0\right) \int_\Omega \frac{dx}{|\det(\nabla u(x))|}.$$

Observing that, at leading order, $N \approx \frac{|\Omega|}{\varepsilon^d |Q(\ell)|}$, where $|Q(\ell)|$ is the volume of the unit cell $Q(\ell)$ of ℓ, this proves (ii).

We next prove (iii): fixing a positive parameter α (which in the end will go to zero), we know that for $|x|$ large enough, $|W_0(x) - \frac{a}{|x|^p}| \leq \frac{\alpha}{|x|^p}$. Using the regularity of y, we thus have, for $\frac{\varepsilon}{\delta}$ large enough,

$$\left|W_0\left(\frac{u(\varepsilon i) - u(\varepsilon j)}{\delta}\right) - \frac{a\delta^p}{|u(\varepsilon i) - u(\varepsilon j)|^p}\right| \leq \frac{C\alpha\delta^p}{|i-j|^p},$$

where C depends only on u. Hence, we deduce easily that

$$\left|\left(\frac{\varepsilon}{\delta}\right)^p \mathcal{E}_{\varepsilon,\delta}(u) - \frac{1}{2N}\sum_{i\neq j}\frac{a\varepsilon^p}{|u(\varepsilon i)-u(\varepsilon j)|^p}\right| \leq C\alpha\frac{1}{2N}\sum_{i\neq j}\frac{1}{|i-j|^p} \leq C\alpha\sum_{j\in\ell\setminus\{0\}}\frac{1}{|j|^p}. \quad (26)$$

We next apply (i) with $W_0(x) = \frac{1}{|x|^p}$ to conclude that the second term of the right-hand side of (26) converges to the desired formula. There only remains to point out that (26) is valid for any $\alpha > 0$, as far as $\frac{\varepsilon}{\delta}$ is chosen large enough, which concludes the proof. $\Diamond$

Remark 2.2 *The regularity assumption we have made on u could be slightly relaxed. Indeed, u being a C^1-diffeomorphism is clearly sufficient to make the above proof available. However, and although this assumption is reasonable (see [18]), the Taylor expansion we use here could not be carried out if only lower regularity was assumed. If for example we allow jumps in the gradient, it might be possible to obtain a concentration of energy on the jump set (see [13]).*

2.2 Higher order terms

We have studied in Subsection 2.1 the limit of the energy as ε and δ go to zero, that is, the zero order term of a development of this energy in powers of ε. We give now a derivation of higher order terms of this development, limiting ourselves to order two, although the computations could be carried out at any order.

Before stating this result in Theorem 2.3 below, we need some definition. Let Ω be a piecewise C^1 open bounded subset of $\mathbf{R}^d$, and let $x \in \partial\Omega$. Denote by $\Gamma(x)$ the tangent plane at x, and define

$$\mu_{\Gamma(x),\ell} = \lim_{\varepsilon\to 0}\left(\varepsilon^{d-1}\sum_{k\in A_\varepsilon(\Gamma(x))}\mathcal{N}_\varepsilon(k)\delta_k\right), \quad (27)$$

with $A_\varepsilon(\Gamma(x)) = \{d(i,\frac{1}{\varepsilon}\Gamma(x)), \quad i \in \ell\cap\frac{1}{\varepsilon}(\Gamma(x)^-\cap\Omega)\}$, the number $\mathcal{N}_\varepsilon(k)$ is $\mathcal{N}_\varepsilon(k) = \#\{i \in \ell\cap\frac{1}{\varepsilon}(\Gamma(x)^-\cap\Omega), \quad d(i,\frac{1}{\varepsilon}\Gamma(x)) = k\}$, the set $\Gamma(x)^-$ being equal to $\Gamma(x)^- = \{z+\nu(x)t, \quad t \in (-\infty,0), \quad z \in \Gamma(x)\}$, where $\nu(x)$ is the outer normal of Ω at x.

Theorem 2.3 *Let W_0 be a function defined on $\mathbf{R}^d\setminus\{0\}$, such that for all $x \neq 0$, $W_0(x) = W_0(-x)$, which is smooth on the exterior of any ball B_R, for any $R > 0$, and such that there exists $C \geq 0$, $R_0 > 0$ and $a > 2$ satisfying*

$$\forall k \in \mathbf{N}, \quad \forall x \in (B_{R_0})^c, \quad |D^k W_0(x)| \leq \frac{C}{|x|^{d+k+a}}. \quad (28)$$

Let Ω be a piece-wise C^1 open bounded subset of $\mathbf{R}^d$, and let u be a C^∞-diffeomorphism defined on Ω, with values in $\mathbf{R}^d$. We assume in addition that there exists a sequence $\varepsilon_n > 0$ converging to zero such that, for all integer n, we have $\#(\varepsilon_n\ell\cap\Omega) = \frac{|\Omega|}{\varepsilon_n^d|Q(\ell)|}$, where $|Q(\ell)|$ is the volume of the unit cell of the lattice ℓ. Consider $\mathcal{E}_{\delta,\varepsilon}$ the energy defined by (19). Then we have, restricting ε to the sequence ε_n:

(i) If $\delta = \varepsilon$, then

$$\mathcal{E}_{\varepsilon,\delta}(u) = \frac{1}{2|\Omega|}\int_\Omega \sum_{j\in\ell\setminus\{0\}} W_0(\nabla u(x)(j))dx - \frac{\varepsilon}{2|\Omega|}\int_{\partial\Omega}\left(\int_0^\infty \sum_{j\in\ell,\ j\nu\geq k} W_0(\nabla u(x)j)d\mu_{\Gamma(x),\ell}(k)\right)d\sigma(x) - \frac{\varepsilon^2}{24|\Omega|}\int_\Omega \sum_{j\in\ell\setminus\{0\}} D^2W_0(\nabla u(x)j)(D^2u(x)(j,j), D^2u(x)(j,j))dx + \varepsilon^2 F_1(u) + o(\varepsilon^2), \tag{29}$$

where $\Gamma(x)$ is the tangent plane of $\partial\Omega$ at x, and the non-negative measure $d\mu_{\Gamma,\ell}(k)$ is defined by (27) In addition, $F_1(u)$ contains only boundary terms;

(ii) If $\varepsilon \ll \delta$, and if $W_0 \in L^1(\mathbf{R}^3)$, then

$$\left(\frac{\varepsilon}{\delta}\right)^d \mathcal{E}_{\varepsilon,\delta}(u) = \frac{\int_{\mathbf{R}^d} W_0}{2|\Omega|}\int_\Omega \frac{dx}{|\det(\nabla u(x))|} - \frac{\varepsilon}{|\Omega|}\int_{\partial\Omega}\int_0^\infty\left(\int_k^\infty W_0(\nabla u(x)z)d\mu_{\Gamma(x),\ell}(z)\right)dyd\sigma(x) - \frac{\varepsilon^2}{24|\Omega|}\int_\Omega\int_{\mathbf{R}^d} D^2W_0(\nabla u(x)y)(D^2u(x)(y,y), D^2u(x)(y,y))dydx + \varepsilon^2 F_2(u) + o(\varepsilon^2), \tag{30}$$

the measure $d\mu_{\Gamma(x),\ell}$ being defined as in (i), and the term $F_2(u)$ containing only boundary terms.

Let us point out that, although formulas (29) and (30) seem rather complicated, the special case where Ω is the unit cube of $\mathbf{R}^d$, and the lattice ℓ is equal to $\mathbf{Z}^d$, in which case the plane $\Gamma(x)$ is exactly the face of the cube to which x belongs, and the measure $d\mu_{\Gamma(x),\mathbf{Z}^d}$ is easily computed to be $\sum_{p\geq 1}\delta_p$, the sum involving only $p \in \mathbf{N}$. Consequently, in this case, the integrand of the second term of (29) reads:

$$\sum_{k\geq 1}\sum_{j\in\mathbf{Z}^d,\ jn\geq k} W_0(\nabla u(x)j),$$

which may be interpreted, when ∇u is the identity matrix, as the surface energy of a crystal. In a more general setting, the measure $d\mu_{\Gamma(x),\ell}$ may be seen as the average number of points in ℓ and in the half-space containing Ω which are at distance k from $\Gamma(x)$.

Proof: We only give the proof of (i), the proof of (ii) following the same line of arguments. For the sake of simplicity, we assume that the constant a of (28) satisfies $a > 8$. This is only a technical assumption, which allows to simplify the argument below in the present proof. We will next indicate how to deal with the general case ($a > 2$).

We use a cut-off radius $A > 0$, as in the proof of Theorem 2.1, writing

$$\begin{aligned}\mathcal{E}_{\varepsilon,\delta}(u) &= \frac{1}{2N}\Big(\sum_{i\in\ell\cap\frac{1}{\varepsilon}\Omega}\ \sum_{0<|i-j|<A} W_0\Big(\frac{u(\varepsilon i)-u(\varepsilon j)}{\varepsilon}\Big)\\ &\quad+\sum_{i\in\ell\cap\frac{1}{\varepsilon}\Omega}\ \sum_{|i-j|\geq A} W_0\Big(\frac{u(\varepsilon i)-u(\varepsilon j)}{\varepsilon}\Big)\Big),\end{aligned} \tag{31}$$

where all the sums over j concern only $j \in \ell$. Using (28), the second sum is easily bounded by a term of the form $\frac{C}{A^a}$, so that, taking $A = \varepsilon^{-\beta}$, with $\frac{2}{a} < \beta < \frac{1}{4}$, which is possible since $a > 8$, this sum is of strictly lower order than ε^2. Next, we use a Taylor expansion of the expression $W_0\big(\frac{u(\varepsilon i)-u(\varepsilon j)}{\varepsilon}\big)$:

$$\begin{aligned}W_0\Big(\frac{u(\varepsilon i)-u(\varepsilon j)}{\varepsilon}\Big) &= W_0\Big(\nabla u(\varepsilon i)(j-i)\Big)+\frac{\varepsilon}{2}\nabla W_0\Big(\nabla u(\varepsilon i)(j-i)\Big)\Big(D^2u(\varepsilon i)(j-i,j-i)\Big)\\ &\quad+\varepsilon^2\Big[\frac{1}{8}D^2W_0\Big(\nabla u(\varepsilon i)(j-i)\Big)\Big(D^2u(\varepsilon i)\big(j-i,j-i\big),D^2u(\varepsilon i)\big(j-i,j-i\big)\Big)\\ &\qquad+\frac{1}{6}\Big(\nabla u(\varepsilon i)(j-i)\Big)D^3u(\varepsilon i)\big(j-i,j-i,j-i\big)\Big]\\ &\quad+\frac{\varepsilon^3}{72}D^2W_0\Big(\nabla u(\varepsilon i)(j-i)\Big)\Big(D^2u(\varepsilon i)(j-i,j-i),D^3u(\varepsilon i)(j-i,j-i,j-i)\Big)\\ &\qquad+O\Big(\frac{\varepsilon^3A^4}{|j-i|^{d+a+1}}\Big),\end{aligned} \tag{32}$$

where the term $O\Big(\frac{\varepsilon^3A^4}{|j-i|^{d+a+1}}\Big)$ involves constants depending only on W_0, u and Ω. Since the term depending on j may be summed up ℓ uniformly with respect to i, this will lead, when summed up with respect to i and j, to a quantity of order $O(\varepsilon^3A^4) = o(\varepsilon^2)$. We next study the term of order three: we need to show that, summed with respect to i and j, it remains of lower order than ε^2. For this purpose, we estimate it as follows:

$$\begin{aligned}&\Big|\sum_{0<|j-i|<A} D^2W_0\Big(\nabla u(\varepsilon i)(j-i)\Big)\Big(D^2u(\varepsilon i)(j-i,j-i),D^3u(\varepsilon i)(j-i,j-i,j-i)\Big)\Big|\\ &\qquad\leq\sum_{0<|j|<A}\frac{C}{|j|^{d+a+2}}|j|^5=\sum_{0<|j|<A}\frac{C}{|j|^{d+a-3}}\leq\frac{C}{A^{a-3}}.\end{aligned} \tag{33}$$

This shows that the third-order term in (32) is of order $\frac{\varepsilon^3}{A^{a-3}}$, which is neglectable compared

to ε^2, thanks to the definition of A. We may thus write the energy as:

$$\begin{aligned}\mathcal{E}_{\varepsilon,\delta}(u) &= \frac{1}{2N}\sum_{i\in\ell\cap\frac{1}{\varepsilon}\Omega}\sum_{0<|i-j|<A}\Big[W_0\Big(\nabla u(\varepsilon i)(j-i)\Big)\\ &+\frac{\varepsilon}{2}\nabla W_0\Big(\nabla u(\varepsilon i)(j-i)\Big)\Big(D^2u(\varepsilon i)\big(j-i,j-i\big)\Big)\\ &+\frac{\varepsilon^2}{6}\nabla W_0\Big(\nabla u(\varepsilon i)(j-i)\Big)D^3u(\varepsilon i)\big(j-i,j-i,j-i\big)\\ &+\frac{\varepsilon^2}{8}D^2W_0\Big(\nabla u(\varepsilon i)(j-i)\Big)\Big(D^2u(\varepsilon i)\big(j-i,j-i\big),D^2u(\varepsilon i)\big(j-i,j-i\big)\Big)\Big]\\ &+o(\varepsilon^2). \end{aligned} \tag{34}$$

We now notice that in the terms of order ε^2, we may sum up over all $j\in\ell\setminus\{i\}$ since the missing terms sum up to a lower order term. We may in fact do the same thing for the term of order ε. Indeed, the missing terms may be estimated as follows:

$$\left|\frac{\varepsilon}{2}\sum_{|j|\geq A}\nabla W_0\Big(\nabla u(\varepsilon i)j\Big)D^2u(\varepsilon i)\big(j,j\big)\right|\leq\sum_{|j|\geq A}\frac{C\varepsilon|j|^2}{|j|^{d+1+a}}=O\Big(\frac{\varepsilon}{A^{a-1}}\Big)=o(\varepsilon^2), \tag{35}$$

from the definition of A. This estimate is valid for i far enough from the boundary of $\frac{1}{\varepsilon}\Omega$, since otherwise the sum is truncated not at A, but at $d(i,\frac{1}{\varepsilon}\Omega^c)$. On the other hand, these terms are easily seen, through the same kind of estimate, to be boundary terms of higher order.

We leave the first term as it stands for now, dealing with it afterwards. The other terms are easily seen to be Riemann sums, converging, up to higher order *boundary* terms, to the corresponding integrals. We thus have:

$$\begin{aligned}\mathcal{E}_{\varepsilon,\delta}(u) &= \frac{1}{2N}\sum_{i\in\ell\cap\frac{1}{\varepsilon}\Omega}\sum_{0<|i-j|<A}W_0\Big(\nabla u(\varepsilon i)(j-i)\Big)\\ &+ \frac{\varepsilon}{4|\Omega|}\int_\Omega\sum_{j\in\ell\setminus\{0\}}\nabla W_0\big(\nabla u(x)j\big)\big(D^2u(x)(j,j)\big)\,dx\\ &+ \varepsilon^2\Big[\frac{1}{6|\Omega|}\int_\Omega\sum_{j\in\ell\setminus\{0\}}\nabla W_0(\nabla u(x)j)D^3u(x)(j,j,j)dx\\ &\quad+\frac{1}{8|\Omega|}\int_\Omega\sum_{j\in\ell\setminus\{0\}}D^2W_0(\nabla u(x)j)(D^2u(x)(j,j),D^2u(x)(j,j))dx\Big]\\ &+ \varepsilon^2F_1(u)+o(\varepsilon^2), \end{aligned} \tag{36}$$

where $F_1(u)$ is a boundary term. Integrating by parts the first part of the term of order ε^2, one easily sees that it is exactly the corresponding term of (29). Turning to the term of order ε, we see that its integrand is an exact derivative with respect to x, so that it is

equal to:

$$\int_\Omega \sum_{j\in\ell\backslash\{0\}} \nabla W_0\big(\nabla u(x)j\big)\big(D^2u(x)(j,j)\big)dx = \int_{\partial\Omega} \sum_{j\in\ell\backslash\{0\}} W_0(\nabla u(x)j)(jn)d\sigma(x). \qquad (37)$$

Using the fact that $W_0(x) = W_0(-x)$, together with the fact that the set $\ell\backslash\{0\}$ is symmetric with respect to 0, we see that this term cancels. We now deal with the term of order zero: it will naturally give the zero-order term of (29), and also approximating terms of order 1 and 2 a priori. The point here is to show that these terms give the boundary term of (29). Denoting by $\mathcal{E}^0_{\varepsilon,\delta}(u)$ the zero-order term of (36), we write:

$$\begin{aligned}\mathcal{E}^0_{\varepsilon,\delta}(u) &= \frac{1}{2N}\sum_{i\in\ell\cap\frac{1}{\varepsilon}\Omega}\sum_{j\in\ell\backslash\{0\}} W_0(\nabla u(\varepsilon i)j)dx - \frac{1}{2N}\sum_{i\in\ell\cap\frac{1}{\varepsilon}\Omega}\sum_{j\notin\frac{1}{\varepsilon}\Omega} W_0(\nabla u(\varepsilon i)(j-i))\\ &\quad -\frac{1}{2N}\sum_{i\in\frac{1}{\varepsilon}\Omega}\sum_{j\in\frac{1}{\varepsilon}\Omega\cap B_A(i)^c} W_0(\nabla u(\varepsilon i)(j-i)). \qquad (38)\end{aligned}$$

Here, all the sums are restricted to points belonging to ℓ. The third term is easily bounded as follows:

$$\left|\frac{1}{2N}\sum_{i\in\ell\cap\frac{1}{\varepsilon}\Omega}\sum_{j\in\frac{1}{\varepsilon}\Omega\cap B_A(i)^c} W_0(\nabla u(\varepsilon i)(j-i))\right| \le C\sum_{|j|>A}\frac{1}{|j|^{a+d}} \le \frac{C}{A^a} = o(\varepsilon^2).$$

The two remaining terms will respectively give the terms of order zero and one in (29). In order to prove this claim, we denote by f the function $f(x) = \sum_{j\neq 0} W_0(\nabla u(x)j)$, and write it as:

$$\begin{aligned}\frac{\varepsilon^3}{2|\Omega|}\sum_{i\in\ell\cap\frac{1}{\varepsilon}\Omega} f(\varepsilon i) &= \frac{1}{2|\Omega|}\int_\Omega f(x)dx + \frac{1}{2|\Omega|}\sum_{i\in\ell\cap\frac{1}{\varepsilon}\Omega}\int_{\varepsilon i+\varepsilon Q(\ell)}(f(\varepsilon i)-f(x))dx,\\ &\quad + \sum_{i\in\ell\cap\frac{1}{\varepsilon}\Omega}\int_{(\varepsilon i+\varepsilon Q(\ell))\cap\Omega^c} f - \sum_{i\in\ell\cap\frac{1}{\varepsilon}\Omega^c}\int_{(\varepsilon i+\varepsilon Q(\ell))\cap\Omega} f. \qquad (39)\end{aligned}$$

where $Q(\ell)$ is the primitive unit cell of ℓ. We next make a Taylor expansion of the second term, that is, $f(\varepsilon i) - f(x) = \nabla f(\varepsilon i)(i-x) - D^2 f(\varepsilon i)(x-i, x-i) + O(\varepsilon^3)$. The first term of this expansion is linear with respect to $x-i$, and thus cancels when integrated over $\varepsilon i + \varepsilon Q(\ell)$. We thus have

$$\frac{\varepsilon^3}{2|\Omega|}\sum_{i\in\ell\cap\frac{1}{\varepsilon}\Omega} f(\varepsilon i) = \frac{1}{|\Omega|}\int_\Omega f(x)dx - \frac{\varepsilon^5}{2|\Omega|}\sum_{i\in\ell\cap\frac{1}{\varepsilon}\Omega}\int_{Q(\ell)} D^2 f(\varepsilon i)(y,y)dy + O(\varepsilon^3).$$

We recognize here again in the second term a Riemann sum, so that it may be replaced, up to terms which are neglectable before ε^2, by $\varepsilon^2\int_\Omega\int_{Q(\ell)} D^2 f(x)(y,y)dydx$. This term being an integral of a derivative with respect to x, it will give only a boundary term of order ε^2. We now turn to the last terms of (39), which are boundary terms, since they

clearly involve only terms such that $d(i, \frac{1}{\varepsilon}\partial\Omega) < 2\varepsilon$. Next, we notice that each term of this difference is a Riemann sum of the boundary, and thus may be replaced, up to boundary terms of order ε^2, by the corresponding integrals, which are equal.

We finally deal with the remaining term, that is, the second term of (38). Since the treatment of this term is rather delicate, we provide a proof in the case when Ω is a polyhedron. The extension to the general case follows the same argument with some straightforward technical adaptations that we omit. The first point is that, since j is restricted to belong to $\frac{1}{\varepsilon}\Omega^c$, and using once again that ∇u^{-1} is bounded uniformly on Ω, we may reduce this sum to terms which are not far from the boundary:

$$-\frac{1}{2N}\sum_{i\in\ell\cap\frac{1}{\varepsilon}\Omega}\sum_{j\notin\frac{1}{\varepsilon}}W_0\big(\nabla u(\varepsilon i)(j-i)\big) = -\frac{1}{2N}\sum_{i\in\ell\cap\partial_\varepsilon\Omega}\sum_{j\notin\frac{1}{\varepsilon}\Omega}W_0\big(\nabla u(\varepsilon i)(j-i)\big) + o(\varepsilon^2),$$

where $\partial_\varepsilon\Omega = \{y \in \frac{1}{\varepsilon}\Omega, \quad d(y, \partial(\frac{1}{\varepsilon}\Omega)) < \frac{1}{\sqrt{\varepsilon}}\}$. This expression shows that this is going to be a boundary term. Next, we separate the boundary of Ω into P different faces, denoted by Γ_p, with $1 \le p \le P$. We now consider only one face, putting all them together in the end:

$$E_{\Gamma_p}(u) = -\frac{1}{2N}\sum_{i\in\ell\cap\Gamma_p^\varepsilon}\sum_{j+i\in\ell\cap\frac{1}{\varepsilon}\Omega^c}W_0\big(\nabla u(\varepsilon i)j\big),$$

where Γ_p^ε is the set of points in $\frac{1}{\varepsilon}\Omega$ which are at distance smaller than $\frac{1}{\sqrt{\varepsilon}}$ from $\frac{1}{\varepsilon}\Gamma_p$. Now, considering the set to which j belongs, it may be described, up to a term of order ε^2, by the constraints $j \in \ell$ and $(j + i - \pi_{\frac{1}{\varepsilon}\Gamma_p}(i))\nu \ge 0$, where ν is the outer normal of the face Γ_p, and $\pi_{\frac{1}{\varepsilon}\Gamma_p}$ is the orthogonal projection on the hyper-plane $\frac{1}{\varepsilon}\Gamma_p$. Now, since $d(i, \frac{1}{\varepsilon}\Gamma_p) = (\pi_{\frac{1}{\varepsilon}\Gamma_p}(i) - i)\nu$, this property also reads $j\nu \ge d(i, \frac{1}{\varepsilon}\Gamma_p)$. Hence,

$$E_{\Gamma_p}(u) = -\frac{\varepsilon^d}{2|\Omega|}\sum_{i\in\ell\cap\Gamma_p^\varepsilon}\sum_{j\in\ell,\, jn\ge d(i,\frac{1}{\varepsilon}\Gamma_p)}W_0\big(\nabla u(\varepsilon i)j\big) + O(\varepsilon^2).$$

We next approximate, up to order ε, the sum over j by the same one where εi is replaced by $\pi_{\Gamma_p}(\varepsilon i)$. This may be done using a Taylor expansion, and the correcting term is shown to be of order ε^2 when summed up with respect to i using the fact that $a > 2$. The term we want to treat now is thus:

$$E_{\Gamma_p}(u) = -\frac{\varepsilon^d}{2|\Omega|}\sum_{i\in\ell\cap\Gamma_p^\varepsilon}\sum_{j\in\ell,\, jn\ge d(i,\frac{1}{\varepsilon}\Gamma_p)}W_0\big(\nabla u(\pi_{\Gamma_p}(\varepsilon i))j\big) + O(\varepsilon^2).$$

Assume for a while that ∇u is constant and equal to F on Γ_p. Then, we now define the set $A_\varepsilon^p(\Gamma_p) = \{d(i, \frac{1}{\varepsilon}\Gamma_p), \quad i \in \ell \cap \Gamma_p^\varepsilon\}$, and $\mathcal{N}_\varepsilon^p(k) = \#\{i \in \Gamma_p^\varepsilon \cap \ell, \quad d(i, \frac{1}{\varepsilon}\Gamma_p) = k\}$, and using these notations, we write the above energy as

$$E_{\Gamma_p}(u) = -\frac{\varepsilon^d}{2|\Omega|}\sum_{k\in A_\varepsilon^p(\Gamma_p)}\mathcal{N}_\varepsilon^p(k)\sum_{j\in\ell,\, jn\ge k}W_0\big(Fj\big) + O(\varepsilon^2).$$

There only remains to point out that the number $\mathcal{N}_\varepsilon^p(k)$ is equal to the number $|\Gamma_p|\mathcal{N}_\varepsilon(k)$ appearing in (27), up to a correcting term of order ε^{2-d}. Here $|\Gamma_p|$ is the $d-1$-dimensional measure of the face Γ_p. We therefore conclude in this special case:

$$E_{\Gamma_p}(u) = -\frac{\varepsilon|\Gamma_p|}{2|\Omega|}\int_0^\infty \Big(\sum_{j\in\ell,\, jn\geq k} W_0(\nabla u(x)j)\Big)\, d\mu_{\Gamma_p,\ell}(k),$$

which matches exactly the second term of (29). Here, x is any point of Γ_p. In order to conclude, we only need to point out that if ∇u is not a constant on Γ_p, a similar but more tedious analysis leads to the second term of (29) through a Riemann sum over Γ_p. Next, using an approximation of Ω by a polyhedron, we conclude in the general case.

We now explain how the above argument may be adapted to the case where $a \leq 8$. Note that the points where we have used the assumption $a > 8$ concern only the bulk term, and not the surface terms. In the bulk term, the point is the choice of β, i.e of A, the cut-off radius used in (31). One needs $\beta > \frac{2}{a}$ so that the remainder term in (31) be of order strictly lower than ε^2. If $a \leq 8$, this implies that the remainder of (32) is no more of order $o(\varepsilon^2)$. Hence, one needs to expand at an order higher than 2, say q. And the remainder, which is of order $O(\frac{\varepsilon^q A^{q+1}}{|j-i|^{d+a+1}})$, leads, when summed up over j, to a term of order $O(\varepsilon^{q-1-\beta q})$. Hence, if β is chosen strictly lower than 1, which possible since $a > 2$, this term is of order strictly lower than ε^2 for q large enough. There only then remains to deal with the additional terms of the development, which is done using their exact expression, as was done in (33) for the term of order three. $\Diamond$

Note that as it is clear in the above proof, the development could be carried on at any order. However, even the surface term of order ε is a little cumbersome to establish, and its expression seems to be difficult to use except in special cases. This indicates that higher order surface terms are likely to be hard to compute and to use. On the contrary, if one only looks for bulk terms, the development is within reach. (In such a case, the assumption (28) would involve $a > q$, q being the order at which we want to develop.)

Another point is that the term of order ε is a boundary term, even if the assumption $W_0(x) = W_0(-x)$ is dropped. However, in this case, the right-hand side of (37) would appear in addition to the term of (29).

Finally, let us point out that this order one term shows a minus sign because (and it is apparent in the above proof) it is the correction of the bulk term of order zero, to which we have added terms in order to have the whole sum over ℓ when x is close to the boundary. It may be therefore interpreted as the *opposite* of the surface energy of the crystal.

3 Thomas-Fermi type models

We deal in this Section with Thomas-Fermi type models, where the quantum nature of the electrons is (partially) taken into account, whereas the nuclei are supposed to be classical particles.

We first present the Thomas-Fermi-von Weizsäcker (TFW) model, define it for molecules, and then explain how it translates into TFW theory for infinite periodic (solid-state)

systems through the thermodynamic limit process [14]. We also show the link between this thermodynamic limit process and the present scheme.

3.1 Presentation of the models

We briefly present in this subsection the Thomas-Fermi-von Weizsäcker (TFW) model, recalling that all we are going to do for this model is clearly adaptable to Thomas-Fermi (TF), and even to Thomas-Fermi-Dirac-von Weizsäcker model. We refer to [29] for precisions on these models.

The TFW energy is defined, for a set of M nuclei of positions $\{X_i\}_{1\leq i\leq M}$ and charges $\{Z_i\}_{1\leq i\leq M}$, and a set of electrons defined by their total density $\rho \geq 0$ (such that $\sqrt{\rho} \in H^1(\mathbf{R}^3)$), by

$$E^{\mathrm{TFW}}(\{X_i, Z_i\}, \rho) = \frac{\hbar^2}{m}\left(\int_{\mathbf{R}^3} |\nabla\sqrt{\rho}|^2 + \int_{\mathbf{R}^3} \rho^{5/3}\right) + \frac{e^2}{4\pi\varepsilon_0}\left(-\sum_{i=1}^{M}\int_{\mathbf{R}^3} \frac{Z_i\rho(x)}{|x-X_i|}dx + \frac{1}{2}\int_{\mathbf{R}^3}\frac{\rho(x)\rho(y)}{|x-y|}dxdy + \frac{1}{2}\sum_{i\neq j}\frac{Z_iZ_j}{|X_i-X_j|}\right), \quad (40)$$

where $\hbar$ is Planck's constant, e the elementary charge, m the mass of an electron and ε_0 the dielectric permittivity constant. Note that the TFW model is usually stated in a unit system where the coefficients $\frac{\hbar^2}{m}$ and $\frac{e^2}{4\pi\varepsilon_0}$ of (40) are both equal to 1, but here we need to scale the characteristic length of the model with respect to the atomic spacing, as was done in Section 2 for two-body energies. Let us also point out that we have skipped here dimensionless constants which should appear in front of the first two terms of (40) (see [43] for the details), since they are mathematically irrelevant here.

The integer N being the total number of electrons, the density ρ is subjected to the constraint $\int \rho = N$. When the electrons are in their ground state, they minimize the above energy, i.e they are a solution of the minimization problem:

$$\mathcal{E}^{\mathrm{TFW}}(\{X_i, Z_i\}) = \inf\left\{E^{\mathrm{TFW}}(\{X_i, Z_i\}, \rho), \quad \rho \geq 0, \quad \sqrt{\rho} \in H^1(\mathbf{R}^3), \quad \int_{\mathbf{R}^3}\rho = N\right\}. \quad (41)$$

Here, we assume that we deal with a set of N identical atoms, and fix the nuclear charge to $Z_i = 1$, although none of these assumptions are limitations. The important assumption is that the nuclei are periodically distributed, that is, as in Section 2, $\{X_i\} = \varepsilon\ell \cap \Omega$, where ℓ is the periodic lattice on which the nuclei are distributed, ε the inter-atomic distance, and Ω the Lipschitz open set defining the solid we are studying.

We next point out that the characteristic length of the system is easily shown by a dimensional analysis to be $\delta = \frac{\hbar^2 4\pi\varepsilon_0}{e^2 m}$. Hence, setting $E_0 = \frac{\hbar^2}{m}$, (40) translates into:

$$E_\delta^{\mathrm{TFW}}(\{X_i\}, \rho) = E_0\left[\int_{\mathbf{R}^3} |\nabla\sqrt{\rho}|^2 + \int_{\mathbf{R}^3}\rho^{5/3} + \frac{1}{\delta}\left(-\sum_{i=1}^{M}\int_{\mathbf{R}^3}\frac{\rho(x)}{|x-X_i|}dx + \frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3}\frac{\rho(x)\rho(y)}{|x-y|}dxdy + \frac{1}{2}\sum_{i\neq j}\frac{1}{|X_i-X_j|}\right)\right], \quad (42)$$

and (41) similarly. Assuming now that the set of nuclei $\{X_i\} = \varepsilon\ell \cap \Omega$ is deformed by a C^∞-diffeomorphism u, we thus define

$$\mathcal{E}^{\rm TFW}_{\varepsilon,\delta}(u) = \frac{1}{N}\inf\left\{E^{\rm TFW}_\delta(u(\varepsilon\ell\cap\Omega),\rho), \quad \rho\geq 0, \quad \sqrt{\rho}\in H^1(\mathbf{R}^3), \quad \int_{\mathbf{R}^3}\rho = N\right\}, \quad (43)$$

where N is the total number of nuclei (equal to the number of electrons), that is, $N = \#(\varepsilon\ell\cap\Omega)$. Equation (43) is the equivalent of (19) in the present case of TFW theory.

We recall that given a set of any finite nuclei $\{X_i\}_{1\leq i\leq N}$, the minimization problem (41) has a unique solution ρ. We refer to [6] for the proof of this result. The function $\mathcal{E}^{\rm TFW}_{\varepsilon,\delta}(u)$ is thus well-defined by (43).

3.2 Infinite periodic systems

The problem of the thermodynamic limit of the above (TFW) model is closely linked with the problem we are dealing with here. Indeed, setting $\tilde\rho(x) = \varepsilon^3\rho(\varepsilon x)$ and changing variables in (42), we get

$$E^{\rm TFW}_\delta(u(\varepsilon\ell\cap\Omega),\rho) = E_0\left[\frac{1}{\varepsilon^2}\left(\int_{\mathbf{R}^3}|\nabla\sqrt{\tilde\rho}|^2 + \int_{\mathbf{R}^3}\tilde\rho^{5/3}\right)\right.$$
$$\left. + \frac{1}{\delta\varepsilon}\left(-\sum_{i\in\ell\cap\frac{1}{\varepsilon}\Omega}\int_{\mathbf{R}^3}\frac{\tilde\rho(x)}{|x-\frac{u(\varepsilon i)}{\varepsilon}|}dx + \frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3}\frac{\tilde\rho(x)\tilde\rho(y)}{|x-y|}dxdy + \frac{1}{2}\sum_{i\neq j\in\ell\cap\frac{1}{\varepsilon}\Omega}\frac{1}{|\frac{u(\varepsilon i)-u(\varepsilon j)}{\varepsilon}|}\right)\right]. \quad (44)$$

In the special case where the function u is linear, $\frac{u(\varepsilon i)}{\varepsilon}$ simplifies into $u(i)$, so that the problem we address here is exactly the problem of finding the limit of the ground state TFW energy as the set of nuclei fills in the lattice $u(\ell)$, which is the thermodynamic limit problem for the TFW model, as dealt with in [14, 15], up to fact that the constants involved in (44) scale properly, namely $\frac{1}{\varepsilon^2}\sim\frac{1}{\delta\varepsilon}$, i.e $\delta\sim\varepsilon$, which is the equivalent of (i) of Theorem 2.1. We recall here the results of [14], which link the TFW energy (44) with the one for an infinite periodic system. Let ℓ be a periodic lattice. Then, for any $\tilde\rho$ such that $\sqrt{\tilde\rho}\in H^1_{\rm per}(\ell)$ (this is the set of functions belonging to $H^1_{\rm loc}(\mathbf{R}^3)$ which are ℓ-periodic):

$$\begin{aligned} E^{\rm TFW}(\tilde\rho,\ell) &= \int_{Q(\ell)}|\nabla\sqrt{\tilde\rho}|^2 + \int_{Q(\ell)}\tilde\rho^{5/3} - \int_{Q(\ell)}\tilde\rho G_\ell \\ &\quad + \frac{1}{2}\int_{Q(\ell)}\int_{Q(\ell)}\tilde\rho(x)G_\ell(x-y)\tilde\rho(y)dxdy, \end{aligned} \quad (45)$$

where $Q(\ell)$ is the primitive unit cell (or any unit cell) of the lattice ℓ, and G_ℓ may be seen as the ℓ-periodic version of the Coulomb potential, and is defined by the following

$$\left\{\begin{array}{l} -\Delta G_\ell = 4\pi\left(\delta_0 - \frac{1}{|Q(\ell)|}\right) \quad \text{in} \quad Q(\ell), \\ G_\ell \quad \text{is} \quad \ell-\text{periodic}, \quad \lim\limits_{|x|\to 0}\left(G_\ell(x) - \frac{1}{|x|}\right) = 0. \end{array}\right. \quad (46)$$

Theorem 3.1 (Thermodynamic limit of the TFW model, [14])
Let Ω be a Lipschitz open bounded subset of $\mathbf{R}^3$. Denote by $E^{\rm TFW}(\ell \cap \frac{1}{\varepsilon}\Omega, \tilde\rho)$ the rescaled TFW energy, that is, (44) with $E_0 = \varepsilon^2$, $\delta = \varepsilon$ and $u = Id$:

$$\begin{aligned} E^{\rm TFW}(\ell \cap \frac{1}{\varepsilon}\Omega, \tilde\rho) &= \int_{\mathbf{R}^3} |\nabla\sqrt{\tilde\rho}|^2 + \int_{\mathbf{R}^3} \tilde\rho^{5/3} - \sum_{i\in\ell\cap\frac{1}{\varepsilon}\Omega} \int_{\mathbf{R}^3} \frac{\tilde\rho(x)}{|x-i|}dx \\ &\quad + \frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3} \frac{\tilde\rho(x)\tilde\rho(y)}{|x-y|}dxdy + \frac{1}{2}\sum_{i\neq j\in\ell\cap\frac{1}{\varepsilon}\Omega} \frac{1}{|i-j|}, \end{aligned} \tag{47}$$

and denote

$$E^{\rm TFW}(\ell \cap \frac{1}{\varepsilon}\Omega) = \frac{1}{N}\inf\Big\{ E_\varepsilon(\ell \cap \frac{1}{\varepsilon}\Omega, \tilde\rho), \quad \tilde\rho \geq 0, \quad \sqrt{\tilde\rho} \in H^1(\mathbf{R}^3), \quad \int_{\mathbf{R}^3} \tilde\rho = N \Big\},$$

with $N = \#(\ell \cap \frac{1}{\varepsilon}\Omega)$. Then, we have

$$\lim_{\varepsilon\to 0} E^{\rm TFW}(\ell \cap \frac{1}{\varepsilon}\Omega) = E^{\rm TFW}(\ell),$$

where $E^{\rm TFW}(\ell)$ is defined by the following minimization problem:

$$E^{\rm TFW}(\ell) = \inf\Big\{ E^{\rm TFW}(\ell, \tilde\rho), \quad \tilde\rho \geq 0, \quad \sqrt{\tilde\rho} \in H^1_{\rm per}(\ell), \quad \int_{Q(\ell)} \tilde\rho = 1 \Big\}, \tag{48}$$

the periodic energy $E^{\rm TFW}(\ell, \tilde\rho)$ being defined in (45), $Q(\ell)$ being a primitive unit cell of the lattice ℓ, and $H^1_{\rm per}(\ell)$ being the set of function in $H^1_{\rm loc}(\mathbf{R}^3)$ which are ℓ-periodic.

In addition, the density $\tilde\rho_\varepsilon$ solution of the minimization problem $E^{\rm TFW}(\ell\cap\frac{1}{\varepsilon}\Omega)$ converges to the solution of $E^{\rm TFW}(\ell)$, uniformly on any set of the form $(\frac{1}{\varepsilon} - \gamma_\varepsilon)\Omega$, where $1 \ll \gamma_\varepsilon \leq \frac{1}{\varepsilon}$.

The energy $E^{\rm TFW}(\tilde\rho, \ell)$ appearing above is defined as follows, The proof of Theorem 3.1 as presented in chapter 5 of [14] is based on the convergence and uniqueness of the solution of the Euler-Lagrange equation of minimization problems $E^{\rm TFW}(\ell \cap \frac{1}{\varepsilon}\Omega)$ and $E^{\rm TFW}(\ell)$. The first one converges in some sense to the second, so that their solutions also converge. This is why we now write down the Euler-Lagrange equation of the minimization problem defining $\mathcal{E}^{\rm TFW}_{\varepsilon,\delta}(u)$ (43). Setting $v = \sqrt{\tilde\rho}$, it reads:

$$-\Delta v + \frac{5}{3}v^{7/3} + \Big(v^2 * \frac{1}{|x|} - \sum_{i\in\ell\cap\frac{1}{\varepsilon}\Omega} \frac{1}{|x-i|} + \theta \Big) v = 0,$$

where θ is the Lagrange multiplier associated with the constraint $\int\tilde\rho = N$. Setting $\phi = -v^2 * \frac{1}{|x|} + \sum_{i\in\ell\cap\frac{1}{\varepsilon}\Omega} \frac{1}{|x-i|} - \theta$, we thus have:

$$\left\{ \begin{array}{l} -\Delta v + \frac{5}{3}v^{7/3} - \phi v = 0, \\ -\Delta\phi = 4\pi\Big(\displaystyle\sum_{i\in\ell\cap\frac{1}{\varepsilon}\Omega} \delta_i - v^2 \Big). \end{array} \right. \tag{49}$$

In the periodic case, the sum over $\ell \cap \frac{1}{\varepsilon}\Omega$ is replaced by a sum over the whole of ℓ. Note that as ε goes to 0, the system (49) converges to the periodic one. Our aim in the following subsection is to adapt the proof of Theorem 3.1 to the case when u is not a linear transformation, but a general C^∞-diffeomorphism.

3.3 Convergence theorem

We give in this subsection the equivalent of Theorem 2.1, together with its proof:

Theorem 3.2 *Let Ω be a Lipschitz open set of $\mathbf{R}^3$, and let u be a C^∞-diffeomeorphism defined on Ω, and ℓ a periodic lattice. Suppose that the volume of the primitive unit cell of ℓ is normalized, i.e $|Q(\ell)| = 1$. Consider the energy $\mathcal{E}_{\varepsilon,\delta}(u)$ defined by (42)-(43). Then, we have:*

(i) If $\varepsilon = \delta$, and if $E_0 = \varepsilon^2$, then we have the following convergence:

$$\lim_{\varepsilon\to 0} \mathcal{E}_{\varepsilon,\delta}(u) = \frac{1}{|\Omega|}\int_\Omega E^{\mathrm{TFW}}(\nabla u(x)\ell)dx, \tag{50}$$

where E^{TFW} is the rescaled TFW energy defined by (48)-(45)-(46).

(ii) If $\varepsilon \ll \delta$, and if $E_0 = \varepsilon^2$, then we have the following convergence:

$$\lim_{\varepsilon\to 0} \mathcal{E}_{\varepsilon,\delta}(u) = \frac{1}{|\Omega|}\int_\Omega \frac{dx}{|\det(\nabla u(x))|^{2/3}}. \tag{51}$$

(iii) If $\delta \ll \varepsilon$, and if $E_0 = \delta^2$, then $\mathcal{E}_{\varepsilon,\delta}(u)$ converges to a constant independent of u. This constant may be identified as the rescaled atomic TFW energy [30].

Proof: We start with the proof of (i). We denote by ρ the solution of the minimization problem (42)-(43) defining $\mathcal{E}_{\varepsilon,\delta}(u)$, and by $\tilde\rho$ the rescaled electronic density, that is, $\tilde\rho(x) = \varepsilon^3\rho(\varepsilon x)$. The proof will be carried out in three steps:

Step 1: We have the following convergence:

$$\lim_{\varepsilon\to 0}\left\| \tilde\rho\big(\cdot + \frac{1}{\varepsilon}u(\varepsilon i)\big) - \rho_{\nabla u(\varepsilon i)\ell}\right\|_{L^\infty(\nabla u(\varepsilon i)Q(\ell))} = 0, \tag{52}$$

the convergence being uniform with respect to $i \in \ell \cap (\frac{1}{\varepsilon} - \frac{1}{\sqrt{\varepsilon}})\Omega$. Here, for any periodic lattice ℓ', the density $\rho_{\ell'}$ is the corresponding TFW electronic density, i.e the solution of (48)-(45)-(46).

In order to show (52), we argue by contradiction (this proof is an adaptation of that of Theorem 5.9 in [14]). Assuming that it does not hold, we deduce the existence of some $x_\varepsilon \in \nabla u(\varepsilon i)Q(\ell)$ such that

$$\left| v(x_\varepsilon + \frac{u(\varepsilon i)}{\varepsilon}) - v_{\nabla u(\varepsilon i)\ell}(x_\varepsilon)\right| \geq \alpha > 0,$$

for some α independent of ε, where $v = \sqrt{\rho}$, and $v_{\nabla u(\varepsilon i)\ell} = \sqrt{\rho_{\nabla u(\varepsilon i)\ell}}$. Using the regularity of u, we point out that the sequence x_ε is compact, so that, up to a subsequence, we may assume that it converges to some $x_0 \in \bigcup_{0<\varepsilon\leq 1} \bigcup_{i\in\ell\cap\frac{1}{\varepsilon}\Omega} \nabla u(\varepsilon i)Q(\ell)$. We recall now that v satisfies the Euler-Lagrange equation of the minimization problem (42)-(43), that is, the equivalent of (49):

$$\left\{\begin{array}{l} -\Delta v + \frac{5}{3}v^{7/3} - \phi v = 0, \\ -\Delta\phi = 4\pi\Big(\sum_{j\in\ell\cap\frac{1}{\varepsilon}\Omega} \delta_{\frac{u(\varepsilon j)}{\varepsilon}} - v^2\Big), \end{array}\right. \tag{53}$$

where the effective potential ϕ may also be defined by $\phi = \sum_{j\in\ell\cap\frac{1}{\varepsilon}\Omega} \frac{1}{|x-\frac{u(\varepsilon j)}{\varepsilon}|} - v^2 * \frac{1}{|x|} - \theta$, the constant θ being the Lagrange multiplier associated to the constraint $\int v^2 = N$ in (43).

Using elliptic regularity results, it is then possible, using the methods of [14] (Propositions 3.8 and 3.12), to show that there exists a constant C independent of ε such that

$$\|v\|_{L^\infty(\mathbf{R}^3)} + \|\phi\|_{L^p_{\rm unif}(\mathbf{R}^3)} + \|\phi\|_{L^\infty(\frac{1}{\varepsilon}\Omega^c)} \leq C, \tag{54}$$

for any $p < 3$. Inserting this information in the first equation of (53), this also implies that v is uniformly continuous on $\mathbf{R}^3$, uniformly with respect to ε. Hence, for sufficiently small an ε, we have

$$\Big|v\big(x_0 + \frac{u(\varepsilon i)}{\varepsilon}\big) - v_{\nabla u(\varepsilon i)\ell}(x_0)\Big| \geq \frac{\alpha}{2}. \tag{55}$$

Now, the bounds we have on v and ϕ are valid for $v(\cdot + \frac{u(\varepsilon i)}{\varepsilon})$ and $\phi(\cdot + \frac{u(\varepsilon i)}{\varepsilon})$, and thus allow to assume, using elliptic regularity and Rellich's theorem, that they converge, up to a subsequence once more, to some $\overline{v}$ and $\overline{\phi}$ in $L^\infty_{\rm loc}(\mathbf{R}^3)$ and $L^p_{\rm loc}(\mathbf{R}^3)$, respectively. We also point out that εi belongs to $\overline{\Omega}$, which is compact, so that we may assume that it converges to some $y \in \overline{\Omega}$. We thus have:

$$\left\{\begin{array}{lll} v\big(\cdot + \frac{u(\varepsilon i)}{\varepsilon}\big) \longrightarrow \overline{v} & \text{in} & L^\infty_{\rm loc}(\mathbf{R}^3), \\ \phi\big(\cdot + \frac{u(\varepsilon i)}{\varepsilon}\big) \longrightarrow \overline{\phi} & \text{in} & L^p_{\rm loc}(\mathbf{R}^3), \\ \varepsilon i \longrightarrow y \in \overline{\Omega}. & & \end{array}\right.$$

We may then pass to the limit in the system satisfied by $v\big(\cdot + \frac{u(\varepsilon i)}{\varepsilon}\big)$ and $\phi\big(\cdot + \frac{u(\varepsilon i)}{\varepsilon}\big)$, that is,

$$\left\{\begin{array}{l} -\Delta v\big(\cdot + \frac{u(\varepsilon i)}{\varepsilon}\big) + -\frac{5}{3}v\big(\cdot + \frac{u(\varepsilon i)}{\varepsilon}\big)^{7/3} - \phi v\big(\cdot + \frac{u(\varepsilon i)}{\varepsilon}\big) = 0, \\ -\Delta\phi\big(\cdot + \frac{u(\varepsilon i)}{\varepsilon}\big) = \sum_{j\in\ell\cap\frac{1}{\varepsilon}\Omega} \delta_{\frac{u(\varepsilon j)}{\varepsilon} - \frac{u(\varepsilon i)}{\varepsilon}} - v\big(\cdot + \frac{u(\varepsilon i)}{\varepsilon}\big)^2. \end{array}\right.$$

Note here that the measure $\sum_{j\in\ell\cap\frac{1}{\varepsilon}\Omega}\delta_{\frac{u(\varepsilon j)}{\varepsilon}-\frac{u(\varepsilon i)}{\varepsilon}}$ converges to the measure $\sum_{j\in\ell}\delta_{\nabla u(y)j}$ in $\mathcal{D}'(\mathbf{R}^3)$, because $\lim_{\varepsilon\to 0} d(i,\frac{1}{\varepsilon}\Omega^c)=+\infty$. Therefore, we have:

$$\left\{\begin{array}{l} -\Delta\overline{v}+\frac{5}{3}\overline{v}^{7/3}-\overline{\phi}-\overline{v}=0,\\ -\Delta\overline{\phi}=4\pi\Big(\sum_{j\in\ell}\delta_{\nabla u(y)j}-\overline{v}^2\Big).\end{array}\right.$$

This system has a unique solution $(v_{\nabla u(y)\ell},\phi_{\nabla u(y)\ell})$ in $L^\infty(\mathbf{R}^3)\times L^1_{\rm unif}(\mathbf{R}^3)$, according to Theorem 6.5 of [14], and therefore we should have $\overline{v}=v_{\nabla u(y)\ell}$. We now reach a contradiction with (55) if we can pass to the limit in (55), that is, if $v_{M\ell}$ is a continuous function of the matrix M. This result is easily shown by repeating the same argument as above. This completes the proof of (52).

Step 2: We have the following convergence:

$$\lim_{\varepsilon\to 0}\Big\|\phi\big(\cdot+\frac{u(\varepsilon i)}{\varepsilon}\big)-\phi_{\nabla u(\varepsilon i)\ell}\Big\|_{L^\infty(\nabla u(\varepsilon i)Q(\ell))}=0, \tag{56}$$

the convergence being uniform with respect to $i\in(\frac{1}{\varepsilon}-\frac{1}{\sqrt{\varepsilon}})\Omega$. Here, for any lattice ℓ', $\phi_{\ell'}$ is the effective potential associated to the density $\rho_{\ell'}$, solution of (48)-(45)-(46). In other words, $v_{\ell'}=\sqrt{\rho_{\ell'}}$ and $\phi_{\ell'}$ are the unique solutions in $L^\infty(\mathbf{R}^3)$ and $L^1_{\rm unif}(\mathbf{R}^3)$ respectively, of the system

$$\left\{\begin{array}{l} -\Delta v+\frac{5}{3}v^{7/3}-\phi v=0,\\ -\Delta\phi=4\pi\Big(\sum_{j\in\ell'}-\delta_j-v^2\Big).\end{array}\right.$$

We skip the proof of (56), since it is an easy adaptation of the one of (52).

Step 3: convergence of the energy. We are now in position to show the desired convergence result. In order to do so, we split the expression of the energy into different terms, which we treat separately. We first show:

$$E_1(\tilde\rho):=\frac{1}{N}\int_{\mathbf{R}^3}\tilde\rho^{5/3}\longrightarrow\frac{1}{|\Omega|}\int_\Omega\Big(\int_{\nabla u(x)Q(\ell)}\rho^{5/3}_{\nabla u(x)\ell}(z)dz\Big)dx,\quad\text{as}\quad\varepsilon\to 0. \tag{57}$$

We separate this integral into a sum of integrals over domains which will *in fine* converge to the unit cell $\nabla u(x)Q(\ell)=Q(\nabla u(x)\ell)$:

$$E_1(\tilde\rho):=\frac{1}{N}\sum_{j\in\ell\cap\frac{1}{\varepsilon}\Omega}\int_{\frac{1}{\varepsilon}u(\varepsilon j+\varepsilon Q(\ell))}\tilde\rho^{5/3}+\frac{1}{N}\sum_{j\in\ell\cap\frac{1}{\varepsilon}\Omega^c}\int_{\frac{1}{\varepsilon}u(\varepsilon j+\varepsilon Q(\ell))}\tilde\rho^{5/3}.$$

We first deal with the first sum: we have

$$\begin{aligned}\int_{\frac{1}{\varepsilon}u(\varepsilon j+\varepsilon Q(\ell))}\tilde\rho^{5/3} &= \int_{\frac{1}{\varepsilon}(u(\varepsilon j+\varepsilon Q(\ell))-u(\varepsilon j))}\tilde\rho^{5/3}(z+\frac{1}{\varepsilon}u(\varepsilon j))dz\\ &= \int_{\nabla u(\varepsilon j)Q(\ell)}\rho^{5/3}_{\nabla u(\varepsilon j)\ell}(z)dz+o(1),\end{aligned}$$

uniformly with respect to $j \in (\frac{1}{\varepsilon} - \frac{1}{\sqrt{\varepsilon}})\Omega$ according to (52) and the fact that $\Big|\nabla u(\varepsilon j)Q(\ell) \setminus \frac{1}{\varepsilon}\big(u(\varepsilon j+\varepsilon Q(\ell))-u(\varepsilon j)\big)\Big| + \Big|\frac{1}{\varepsilon}\big(u(\varepsilon j+\varepsilon Q(\ell))-u(\varepsilon j)\big) \setminus \nabla u(\varepsilon j)Q(\ell)\Big|$ converges to 0 uniformly with respect to $j \in (\frac{1}{\varepsilon} - \frac{1}{\sqrt{\varepsilon}})\Omega$. Hence, using that $\tilde{\rho}$ is bounded independently of ε to show that boundary terms $j \in \frac{1}{\varepsilon}\Omega \setminus (\frac{1}{\varepsilon} - \frac{1}{\sqrt{\varepsilon}})\Omega$ have a neglectable contribution, we deduce that

$$E_1(\tilde{\rho}) = \frac{1}{N} \sum_{j \in \ell \cap \frac{1}{\varepsilon}\Omega} \int_{\nabla u(\varepsilon j)Q(\ell)} \rho_{\nabla u(\varepsilon j)\ell}^{5/3} + \frac{1}{N} \sum_{j \in \ell \cap \frac{1}{\varepsilon}\Omega^c} \int_{\frac{1}{\varepsilon}u(\varepsilon j+\varepsilon Q(\ell))} \tilde{\rho}^{5/3} + o(1).$$

The first sum may be identified as the Riemann sum converging to the desired integral. Hence, in order to conclude the proof of (57), we only need to show that the second sum converges to 0. In order to do so, we point out that the same argument as above allows to show that

$$\begin{aligned} 1 = \frac{1}{N}\int_{\mathbf{R}^3} \tilde{\rho} &= \frac{1}{N} \sum_{j \in \ell \cap \frac{1}{\varepsilon}\Omega} \int_{\nabla u(\varepsilon j)Q(\ell)} \rho_{\nabla u(\varepsilon j)\ell} + \frac{1}{N} \sum_{j \in \ell \cap \frac{1}{\varepsilon}\Omega^c} \int_{\nabla u(\varepsilon j)Q(\ell)} \tilde{\rho} + o(1) \\ &= 1 + \int_{\frac{1}{\varepsilon}\Omega^c} \tilde{\rho} + o(1), \end{aligned}$$

so that

$$\lim_{\varepsilon \to 0} \int_{\frac{1}{\varepsilon}\Omega^c} \tilde{\rho} = 0. \tag{58}$$

This, together with the fact that $\tilde{\rho}$ is uniformly bounded in $\mathbf{R}^3$, allows to show that $\int_{\frac{1}{\varepsilon}\Omega^c} \tilde{\rho}^{5/3} = o(1)$, concluding the proof of (57).

We now turn to the second term of the energy, and show the following convergence:

$$E_2(\tilde{\rho}) := \frac{1}{N}\int_{\mathbf{R}^3} |\nabla\sqrt{\tilde{\rho}}|^2 \longrightarrow \frac{1}{|\Omega|}\int_\Omega \left(\int_{\nabla u(x)Q(\ell)} |\nabla\sqrt{\rho_{\nabla u(x)\ell}}|^2\right) dx \tag{59}$$

We proceed here in the same way as for (57), showing first that the exterior contribution is neglectable. In order to do so, we recall that, using the same notations as in step 1, we have

$$-\Delta v + \frac{5}{3}v^{7/3} - \phi v = 0,$$

so that, multiplying this equation by v and integrating over $\frac{1}{\varepsilon}\Omega^c$, we have

$$\frac{1}{N}\int_{\frac{1}{\varepsilon}\Omega^c} (-\Delta v)v = \frac{1}{N}\int_{\frac{1}{\varepsilon}\Omega^c} \phi\tilde{\rho} - \frac{1}{N}\int_{\frac{1}{\varepsilon}\Omega^c} \frac{5}{3}\tilde{\rho}^{5/3} = o(1),$$

according to (54) and (58). Next, we use elliptic regularity to show that $\frac{1}{N}\int_{\partial(\frac{1}{\varepsilon}\Omega)} v\frac{\partial v}{\partial n} = o(1)$, thereby proving that

$$\lim_{\varepsilon \to 0} \frac{1}{N}\int_{\frac{1}{\varepsilon}\Omega^c} |\nabla v|^2 = 0.$$

Now, using elliptic regularity here again, one easily sees that ∇v is bounded in $L^2_{\rm unif}(\mathbf{R}^3)$, so that

$$E_2(\tilde\rho) = \frac{1}{N} \sum_{j\in\ell\cap(\frac{1}{\varepsilon}-\frac{1}{\sqrt{\varepsilon}})\Omega} \int_{\frac{1}{\varepsilon}u(\varepsilon j+\varepsilon Q(\ell))} |\nabla v|^2 + o(1).$$

Following the proof of (57), what we need here in order to conclude is the following convergence result:

$$\Big\| \nabla v - \nabla v_{\nabla u(\varepsilon i\ell)} \Big\|_{L^2(\nabla u(\varepsilon i)Q(\ell))} \longrightarrow 0 \quad \text{as} \quad \varepsilon\to 0,$$

uniformly with respect to $i \in (\frac{1}{\varepsilon} - \frac{1}{\sqrt{\varepsilon}})\Omega$. This result is easily proved using (52) and (56) and the first equation of (53). This allows to conclude the proof of (59).

We finally deal with the electrostatic terms of the energy, which is more intricate than (57) and (59). We recall that the electrostatic energy reads:

$$\frac{1}{N}\Big(- \sum_{i\in\ell\cap\frac{1}{\varepsilon}\Omega} \int_{\mathbf{R}^3} \frac{\tilde\rho(x)}{|x-\frac{u(\varepsilon i)}{\varepsilon}|}dx + \frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3} \frac{\tilde\rho(x)\tilde\rho(y)}{|x-y|}dxdy + \frac{1}{2} \sum_{i\neq j\in\ell\cap\frac{1}{\varepsilon}\Omega} \frac{\varepsilon}{|u(\varepsilon i)-u(\varepsilon j)|}\Big)$$
$$= -\frac{1}{2N}\int_{\mathbf{R}^3}\phi\tilde\rho + \frac{1}{2N}\sum_{i\in\ell\cap\frac{1}{\varepsilon}\Omega}\Big(\lim_{x\to\frac{u(\varepsilon i)}{\varepsilon}} \big(\phi(x) - \frac{1}{|x-\frac{u(\varepsilon i)}{\varepsilon}|}\big)\Big). \quad (60)$$

Here we have used the definition of ϕ, that is, $\phi = \displaystyle\sum_{i\in\ell\cap\frac{1}{\varepsilon}\Omega} \frac{1}{|x-\frac{u(\varepsilon i)}{\varepsilon}|} - \tilde\rho * \frac{1}{|x|} - \theta$. We may deal separately with each term of the right-hand side of (60). The first term is easily treated using the same arguments as for (57), based on (52), (56) and (54), showing:

$$E_3(\tilde\rho) := -\frac{1}{2N}\int_{\mathbf{R}^3}\phi\tilde\rho \longrightarrow -\frac{1}{2|\Omega|}\int_\Omega \Big(\int_{\nabla u(x)Q(\ell)} \phi_{\nabla u(x)\ell}\rho_{\nabla u(x)\ell}\Big)dx \quad \text{as} \quad \varepsilon\to 0. \quad (61)$$

We now deal with the last term of (60), and show the following:

$$E_4(\tilde\rho) := \frac{1}{2N}\sum_{i\in\ell\cap\frac{1}{\varepsilon}\Omega}\Big(\lim_{y\to\frac{u(\varepsilon i)}{\varepsilon}} \big(\phi(y) - \frac{1}{|y-\frac{u(\varepsilon i)}{\varepsilon}|}\big)\Big) \longrightarrow \frac{1}{2|\Omega|}\int_\Omega \Big(\lim_{y\to 0}\big(\phi_{\nabla u(x)\ell}(y) - \frac{1}{|y|}\big)\Big)dx \quad (62)$$

as $\varepsilon\to 0$. Here again, we copy the proof of (57), separating into terms $i \in (\frac{1}{\varepsilon} - \frac{1}{\sqrt{\varepsilon}})\Omega$ and those belonging to $\frac{1}{\varepsilon}\Omega \setminus (\frac{1}{\varepsilon} - \frac{1}{\sqrt{\varepsilon}})\Omega$. For the first part, the use of (56) allows to conclude. In order to show that the remaining terms are neglectable, i.e that

$$\frac{1}{N}\sum_{i\in\ell\cap(\frac{1}{\varepsilon}\Omega\setminus\frac{1}{\sqrt{\varepsilon}}\Omega)} \Big(\lim_{y\to 0}\big(\phi(y+\frac{u(\varepsilon i)}{\varepsilon}) - \frac{1}{|y|}\big)\Big) = o(1), \quad (63)$$

we use the second equation of (53), and (54), getting

$$\Big| -\Delta\big(\phi(x+\frac{u(\varepsilon i)}{\varepsilon}) - \frac{1}{|x|}\big)\Big| \le C$$

on some ball B_α, with $\alpha > 0$ and C independent of i and ε, provided ε is sufficiently small. Hence, using the fact that ϕ is bounded in $L^1_{\rm unif}(\mathbf{R}^3)$ and the mean value inequality, this implies that

$$\left|\phi(x + \frac{u(\varepsilon i)}{\varepsilon}) - \frac{1}{|x|}\right| \leq C \quad \forall x \in B_\alpha.$$

This estimate allows to conclude that (63) holds, ending the proof of (62).

There only remain now to collect (57), (59), (61) and (62), and to point out that, for all $x \in \Omega$,

$$\begin{aligned} &- \int_{\nabla u(x)Q(\ell)} G_{\nabla u(x)Q(\ell)}\rho_{\nabla u(x)\ell} \\ &\qquad + \frac{1}{2}\int_{\nabla u(x)Q(\ell)}\int_{\nabla u(x)Q(\ell)} \rho_{\nabla u(x)\ell}(z)G_{\nabla u(x)\ell}(z-y)\rho_{\nabla u(x)\ell}(y)dydz = \\ &\qquad\qquad - \frac{1}{2}\int_{\nabla u(x)Q(\ell)} \phi_{\nabla u(x)\ell}\rho_{\nabla u(x)\ell} + \frac{1}{2}\lim_{y\to 0}(\phi_{\nabla u(x)\ell}(y) - \frac{1}{|y|}), \end{aligned}$$

to conclude the proof of (i).

We now prove (ii). Here again, we first rescale the density ρ, setting $\tilde\rho(x) = \varepsilon^3\rho(\varepsilon x)$. The energy may then be written as:

$$\begin{aligned} &\mathcal{E}_{\varepsilon,\delta}(u) = \frac{1}{N}\left[\int_{\mathbf{R}^3} |\nabla\sqrt{\tilde\rho}|^2 + \int_{\mathbf{R}^3}\tilde\rho^{5/3}\right. \\ &\left. + \frac{\varepsilon}{\delta}\Big(-\sum_{j\in\ell\cap\frac{1}{\varepsilon}\Omega}\int_{\mathbf{R}^3}\frac{\tilde\rho(x)}{|x-\frac{u(\varepsilon j)}{\varepsilon}|} + \frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3}\frac{\tilde\rho(x)\tilde\rho(y)}{|x-y|}dxdy + \frac{1}{2}\sum_{i\neq j\in\ell\cap\frac{1}{\varepsilon}\Omega}\frac{\varepsilon}{|u(\varepsilon i)-u(\varepsilon j)|}\Big)\right], \end{aligned}$$

Next, we follow exactly the steps of the proof of (i), except that here, ε and δ appear as parameters in the system satisfied by $v = \sqrt{\tilde\rho}$ and $\phi = \displaystyle\sum_{j\in\ell\cap\frac{1}{\varepsilon}\Omega}\frac{1}{|x-\frac{u(\varepsilon j)}{\varepsilon}|} - v^2 * \frac{1}{|x|} + \frac{\delta}{\varepsilon}\theta$. We give the main ingredients, skipping their proofs since they involve the same arguments as above:

$$\|v\|_{L^\infty(\mathbf{R}^3)} + \frac{\varepsilon}{\delta}\big(\|\phi\|_{L^p_{\rm unif}(\mathbf{R}^3)} + \|\phi\|_{L^\infty(\frac{1}{\varepsilon}\Omega^c)}\big) \leq C,$$

for any $p < 3$, and

$$\lim_{\varepsilon\ll\delta\to 0}\left\|\tilde\rho\big(\cdot + \frac{u(\varepsilon i)}{\varepsilon}\big) - \frac{\varepsilon}{|u(\varepsilon i + \varepsilon Q(\ell))|}\right\|_{L^\infty(\nabla u(\varepsilon i)Q(\ell))} = 0,$$

$$\lim_{\varepsilon\ll\delta\to 0}\left\|\frac{\varepsilon}{\delta}\phi\big(\cdot + \frac{u(\varepsilon i)}{\varepsilon}\big) - \frac{\varepsilon^{2/3}}{|u(\varepsilon i + \varepsilon Q(\ell))|^{2/3}}\right\|_{L^2(\nabla u(\varepsilon i)Q(\ell))} = 0,$$

uniformly with respect to $i \in \ell\cap(\frac{1}{\varepsilon} - \frac{1}{\sqrt{\varepsilon}})\Omega$. With these convergence results, one then easily shows that all terms of the energy converge to 0 except the term $\int\tilde\rho^{5/3}$, which converges to the desired quantity.

Let us now prove (iii). Here again, it is possible to study the convergence of the density and deduce from it the convergence of the energy. But we will provide an alternate and more direct proof using the fact that we deal with a minimization problem. Once again we rescale ρ, but here the rescaling parameter will be δ instead of ε. We thus set $\tilde{\rho}(x) = \delta^3 \rho(\delta x)$. Then, the energy reads:

$$\mathcal{E}_{\varepsilon,\delta}(u) = \frac{1}{N}\Big(\int_{\mathbf{R}^3} |\nabla \sqrt{\tilde{\rho}}|^2 + \int_{\mathbf{R}^3} \tilde{\rho}^{5/3} - \sum_{j \in \ell \cap \frac{1}{\varepsilon}\Omega} \int_{\mathbf{R}^3} \frac{\tilde{\rho}(x)}{|x - \frac{u(\varepsilon j)}{\delta}|} + \frac{1}{2} \int_{\mathbf{R}^3} \int_{\mathbf{R}^3} \frac{\tilde{\rho}(x)\tilde{\rho}(y)}{|x-y|} dxdy + \frac{1}{2} \sum_{i \neq j \in \ell \cap \frac{1}{\varepsilon}\Omega} \frac{\delta}{|u(\varepsilon i) - u(\varepsilon j)|} \Big) = \frac{1}{N} E^{\mathrm{TFW}}\big(\frac{u(\varepsilon \ell \cap \Omega)}{\delta}\big),$$

the term $E^{\mathrm{TFW}}\big(\frac{u(\varepsilon\ell\cap\Omega)}{\delta}\big)$ denoting the solution of the minimization problem

$$E^{\mathrm{TFW}}\big(\frac{u(\varepsilon \ell \cap \Omega)}{\delta}\big) = \inf\Big\{ E^{\mathrm{TFW}}\big(\frac{u(\varepsilon \ell \cap \Omega)}{\delta}, \tilde{\rho}\big), \quad \tilde{\rho} \geq 0, \quad \sqrt{\tilde{\rho}} \in H^1(\mathbf{R}^3), \quad \int_{\mathbf{R}^3} \tilde{\rho} = N \Big\}, \tag{64}$$

the energy $E^{\mathrm{TFW}}\big(\frac{u(\varepsilon\ell\cap\Omega)}{\delta}, \tilde{\rho}\big)$ being the rescaled TFW energy (47).

Let now ρ_0 be a non-negative radial compactly-supported smooth function of total mass 1. Using the function $\eta(x) = \sum_{j \in \frac{u(\varepsilon\ell\cap\Omega)}{\delta}} \rho_0(x-j)$, as a test function for the minimization problem (64), we have:

$$\mathcal{E}_{\varepsilon,\delta}(u) \leq \frac{1}{N} E^{\mathrm{TFW}}\big(\frac{u(\varepsilon \ell \cap \Omega)}{\delta}, \eta\big).$$

We now point out that, for $\frac{\varepsilon}{\delta}$ large enough, the terms of the sum defining η have disjoint supports, so that we have:

$$\int_{\mathbf{R}^3} |\nabla \sqrt{\eta}|^2 + \int_{\mathbf{R}^3} \eta^{5/3} = N \int_{\mathbf{R}^3} |\nabla \sqrt{\rho_0}|^2 + N \int_{\mathbf{R}^3} \rho_0^{5/3}.$$

Next, in order to compute the electrostatic terms, we point out that since ρ_0 is radially symmetric, has compact support and total mass one, the function $\rho_0 * \frac{1}{|x|} - \frac{1}{|x|}$ has its support included in that of ρ_0. Therefore, we have if $\frac{\varepsilon}{\delta}$ is large enough:

$$-\frac{1}{2} \sum_{j \in \ell \cap \frac{1}{\varepsilon}\Omega} \int_{\mathbf{R}^3} \frac{\eta(x)}{|x - \frac{u(\varepsilon j)}{\delta}|} dx + \frac{1}{2} \int_{\mathbf{R}^3} \int_{\mathbf{R}^3} \frac{\eta(x)\eta(y)}{|x-y|} dxdy = -\frac{1}{2} \int_{\mathbf{R}^3} \eta(x) \sum_{j \in \ell \cap \frac{1}{\varepsilon}\Omega} \Big(\frac{1}{|x - \frac{u(\varepsilon j)}{\delta}|} - \big(\rho_0 * \frac{1}{|x|}\big)(x - \frac{u(\varepsilon j)}{\delta}) \Big) dx = \frac{N}{2} \int_{\mathbf{R}^3} \rho_0(x) \big(-\frac{1}{|x|} + \rho_0 * \frac{1}{|x|} \big) dx.$$

Similarly,

$$-\frac{1}{2}\sum_{j\in\ell\cap\frac{1}{\varepsilon}\Omega}\int_{\mathbf{R}^3}\frac{\eta(x)}{|x-\frac{u(\varepsilon j)}{\delta}|}dx+\frac{1}{2}\sum_{i\neq j\in\ell\cap\frac{1}{\varepsilon}\Omega}\frac{\delta}{|u(\varepsilon i)-u(\varepsilon j)|}=-\frac{N}{2}\int_{\mathbf{R}^3}\frac{\rho_0(x)}{|x|}dx.$$

Collecting these computations, we thus have:

$$\mathcal{E}_{\varepsilon,\delta}(u)\leq\int_{\mathbf{R}^3}|\nabla\sqrt{\rho_0}|^2+\int_{\mathbf{R}^3}\rho_0^{5/3}-\int_{\mathbf{R}^3}\frac{\rho_0(x)}{|x|}dx+\frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3}\frac{\rho_0(x)\rho_0(y)}{|x-y|}dxdy, \tag{65}$$

for any smooth radially symmetric $\rho_0\geq 0$ having compact support. We now define the TFW atomic energy:

$$I_{\rm at}^{\rm TFW}(\lambda)=\inf\Big\{E_{\rm at}^{\rm TFW}(\rho),\quad \rho\geq 0,\quad \sqrt{\rho}\in H^1(\mathbf{R}^3),\quad \int_{\mathbf{R}^3}\rho=\lambda\Big\}, \tag{66}$$

with

$$E_{\rm at}^{\rm TFW}(\rho)=\int_{\mathbf{R}^3}|\nabla\sqrt{\rho}|^2+\int_{\mathbf{R}^3}\rho^{5/3}-\int_{\mathbf{R}^3}\frac{\rho(x)}{|x|}dx+\frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3}\frac{\rho(x)\rho(y)}{|x-y|}dxdy. \tag{67}$$

This minimization problem has been studied in [6], where it is shown that it has a unique minimizer for all $\lambda\leq\lambda_c$, for some $\lambda_c>1$, which is radially symmetric. Hence, in (65), we may use a sequence of functions ρ_0 converging to the unique minimizer of (66), getting

$$\limsup_{\delta\ll\varepsilon\to 0}\mathcal{E}_{\varepsilon,\delta}(u)\leq I_{\rm at}^{\rm TFW}(1). \tag{68}$$

There only remains to prove the reverse inequality. In order to do so, we come back to the function ρ which achieves the minimum defining $\mathcal{E}_{\varepsilon,\delta}(u)$, and the corresponding rescaled density $\tilde{\rho}=\delta^3\rho(\delta x)$. Setting $v=\sqrt{\tilde{\rho}}$, we write down the Euler-Lagrange equation satisfied by v, that is:

$$\begin{cases}-\Delta v+\frac{5}{3}v^{7/3}-\phi v=0,\\ -\Delta\phi=4\pi\Big(\sum\limits_{j\in\ell\cap\frac{1}{\varepsilon}\Omega}\delta_{\frac{u(\varepsilon j)}{\delta}}-v^2\Big).\end{cases}$$

Using this system of equations, it is possible to adapt the methods introduced in [14] (Propositions 3.8, 3.10 and 3.12), in order to have

$$\|v\|_{L^\infty(\mathbf{R}^3)}+\|\phi\|_{L^p_{\rm unif}(\mathbf{R}^3)}\leq C,$$

for any $p<3$, with C independent of ε and δ. Using elliptic regularity and Rellich theorem, we may thus assume that for all $j\in\ell\cap\frac{1}{\varepsilon}\Omega$, $\sqrt{\tilde{\rho}}(\cdot+\frac{u(\varepsilon j)}{\delta})$ converges weakly in $H^1_{\rm loc}(\mathbf{R}^3)$ and strongly in $L^2_{\rm loc}(\mathbf{R}^3)$ to some $v_j=\sqrt{\rho_j}$. Fixing a radius $R>0$, we have, for $\frac{\varepsilon}{\delta}$ large enough:

$$\liminf_{\delta\ll\varepsilon\to 0}\int_{B_{\sqrt{\frac{\varepsilon}{\delta}}(\frac{u(\varepsilon j)}{\delta})}}|\nabla\sqrt{\tilde{\rho}}|^2\geq\liminf_{\delta\ll\varepsilon\to 0}\int_{B_R(\frac{u(\varepsilon j)}{\delta})}|\nabla\sqrt{\tilde{\rho}}|^2\geq\int_{B_R}|\nabla\sqrt{\rho_j}|^2,$$

and similarly for $\int \rho^{5/3}$. Hence, letting R go to infinity, we have

$$\liminf_{\delta \ll \varepsilon \to 0} \frac{1}{N}\left(\int_{\mathbf{R}^3} |\nabla \sqrt{\tilde{\rho}}|^2 + \int_{\mathbf{R}^3} \rho^{5/3}\right) \geq \liminf_{\varepsilon \to 0} \frac{1}{N} \sum_{j \in \ell \cap \frac{1}{\varepsilon}\Omega} \left(\int_{\mathbf{R}^3} |\nabla \sqrt{\rho_j}|^2 + \int_{\mathbf{R}^3} \rho_j^{5/3}\right).$$

Next, we use the bounds we have on ϕ and ρ, getting that $\Delta(\phi - \frac{1}{|x - \frac{u(\varepsilon i)}{\delta}|})$ is bounded in $L^\infty(B_{\sqrt{\frac{\varepsilon}{\delta}}})$, so that $\phi(x + \frac{u(\varepsilon j)}{\delta}) - \frac{1}{|x|}$ converges in $L^\infty_{\rm loc}(\mathbf{R}^3)$ to some $\phi_j - \frac{1}{|x|} \in L^\infty(\mathbf{R}^3)$ such that ϕ_j satisfies $-\Delta \phi_j = \delta_0 - \rho_j$. We now point out that the method used in [7] (Propositions 4.2 and 4.3) is easily adapted to the present case, and yields:

$$\max\big(\phi(x), |v(x)|^{4/3}\big) \leq \frac{C}{|x - \frac{u(\varepsilon i)}{\delta}|^2} + \sum_{j \in \ell \cap \frac{1}{\varepsilon}\Omega} \frac{C}{|x - \frac{u(\varepsilon j)}{\delta}|^4},$$

for all x such that $|x - \dfrac{u(\varepsilon i)}{\delta}| \leq \inf\limits_{j \in \ell \cap \frac{1}{\varepsilon}\Omega \setminus \{i\}} |x - \dfrac{u(\varepsilon j)}{\delta}|$. This allows us to pass to the limit in the term $-\int \rho\phi$, getting

$$\begin{aligned}
\liminf_{\delta \ll \varepsilon \to 0} \frac{1}{N}\left(-\int_{\mathbf{R}^3} \tilde{\rho}\phi\right) &= \liminf_{\delta \ll \varepsilon \to 0} \frac{1}{N} \sum_{j \in \ell \cap \frac{1}{\varepsilon}\Omega} \left(-\int_{B_{\sqrt{\frac{\delta}{\varepsilon}}(\frac{u(\varepsilon j)}{\delta})}} \tilde{\rho}\phi\right) \\
&= \liminf_{\varepsilon \to 0} \frac{1}{N} \sum_{j \in \ell \cap \frac{1}{\varepsilon}\Omega} \left(-\int_{\mathbf{R}^3} \rho_j \phi_j .\right).
\end{aligned}$$

Finally, it is easy to adapt the proof of step 2 of (i) in order to show that the convergence of $\phi(x + \frac{u(\varepsilon j)}{\delta}) - \frac{1}{|x|}$ to $\phi_j - \frac{1}{|x|}$ is uniform with respect to $j \in \ell \cap (\frac{1}{\varepsilon} - \frac{1}{\sqrt{\varepsilon}})\Omega$, getting

$$\lim \frac{1}{N} \sum_{j \in \ell \cap \frac{1}{\varepsilon}\Omega} \lim_{x \to 0} \big(\phi(x + \frac{u(\varepsilon j)}{\delta}) - \frac{1}{|x|}\big) = \lim \frac{1}{N} \sum_{j \in \ell \cap \frac{1}{\varepsilon}\Omega} \lim_{x \to 0} \big(\phi_j(x) - \frac{1}{|x|}\big).$$

Hence, pointing out that $\phi_j = \frac{1}{|x|} - \rho_j * \frac{1}{|x|} + \theta_j$, for some constant θ_j, we deduce that $-\frac{1}{2}\int_{\mathbf{R}^3} \rho_j \phi_j + \frac{1}{2} \lim_{x \to 0}(\phi_j - \frac{1}{|x|}) = -\int \frac{\rho(x)}{|x|} dx + \frac{1}{2}\int\int \frac{\rho(x)\rho(y)}{|x-y|} dxdy$. Gathering all these results, we have

$$\liminf_{\delta \ll \varepsilon \to 0} \mathcal{E}_{\varepsilon,\delta}(u) \geq \liminf_{\varepsilon \to 0} \frac{1}{N} \sum_{j \in \ell \cap \frac{1}{\varepsilon}\Omega} E^{\rm TFW}_{\rm at}(\rho_j) \geq \liminf_{\varepsilon \to 0} \frac{1}{N} \sum_{j \in \ell \cap \frac{1}{\varepsilon}\Omega} I^{\rm TFW}_{\rm at}(\lambda_j),$$

with $\lambda_j = \int \rho_j$. Now, the function $I^{\rm TFW}_{\rm at}(\lambda)$ is convex non-increasing with respect to $\lambda \in \mathbf{R}^+$. Since in addition $\frac{1}{N}\sum \lambda_j \leq 1$, we conclude that

$$\liminf_{\delta \ll \varepsilon \to 0} \mathcal{E}_{\varepsilon,\delta}(u) \geq I^{\rm TFW}_{\rm at}(1). \tag{69}$$

This concludes the proof of (iii). $\Diamond$

Remark 3.3 *Let us point out that the method used in the proof of (iii), based on variational methods, could be used in the proof (i) and (ii) as well. However, and although it seems more natural, it would be considerably more delicate.*

4 Possible extensions

We indicate in this section some direct consequences of the above results, and natural extensions of them. There are mainly two types of extensions: those concerning the microscopic model (the electronic problem), and those concerning the geometry of the atoms.

4.1 Changing the model describing the electrons

In Section 3, we have dealt with Thomas-Fermi type models, which are very crude theories compared to the model they are supposed to approximate, namely, Schrödinger equation. (The approximation of two-body potentials, used in Section 2, is even cruder.)

However, the methods used in this section are intimately linked with the thermodynamic limit problem [14, 30]. More precisely, it seems that the existence of a thermodynamic limit allows one to pass to the limit $\varepsilon = \delta \to 0$, at least in the two cases of two-body potentials and Thomas-Fermi type models. Hence, formulas (21) and (50) are likely to be adaptable to other models, such as for instance Hartree-Fock models [31, 32]. In this case, although the thermodynamic limit has not yet been fully justified, it is possible (see [16]) to derive it formally. Therefore, the elastic energy

$$\mathcal{E}(u) = \frac{1}{|\Omega|} \int_\Omega E^{\mathrm{HF}}(\nabla u(x)\ell) dx,$$

where $E^{\mathrm{HF}}(\ell)$ is the Hartree-Fock energy of the lattice ℓ, defined in [16], is a good candidate to be the elastic Hartree-Fock energy. The same remarks hold for any quantum model.

In the case of the true Schrödinger equation, the difficulty is, as far as we know, that there is no derivation, even formally, of any thermodynamic limit of the model. More precisely, it is clearly possible to derive an energy functional, but the associated variational space is not so easy to guess [20].

Let us make a final remark about these quantum models: in the case of Thomas-Fermi model, that is, when we forget the term $\int |\nabla\sqrt{\rho}|^2$ in the energy (40), we have:

$$E^{\mathrm{TF}}(\{X_i\}, \rho) = \frac{\hbar^2}{m} \int_{\mathbf{R}^3} \rho^{5/3} + \frac{e^2}{4\pi\varepsilon_0} \left(-\sum_{j=1}^{M} \int_{\mathbf{R}^3} \frac{\rho(x)}{|x - X_j|} dx + \frac{1}{2} \int_{\mathbf{R}^3} \int_{\mathbf{R}^3} \frac{\rho(x)\rho(y)}{|x-y|} dx dy + \frac{1}{2} \sum_{i \neq j} \frac{1}{|X_i - X_j|} \right), \quad (70)$$

where we have used the same notations as in (40), setting the nuclear charges Z_j to 1. Let us for a while forget the physical constant, and assume that $\frac{\hbar^2}{m} = 1$ and $\frac{e^2}{4\pi\varepsilon_0} = 1$ in the system of units we use. A simple dimensional argument shows that the power $\frac{5}{3}$ appearing in (70) is in fact equal to $\frac{d+2}{d}$, where d is the dimension of the space (three in our case). Therefore, if we consider the corresponding two-dimensional model, the power we should

use is 2, so that in this case (70) reads:

$$E^{\mathrm{TF}}(\{X_i\},\rho) = \int_{\mathbf{R}^2} \rho^2 + \sum_{j=1}^{M} \int_{\mathbf{R}^2} \rho(x)\log(|x-X_j|)dx \\ -\frac{1}{2}\int_{\mathbf{R}^2}\int_{\mathbf{R}^2} \rho(x)\log(|x-y|)\rho(y)dxdy - \frac{1}{2}\sum_{i\neq j}\log(|X_i-X_j|). \quad (71)$$

Note that, dealing with a two-dimensional model, we have replaced the three-dimensional Coulomb potential $\frac{1}{|x|}$ by the two-dimensional one $-\log(|x|)$. The energy being quadratic with respect to ρ, the Euler-Lagrange equation of the problem

$$E^{\mathrm{TF}}(\{X_i\}) = \inf\Big\{ E^{\mathrm{TF}}(\{X_i\},\rho), \quad \rho\geq 0, \quad \rho\in L^1(\mathbf{R}^2)\cap L^2(\mathbf{R}^2), \\ \log(2+|x|)\rho\in L^1(\mathbf{R}^2), \quad \int_{\mathbf{R}^2}\rho = N\Big\} \quad (72)$$

is linear with respect to ρ. Assuming neutrality, that is, $N=M$, it reads

$$2\rho + \sum_{j=1}^{N}\log(|x-X_i|) - \rho * \log(|x|) + \theta = 0, \quad (73)$$

where θ is the Lagrange multiplier associated to the mass constraint. Now, taking the Laplacian of this equation, we have:

$$-\Delta\rho + \frac{1}{2}\rho = 2\pi\sum_{j=1}^{N}\delta_{X_j}, \quad (74)$$

with $\rho\in L^1(\mathbf{R}^2)$. This equation is easily solved, using the Yukawa potential in dimension two, that is the solution W of $-\Delta W + \frac{1}{2}W = 2\pi\delta_0$ going to zero at infinity. W is nothing else, in fact, than $K_0(\frac{|x|}{\sqrt{2}})$, where K_0 is the Bessel function of the second kind as defined in [1]. Hence, we have the equality:

$$\rho(x) = \sum_{j=1}^{N} W(x-X_j). \quad (75)$$

We now go back to the expression of the energy (70), and using (73) and (75), we have:

$$\begin{aligned} E^{\mathrm{TF}}(\{X_i\},\rho) &= \int_{\mathbf{R}^2}\rho^2 + \frac{1}{2}\int_{\mathbf{R}^2}\rho(x)\Big(\sum_{i=1}^{N}\log|x-X_i| - \rho*\log|x|\Big)dx \\ &\quad + \frac{1}{2}\sum_{j=1}^{N}\Big(\int_{\mathbf{R}^2}\rho(x)\log|x-X_j|dx - \sum_{i\neq j}\log|X_i-X_j|\Big) \\ &= \int_{\mathbf{R}^2}\rho^2 + \frac{1}{2}\int_{\mathbf{R}^2}\rho(-2\rho-\theta) + \frac{1}{2}\sum_{j=1}^{N}\big(2\rho+\theta+\log(|\cdot-X_j|)\big)(X_j) \end{aligned}$$

Thus,

$$\begin{aligned} E^{\mathrm{TF}}(\{X_i\},\rho) &= \sum_{j=1}^{N}\big(\rho+\frac{1}{2}\log(|\cdot-X_j|)\big)(X_j) \\ &= \sum_{i\neq j} W(X_i-X_j)+N\lim_{x\to 0}\big(W(x)+\frac{1}{2}\log(|x|)\big). \end{aligned}$$

Hence, up to an additive constant, the energy (72) may be expressed in terms of the two-body potential W: **the two-dimensional TF model may be recast into a two-body model**, and therefore enters the scope of Section 2. Note that, according to the proof of (ii) of Theorem 3.2, the link between the power p appearing in (51) and the power q appearing in the microscopic energy (40) is $p=q-1$, which ensures that in the present case formulas (22) and (51) become equivalent.

4.2 Changing the microscopic geometry of the atoms

We now give a few remarks about the microscopic arrangement of the atoms: so far, we have assumed that they are periodically distributed. Since this assumption is not always physically satisfactory, the same problem should be addressed in some other cases.

Our first point is a direct improvement of the preceding sections, and is concerned with polycrystalline materials. In this type of solids, we have a mix of different lattices $\ell_1,\ell_2,\dots\ell_K$, with volumic ratios $a_1,a_2,\dots,a_K$. The characteristic length of this mixing is far larger than the atomic one, and far smaller than the macroscopic one. We refer the interested reader to [34, 41, 42] and the references therein. Therefore, introducing an intermediate scale γ such that $\varepsilon\ll\gamma\ll 1$, (we deal here only with the case $\varepsilon=\delta$) one should introduce a tiling of size γ of the set Ω, for instance the unit cells of the lattice $\gamma\mathbf{Z}^3$, setting $Q_j=\Omega\cap(\gamma Q+\gamma j)$, for $j\in\mathbf{Z}^3$, and Q being the unit cube. Then, separating each Q_j into K sets $Q_j^1,Q_j^2,\dots,Q_j^K$ of volumic ratios $a_1,a_2,\dots,a_K$ respectively and assuming that in the set Q_j^k, the atoms are distributed on the set ℓ_k, we thus may use exactly the same computations as those of Theorem 2.1 (i) or Theorem 3.2 (i), getting as elastic energy:

$$\mathcal{E}(u)=\frac{1}{|\Omega|}\sum_{k=1}^{K}\int_\Omega a_k E^{\mathrm{micro}}(\nabla u(x)\ell_k)dx, \tag{76}$$

where the energy functional E^{micro} denotes the corresponding rescaled microscopic energy. One may also very well allow the coefficients a_k to depend on x without any change. Another possible improvement consists in replacing the measure $\sum_{k=1}^K a_k\delta_{\ell_k}$ implicitly used in (76) by any probability measure μ defined in the space of lattices $\mathcal{L}_3(\mathbf{R}^3)$. In this case, Krein-Milmann theorem allows to approximate μ by a sum of Dirac masses as above. The integer K becoming a parameter depending on ε, and going to infinity as $\varepsilon\to 0$, with the condition $\varepsilon\ll\gamma\ll\frac{1}{K}\ll 1$, it is here again possible to adapt our method, finding:

$$\mathcal{E}(u)=\frac{1}{|\Omega|}\int_\Omega\int_{\mathcal{L}_3(\mathbf{R}^3)} E^{\mathrm{micro}}(\nabla u(x)\ell)d\mu_x(\ell)dx. \tag{77}$$

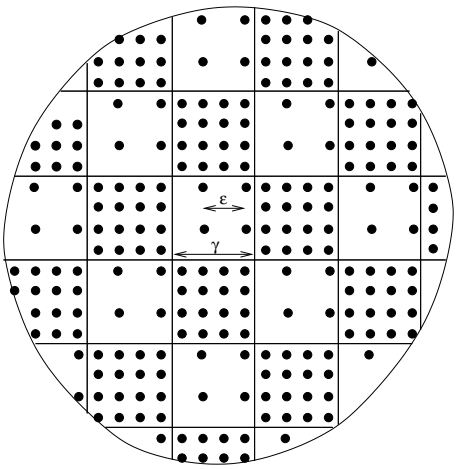

Figure 3: The limiting process allowing to derive (76), with $K = 2$.

Let us point out that the result does not depend on the tiling we choose, as far as it is sufficiently regular (one can for instance replace the lattice $\mathbf{Z}^3$ by any other lattice in the above argument).

The point here is that everything we did in the previous sections extends to this situation, except that we have created interfaces between the grains of each lattice (the cubes Q_j^k in the present case). Now, the condition $\varepsilon \ll \gamma$ implies that the bulk in each Q_j is far more important energetically than these interfaces. However, this remark allows to predict that this presence of different phases should trigger additive terms in the higher order expansion (Theorem 2.3), and in particular a bulk term of order one accounting for these grain boundaries. Worst of all, this term will probably exhibit a dependence on the tiling used. Hence, the expansion at higher order should involve a tiling which is consistent with the physics of grain boundary contacts. All this is beyond our reach today.

One should notice that in the proof of Theorem 2.1 (and implicitly in the one of Theorem 3.2), the important feature about periodicity is translation invariance. Indeed, the crucial point, appart from the Taylor expansion, is the fact that for any lattice ℓ, we have:

$$\forall i \in \ell, \quad \sum_{j \in \ell \setminus \{i\}} W_0(j-i) = \sum_{j \in \ell \setminus \{0\}} W_0(j),$$

as far as W_0 decays fast enough at infinity. One cannot break this property without breaking translation invariance. Conversely, if a sort of translation invariance holds, for instance in the case of almost periodic systems (see [12, 48]), it is possible to adapt our argument. Indeed, in this cas, one would find the same kind of result:

$$\mathcal{E}(u) = \frac{1}{|\Omega|} \int_\Omega E_{W_0}(\nabla u(x)\ell) dx,$$

where $E_{W_0}(\nabla u(x)\ell)$ denotes the two-body energy of the almost periodic set $\nabla u(x)\ell$, that

is,

$$E_{W_0}(\ell) = \lim_{R\to\infty} \frac{1}{\#(B_R \cap \nabla u(x)\ell)} \sum_{i\neq j\in B_R\cap\nabla u(x)\ell} W_0(i-j),$$

which exists because ℓ, hence $\nabla u(x)\ell$, is almost periodic. Note that this quantity does not depend on the center of the ball B_R, even in the case when this center depends on R. This property of existence and uniqueness of an average energy seems to be the crucial one in order to use the method of Theorem 2.1. Of course, some non almost periodic sets enjoy this property (think for instance of the set $\mathbf{Z}^3 \setminus \{0\}$), and the question of the characterization of such sets seems to be open.

5 Convexity and related properties of the homogenized energy

We give here a few remarks about the homogenized energies we have obtained in Section 2 and Section 3. Starting with the zero-order terms (21), (22), (50) and (51), we then study higher order terms obtained in Theorem 2.3.

5.1 Zero-order term

We start with the zero-order terms (21), (22), (50) and (51), first pointing out that each of them exhibits the invariance (16), which is a direct consequence of the Cauchy-Born rule, and in particular:

$$\forall M \in M_+^{3\times 3}, \quad \forall Q \in GL_3(\mathbf{Z}), \quad \mathcal{E}(MQ) = \mathcal{E}(M). \tag{78}$$

Here $M_+^{3\times 3}$ denotes the set of 3 by 3 matrices having positive determinant, and $GL_3(\mathbf{Z})$ the set of matrices having integer entries, positive determinant, and which inverse have integer entries (this set is also equal to the set of matrices having integer entries and determinant equal to ± 1). Equation (78) simply expresses that the lattice defining the microscopic structure of the solid is invariant under a change of basis. Note that this remain valid in the high density limit because $|\det Q| = 1$.

The point is, this invariance prevents any use of the quasiconvexity existence theorems proved by Ball [3], because of the absence of (rapid) growth of the energy at infinity.

According to some remarks in [17] and [24], the invariance (78) prevents any quasiconvexity property (in addition to the absence of rapid growth at infinity). We nevertheless provide a simpler proof of this fact in the particular case of a two-body interaction with radially symmetric potential:

Proposition 5.1 *Let $W_0 : \mathbf{R}^+ \to \mathbf{R} \cup \{+\infty\}$ satisfy the following:*

(a) W_0 is of class C^1 on $[R, +\infty)$ for any $R > 0$;

(b) $\exists a > 0 \quad / \quad \forall t \in [1, +\infty)$, $|W_0(t)| \leq \frac{C}{t^{3+a}}$ and $|W_0'(t)| \leq \frac{C}{t^{4+a}}$, for some constant $C \geq 0$; and

(c) there exists some $t_0 > 0$ such that $W_0'(t_0) \neq 0$, and W_0 is monotone on $[t_0, +\infty)$.

Define the energy

$$E(M) = \sum_{j \in \ell \setminus \{0\}} W_0(|Mj|),$$

for some fixed lattice ℓ, and for any matrix $M \in M_+^{3\times 3}$. Then E is not rank-one convex, thus not quasiconvex.

Let us point out that the conditions imposed on W_0 are fairly general, and include in particular almost all two-body potentials currently used in solid-state physics.

Proof: We assume for the sake of simplicity that $\ell = \mathbf{Z}^3$. For any $z \in \mathbf{R}$, $\quad \lambda, \mu \geq 0$, we define:

$$A(\lambda, \mu, z) = \begin{pmatrix} \lambda & z & 0 \\ 0 & \mu & 0 \\ 0 & 0 & \mu \end{pmatrix},$$

and define the function $\varphi(\lambda, \mu, z) = E(A(\lambda, \mu, z))$. Assuming by contradiction that E is rank-one convex, φ is convex with respect to z. Now, one easily computes, using (78), $\varphi(\lambda, \mu, \lambda n) = \varphi(\lambda, \mu, 0)$, for any integer n. Hence, φ must be independent of z. Differentiating it with respect to z, one thus finds:

$$0 = \sum_{j \neq 0} W_0'\left(\sqrt{(\lambda j_1 + z j_2)^2 + \mu^2 j_2^2 + \mu^2 j_3^2}\right) \frac{(\lambda j_1 + z j_2) j_2}{\sqrt{(\lambda j_1 + z j_2)^2 + \mu^2 j_2^2 + \mu^2 j_3^2}}.$$

We now let λ go to infinity, getting:

$$0 = \sum_{j \in \mathbf{Z}^2 \setminus \{0\}} W_0'\left(\sqrt{(\mu^2 + z^2) j_1^2 + \mu^2 j_2^2}\right) \frac{z j_1^2}{\sqrt{(\mu^2 + z^2) j_1^2 + \mu^2 j_2^2}}.$$

Dividing this equality by z and then taking z to zero, this implies that

$$0 = \sum_{j \in \mathbf{Z}^2 \setminus \{0\}} W_0'(\mu |j|) \frac{j_2^2}{|j|}.$$

Now, choosing $\mu = t_0$, we see that all terms of this sum have the same sign, while some of them are equal to $W_0'(t_0) \neq 0$, which is contradictory. $\Diamond$

However, in the high density case, that is,

$$\mathcal{E}(u) = \frac{1}{|\Omega|} \int_\Omega \frac{dx}{|\det(\nabla u(x))|^p}, \tag{79}$$

with $p = 1$ or $p = \frac{2}{3}$, the function $t \mapsto \frac{1}{t^p}$ being convex in either case with respect to t on $\mathbf{R}^+$, the energy $\mathcal{E}$ is polyconvex [3], hence quasiconvex. The energy being highly degenerate, one needs to add confining terms in order to have some equilibrium state. This kind of problems are dealt with in [44].

Note that in fact in the proof of Proposition 5.1, we have essentially used the fact that a convex function cannot be periodic, unless it is a constant. It is in fact a direct consequence of [23] that a rank-one convex function satisfying (78) must be of the form (79):

Theorem 5.2 (Fonseca, [23]) *Let E be a function defined on $M^{3\times 3}_+$, the set of 3 by 3 matrices having positive determinant.*

(i) Assume that E is bounded below and satisfies (78). Then, E is rank-one-convex if and only if there exists a convex function $g : (0, +\infty) \to \mathbf{R}$ such that

$$E(F) = g(\det F), \quad \forall F \in M^{3\times 3}_+.$$

(ii) If E satisfies $\lim_{\det F \to 0^+} E(F) = +\infty$ and (78), then its lower quasiconvex envelope QE is equal to its rank-one-convex envelope, and there exists a convex function $g : (0, +\infty) \to \mathbf{R}$ such that

$$QE(F) = g(\det F), \quad \forall F \in M^{3\times 3}_+.$$

Therefore, the application of this Theorem to the TFW case allows to conclude that a result similar to that of Proposition 5.1 holds in this case. Indeed, should the corresponding energy be quasiconvex, it would only depend on the determinant of the gradient deformation, according to (i) above. Hence, using

$$M = \begin{pmatrix} \lambda & 0 & 0 \\ 0 & \frac{1}{\sqrt{\lambda}} & 0 \\ 0 & 0 & \frac{1}{\sqrt{\lambda}} \end{pmatrix}$$

as a gradient deformation, the corresponding energy should be independent of λ. This is in contradiction with the fact that as λ goes to zero, the energy goes to infinity. (Because a "great amount" of nuclei get closer and closer in the process. See [7], Proposition 5.2 for a rigourous proof.)

5.2 The boundary term

We now turn to the term of order one in (29) and (30). Here again, we refer to [11] for a detailed study, giving here only a simple example of the role this term may play.

Consider the case $\varepsilon = \delta$, that is (29), discarding all terms of order strictly higher than 1. Assume in addition that $\Omega = Q$ is the unit cube, and that $\ell = \mathbf{Z}^3$. Then, the elastic energy reads:

$$\mathcal{E}(u) = \frac{1}{2}\int_\Omega \sum_{j\neq 0} W_0(\nabla u(x) j)dx - \frac{\varepsilon}{2}\int_{\partial\Omega} \sum_{k\geq 1} \sum_{j\cdot n(x)\geq k} W_0(\nabla u(x) j) d\sigma(x),$$

the sums over j being restricted to $j \in \mathbf{Z}^3$. The consequence of the presence of this first-order term is the breaking of property (78). Indeed, let us consider the example

$$u(x) = \begin{pmatrix} x_1 + px_2 \\ x_2 \\ x_3 \end{pmatrix},$$

where p is an integer. Then, we have

$$\mathcal{E}(u) = \frac{1}{2}\sum_{j\neq 0} W_0(j) - \frac{\varepsilon}{2}\sum_{k\geq 1}\Big(\sum_{|j_1|\geq k} W_0(u(j)) + \sum_{|j_2|\geq k} W_0(u(j)) + \sum_{|j_3|\geq k} W_0(u(j))\Big).$$

Observe now that the last two sums do not depend on p. We are now going to assume that the potential W_0 is radially symmetric, and satisfies:

$$W_0(x) = W_0(|x|) < 0 \quad \text{for} \quad |x| > 1.$$

Hence, we have:

$$\begin{aligned}
\mathcal{E}(u) &= A_0 - \frac{\varepsilon}{2}\sum_{k\geq 1}\sum_{|j_1|\geq k} W_0\Big(\sqrt{(j_1+pj_2)^2 + j_2^2 + j_3^2}\Big) \\
&\geq A_0 - \varepsilon\sum_{k=1}^{p}\sum_{j_3\in\mathbf{Z}} W_0\Big(\sqrt{(p-p)^2 + 1 + j_3^2}\Big) \\
&\geq A_0 - \varepsilon p\sum_{m\in\mathbf{Z}} W_0\Big(\sqrt{1+m^2}\Big) = A_0 + \varepsilon B p,
\end{aligned}$$

where A_0 does not depend on p, and $B > 0$ is independent of ε and p. Therefore, as p goes to infinity, the energy grows like $+\varepsilon p$, going to infinity.

5.3 The second-order term

We now study the second-order term. Let us start with the one-dimensional case, in which (in the case $\varepsilon = \delta$, that is, (i) of Theorem 2.3) the energy reads, if we neglect boundary terms and assume that $\Omega = (0,1)$:

$$\mathcal{E}(u) = \frac{1}{2}\int_0^1 \sum_{j\neq 0} W_0(u'(x)j)dx - \frac{\varepsilon^2}{24}\int_0^1 \sum_{j\neq 0} j^4 W_0(u'(x)j)(u''(x))^2 dx, \tag{80}$$

where the sums are over $\mathbf{Z}\setminus\{0\}$, since we assume for the sake of simplicity that the lattice ℓ is equal to $\mathbf{Z}$. Hence, we have an energy of the form:

$$\mathcal{E}(u) = \int_0^1 E_0(u'(x))dx + \varepsilon^2 h(u'(x))(u''(x))^2 dx,$$

with $h(y) = -\frac{1}{24}\sum_{j\neq 0} j^4 W_0(yj)$, and E_0 is the standard zero-order energy. Thus, if W_0 satisfies the following inequality:

$$\forall y \in \mathbf{R}, \quad \sum_{j\neq 0} j^4 W_0(yj) < 0,$$

then the energy (80) exhibits a convexification term of order 2. The influence of this term on the energy has been studied in details in [4] in the case of the pure displacement problem, that is:

$$I_\Delta = \inf\Big\{\mathcal{E}(u), \quad u(0) = 0, \quad u(1) = 1 + \Delta\Big\},$$

for some $\Delta \in \mathbf{R}$, corresponding to imposing a displacement of length Δ at the right end of the solid, the other end remaining still. It is shown in [4] that when $\varepsilon = 0$, I_Δ exhibits discontinuous critical points, and have no absolute minimizer in a classical sense. When the second-order term is added, and if $h > 0$, then bifurcation phenomenas (with only smooth critical points) occur.

Let us now point out that there exist potentials W for which the corresponding quantity is indeed negative. This is the case for the Morse potential (well suited for a wide range of materials [49, 51]). Indeed, an easy but tedious computation, that we do not reproduce here for the sake of brievity, shows that

Lemma 5.3 *Consider the Morse potential, that is,*

$$W_0(x) = e^{-2(x-r_0)} - 2e^{-(x-r_0)},$$

and assume that the caractestic length r_0 satisfies $r_0 < 5\log(5) - 8\log(2) \approx 2.502$. Then we have:

$$\forall y > 0, \quad \sum_{j\neq 0} j^4 W_0(yj) < 0.$$

On the other hand, it can be shown that the Lennard-Jones potential ($W_0(x) = \frac{1}{x^{12}} - \frac{1}{x^6}$) cannot satisfy this property.

A similar analysis could be carried out in the high density case, that is, (ii) of Theorem 2.3, the second-order term enjoying the same kind of property.

A similar study *should* be possible in the three-dimensional case, but calculations are a lot more involved, and it is not clear whether an ellipticity property can be derived in this case. However, the high density case is more tractable: looking at the second-order term of (30), it is possible to change variables in the integral with respect to y, and obtain:

$$\begin{aligned}
&\mathcal{E}_2(u) := -\frac{\varepsilon^2}{24|\Omega|}\int_\Omega\int_{\mathbf{R}^3} D^2W_0(\nabla u(x)y)(D^2u(x)(y,y), D^2u(x)(y,y))dydx = \\
&\frac{-\varepsilon^2}{24|\Omega|}\iint_{\Omega\times\mathbf{R}^3}\frac{D^2W_0(z)(D^2u(x)(\nabla u(x)^{-1}z, \nabla u(x)^{-1}z), D^2u(x)(\nabla u(x)^{-1}z, \nabla u(x)^{-1}z))dz}{|\det(\nabla u(x))|}dx \\
&= \frac{-\varepsilon^2}{24|\Omega|}\iint_{u(\Omega)\times\mathbf{R}^3} D^2W_0(z)\left[\left(\frac{\nabla v(\xi)}{\det\nabla v(\xi)}\right)^{-1} D^2v(\xi)(z,z), \left(\frac{\nabla v(\xi)}{\det\nabla v(\xi)}\right)^{-1} D^2v(\xi)(z,z)\right]dzd\xi,
\end{aligned}$$

where $v = u^{-1}$. This expression is certainly easiser to study. For instance, if one only looks for radially symmetric deformations, and assuming that W_0 is radially symmetric, then the total energy is bounded from below by a norm of the second derivative of v, hence by a norm of the second derivative of u. For the details, we refer to our forthcoming work [11], where a complete study of this second-order term will be done.

The question remains, in the general three-dimensional setting, and both for (29) and (30), to know wether it is possible to find some situations where the second-order bulk term exhibits ellipticity properties, as was assumed for instance in [5].

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Chapitre 7

Écrantage d'un champ électrique extérieur macroscopique

Ce chapitre reproduit un article écrit en collaboration avec R. Monneau [P9], et accpeté pour publication dans Differential and Integral Equations. Nous y étudions l'effet d'un champ électrique constant sur une plaque décrite par le modèle de Thomas-Fermi-von Weizsäcker, dans la limite où la distance interatomique tend vers 0.

Screening of an Applied Electric Field Inside a Metallic Layer Described by the Thomas-Fermi-von Weizsäcker Model

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Abstract We are interested in the effect of a constant electric field on the electronic structure of a crystal. We model it by a density-functional theory, and derive from this microscopic model macroscopic features of the system by letting the ratio ε between atomic spacing and the size of the crystal go to zero. Although many aspects are disregarded in this approach, we show that the effect of the electric field is negligible inside the crystal and estimate its vanishing rate with respect to the distance from the boundary of the crystal.
AMS Classification: 35A15, 35J20, 35J50, 35Q40.
Keywords: Thomas-Fermi-von Weizsäcker theory, variational methods, electric field, exponential decay.

1 Introduction

We consider a band of crystal immersed in a constant electric field perpendicular to the surface of the crystal. Modeling the electrons by a quantum (hence microscopic) theory, namely the Thomas-Fermi-von Weizsäcker theory, we aim at deriving a macroscopic description of the effect of the electric field on this crystal. In order to do so, we let the ratio ε between the interatomic distance and the width of the crystal band go to zero, accounting for the fact that the first is physically of some orders of magnitude lower than the second.

The main feature of this limiting model is that the effect of the electric field is confined to the boundary of the crystal. Studying this aspect further, we give an estimate of the decaying of this effect in the crystal with respect to ε. However, some non-physical features are also evidenced.

These non-physical features are mainly due to the fact that the model describing the electrons is a static one, thereby preventing the description of any dynamical features. And even static macroscopic phenomena may very well originate from dynamical microscopic ones. Although the type of model we use here has proved to be relevant in some cases related to this one [4, 3], it surely misses some important aspects.

In the following we start by presenting a simplified one-dimensional version of our results, describing in section 2 the full three-dimensional Thomas-Fermi-von Weiszäcker model and the corresponding results. We will drop the proofs of the one-dimensional results which are easy adaptations of the more involved three-dimensional problem. A priori bounds are given in section 4 and the three-dimensional proofs are presented in sections 3 and 4.2. We add in Appendix 5 a homogenization approach by two scale convergence which gives more limited results in our context.

1.1 A one-dimensional microscopic model

1.1.1 Physical description

We consider a one-dimensional crystal. Let us denote by $x \in \mathbf{R}$ the one-dimensional coordinate. We assume that the crystal fills the macroscopic segment:

$$[-1, 1] \subset \mathbf{R},$$

and this crystal is submitted to a constant exterior electric field E. By symmetry considerations, we may assume that this electric field is oriented in the positive direction $x > 0$, i.e. $E \geq 0$ (see fig. 1).

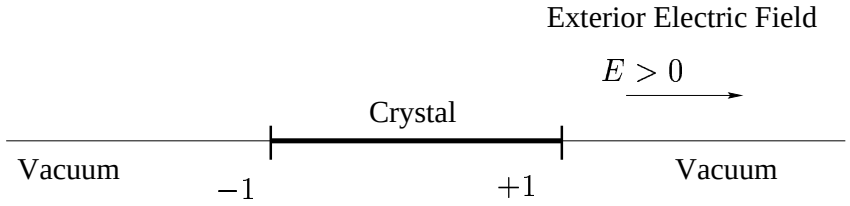

Figure 1: A one-dimensional crystal submitted to a constant exterior electric field

We assume that the crystal is physically described by nuclei and electrons. The nuclei are supposed to be fixed, and to stand at the positions $\{\varepsilon i, \quad i \in \mathbf{Z}, \quad |\varepsilon i| < 1\}$, where ε is the interatomic distance of the crystal. Mathematically, they should be described by Dirac masses, but in order to simplify our presentation, we use a Jellium-like approximation [11], replacing $\varepsilon \sum \delta_{\varepsilon i}$ by $m = \mathbf{1}_{[-1,1]}$. (Note that the first one converges to the second one in the sense of measures.) The density m can be understood as a collection of $\frac{2}{\varepsilon}$ nuclei. Furthermore, each nucleus has a renormalized charge equal to $+\varepsilon$. In particular the charge of the whole set of nuclei is $\int m = 2$ which is equal to the number of nuclei times the elementary renormalized charge ε. As it will be clear in subsection 2.3, the choice of the renormalized charge equal to ε is natural according to physical considerations.

For the examples that we have in mind the microscopic size ε is much smaller than the macroscopic size 1. Typically $\varepsilon \sim 10^{-10}$, so that we expect the limit $\varepsilon \to 0$ to be a good model.

The electrons are described by a renormalized density ρ which satisfies

$$\rho(x) \geq 0 \quad \text{on} \quad \mathbf{R}.$$

In this model we define the usual charge density by the ratio of $m - \rho$ and the charge ε of a nucleus:

$$\sigma = \frac{m - \rho}{\varepsilon}. \tag{1}$$

In particular $\int \sigma = +1$ means that there is one more nucleus than electrons, and $\int \sigma = -1$ means that there is one more electron than nuclei.

We define the Green function of the operator $-\Delta$ as a solution to $-\Delta G = \delta_0$. In the following, the one-dimensional Green function is chosen to be equal to

$$G(x) = -\frac{1}{2}|x|.$$

As a consequence of this choice, the electric potential (up to addition of a constant) is given by $G \star \sigma - Ex$ where we recall that the convolution is defined by the following formula: $G \star \sigma(x) = \displaystyle\int_{-\infty}^{+\infty} dy \quad G(x-y)\sigma(y)$. Then the total electric field is

$$E_{tot} = -\frac{d}{dx}\left(G \star \sigma - Ex\right). \tag{2}$$

1.1.2 The mathematical model

We now present the mathematical microscopic model defining the electronic density ρ as the solution of a minimization problem. In this simplified version of the Thomas-Fermi-von Weiszäcker (TFW) model (see [6, 5, 7] for a presentation of this model and the related mathematical results), we assume that the density ρ minimizes an energy

$$\mathcal{E}_\varepsilon(\rho) = \int_{-\infty}^{+\infty} \varepsilon^4 \left(\frac{d}{dx}\left(\sqrt{\rho}\right)\right)^2 + \varepsilon^2 \rho^{\frac{5}{3}} + \rho \cdot G \star \left(\frac{1}{2}\rho - m\right) + \varepsilon E x \rho$$

on the convex set K_λ defined by ($\lambda > 0$)

$$K_\lambda = \left\{ \rho \geq 0, \quad \sqrt{\rho} \in H^1(\mathbf{R}), \quad |x_3|\rho \in L^1(\mathbf{R}), \qquad \int_{-\infty}^{+\infty} \rho = \lambda \right\}.$$

The point is, $\mathcal{E}_\varepsilon$ is strictly convex on K_λ. The functional $\mathcal{E}_\varepsilon$ is a particular version of the thin film TFW energy presented in [7]. The coefficients in the energy originate from physical constants which may be expressed in terms of ε, as shown in section 2.3. The first term in the integral is a kind of kinetic energy, the second term is a Fermi pressure term, the third term contains the coulombian (in one dimension) interaction of the electrons with themselves and of the electrons with the nuclei, and the last term is the interaction between the electrons and the exterior electric field.

Remark 1.1 *The scaling in ε is such that for $\overline{x} = x/\varepsilon$, $\overline{\rho}(\overline{x}) = \rho(x)$, $\overline{m}(\overline{x}) = m(x)$, we have ρ minimizes $\mathcal{E}_\varepsilon$ if and only if $\overline{\rho}$ minimizes the energy $\mathcal{E}_1$ with $\varepsilon = 1$ and $\overline{m}$ in place of m.*

1.2 Results for the one-dimensional model

Our first result is the

Theorem 1.2 (Crystal Ionized by the Electric Field)
Assume that $0 \leq E < \frac{1}{\varepsilon}$. Then, setting

$$\lambda_c = (1 - \varepsilon E) \left(\int_{\mathbf{R}} m \right)$$

we have:

(i) If $\lambda > \lambda_c$, $\inf_{K_\lambda} \mathcal{E}_\varepsilon = -\infty$.

(ii) If $0 \leq \lambda \leq \lambda_c$, $\inf_{K_\lambda} \mathcal{E}_\varepsilon > -\infty$, and this energy admits a unique minimizer $\rho_\lambda \in K_\lambda$.

>From the fact that $\lambda_c < \int m$ we see that every solution describes a ionized crystal when $E \neq 0$. This fact was already known for the TFW model (as well as in any quantum chemistry model): every molecular system submitted to a constant exterior electric has no stable state. Therefore our model can not give a globally neutral solution in an exterior electric field, so far as ground states are considered. In fact physically such a neutral solution is not the minimizer of an energy: every neutral solution in an exterior electric field is metastable.

Because $\int m = 2$, the ionization is equal to $2\varepsilon E$ but is not negligible at all. Let us recall that the charge in this model is obtained after a division by ε (see (1)). We deduce that the charge corresponding to the ionization is equal to $2E$ (see fig. 2).

In fig. 3 we have represented the situation for a perfect conductor: the electric field vanishes inside the material, but contrarily to the TFW crystal, the material is globally neutral and the charge $E\delta_1(x)$ is compensated by a negative charge $-E\delta_{-1}(x)$ on the other side of the material. As we explained, this compensation is impossible in a TFW model,

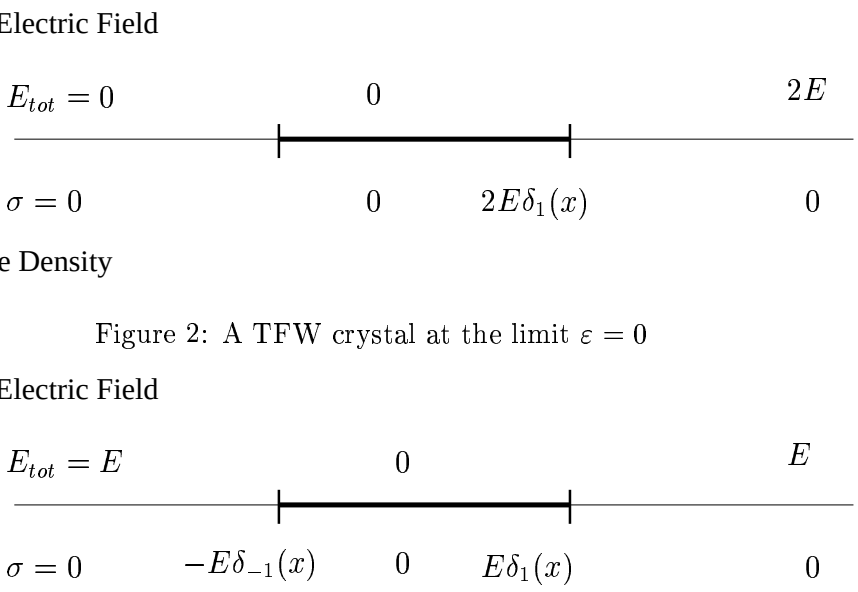

Figure 2: A TFW crystal at the limit $\varepsilon = 0$

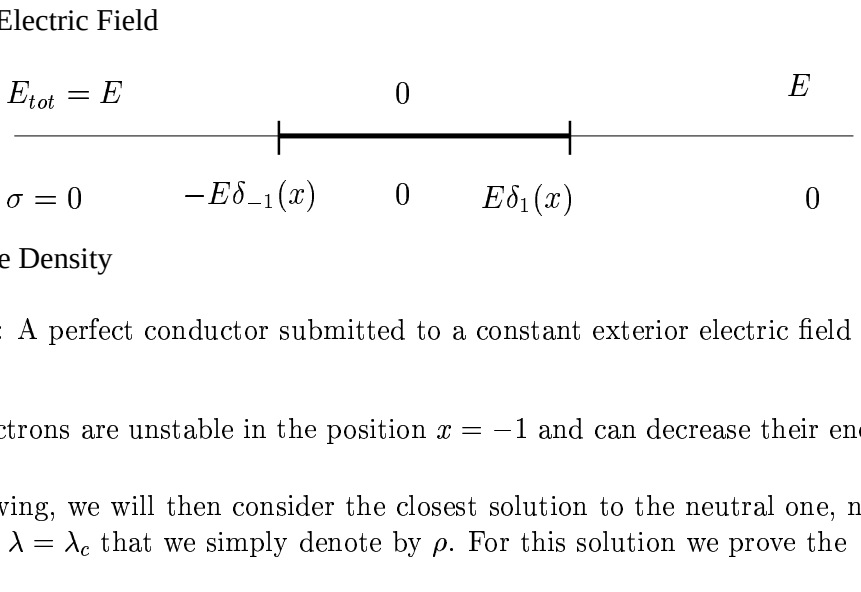

Figure 3: A perfect conductor submitted to a constant exterior electric field

because the electrons are unstable in the position $x = -1$ and can decrease their energy if they go to $-\infty$.

In the following, we will then consider the closest solution to the neutral one, namely the solution for $\lambda = \lambda_c$ that we simply denote by ρ. For this solution we prove the

Theorem 1.3 (Exponential Decay of the Electric Field Inside the Crystal) *Let $0 \leq E < \frac{1}{\varepsilon}$ and $\lambda = \lambda_c$. Then there exist two positive constants C_1, C_2 (which only depend on a bound on E and not on ε) such that the minimizing density ρ and the total electric field E_{tot} (given by equation (2)) satisfy*

$$\left.\begin{array}{l} |\rho(x) - 1| \\ |E_{tot}(x)| \end{array}\right\} \quad \leq \quad C_1 e^{-C_2 \frac{d(x)}{\varepsilon}} \tag{3}$$

where $d(x) = d(x, [-1, 1]^c)$ is the distance of a point x in the crystal to the boundary of the crystal.

This result shows that the interior of the crystal has a behavior of a perfect conductor far enough from its boundaries. In particular the penetration length of the electric field is essentially of the order of a few ε (the size of a cell of the crystal in this simple model).

This result is optimal in the sense that the constants C_1, C_2 can not depend on a bound on εE, because for $E = \frac{1}{\varepsilon}$ the only solution is $\rho = 0$ and (3) would be clearly wrong. Even in the case $E = 0$, this exponential decay result for a TFW-type model seems relevant.

2 The three-dimensional model

2.1 Setting of the problem

We study a band of crystal filling the following subregion of $\mathbf{R}^3$

$$\mathbf{R}^2 \times [-1, 1],$$

and submitted to a constant exterior electric field orthogonal to the crystal

$$E_{ext} = Ee_3,$$

where e_3 is the third vector of the canonical basis.

The nuclei are supposed to be fixed at their positions on a subset of the lattice $\varepsilon\mathbf{Z}^3$. The underlying thin film structure is present through its periodic lattice ℓ_ε:

$$\ell_\varepsilon = \varepsilon\mathbf{Z}^2 \times \{0\},$$

and, unless otherwise stated, all the functions we consider here will be assumed to be ℓ_ε-periodic. We introduce the (periodic) unit cell Γ_ε of the periodic lattice ℓ_ε:

$$\Gamma_\varepsilon = \mathbf{R}^3/\ell_\varepsilon = \left[-\frac{\varepsilon}{2}, \frac{\varepsilon}{2}\right)^2 \times \mathbf{R}.$$

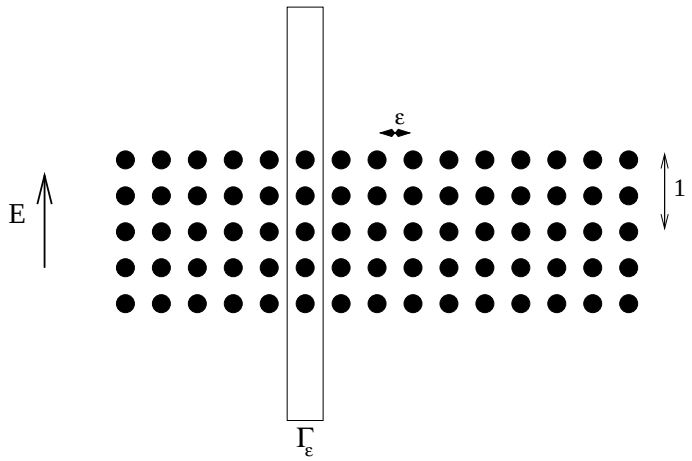

Figure 4: The set of nuclei together with the unit cell Γ_ε (projected on the plane $\{x_2 = 0\}$).

In this three-dimensional model, each nucleus carries a renormalized charge which is fixed equal to ε^3 such that the charge density generated by the nuclei in a cell Γ_ε is defined by

$$m(x) = \sum_{k=-N}^{N} \varepsilon^3 \delta(x - k\varepsilon e_3).$$

for some integer N. In particular we have $2N+1$ nuclei in each cell Γ_ε. As it will be clear is subsection 2.3, the choice of the renormilazed charge ε^3 is natural from physical considerations.

To simplify the presentation we restrict our study to the particular values of ε given by $\varepsilon = \frac{1}{N+\frac{1}{2}}$. For these values, we have $\frac{1}{\varepsilon^2}\int_{\Gamma_\varepsilon} m = 2$ where ε^2 has to be interpreted as the area of a section of Γ_ε, and the nuclei fill the set

$$\varepsilon\mathbf{Z}^3 \cap \Big(\mathbf{R}^2 \times [-1,1]\Big).$$

The electrons are represented by their density ρ, which is a positive ℓ_ε-periodic function. In particular we define the usual volumic charge density on a cell Γ_ε by the ratio of $m-\rho$ by the charge of a nucleus divided by the area of a section of Γ_ε, i.e. $\varepsilon^3/\varepsilon^2 = \varepsilon$:

$$\sigma = \frac{m-\rho}{\varepsilon}$$

The ℓ_ε-periodic Green function G_ε satisfies $-\Delta G_\varepsilon = \delta_0(x) \quad \text{on} \quad \Gamma_\varepsilon$ and is chosen to be equal to

$$G_\varepsilon(x) = -\frac{1}{2\varepsilon^2}|x_3| + \frac{1}{4\pi}\sum_{k\in\varepsilon\mathbf{Z}^2\times\{0\}}\left(\frac{1}{|x-k|} - \frac{1}{\varepsilon^2}\int_{[-\frac{\varepsilon}{2},\frac{\varepsilon}{2}[\times\{0\}}\frac{dy}{|x-y-k|}\right) + \frac{M}{\varepsilon}, \qquad (4)$$

where the constant M is chosen so that $G_\varepsilon(x) - \frac{1}{4\pi|x|} \to 0$ as $x \to 0$. From the definition of G_ε, M is independent of ε. With this definition of the Green function, the electric potential (up to addition of a constant) is given by $G_\varepsilon \star \sigma - Ex_3$ where the convolution product is defined by $G_\varepsilon \star \sigma(x) = \int_{\Gamma_\varepsilon} dy \quad G_\varepsilon(x-y)\sigma(y)$. Then the total electric field is

$$E_{tot} = -\nabla\left(G_\varepsilon \star \sigma - Ex_3\right) \qquad (5)$$

The electronic density is moreover assumed to minimize an energy

$$\mathcal{E}_\varepsilon(\rho) = \int_{\Gamma_\varepsilon} \varepsilon^4 \left|\nabla\sqrt{\rho}\right|^2 + \varepsilon^2\rho^{\frac{5}{3}} + \rho\cdot G_\varepsilon \star \left(\frac{1}{2}\rho - m\right) + \varepsilon E x_3\rho, \qquad (6)$$

which is strictly convex on the convex set K_λ defined for $\lambda > 0$ by

$$K_\lambda = \left\{\rho \geq 0, \quad \sqrt{\rho} \in H^1(\Gamma_\varepsilon), \quad |x_3|\rho \in L^1(\Gamma_\varepsilon), \qquad \frac{1}{\varepsilon^2}\int_{\Gamma_\varepsilon}\rho = \lambda > 0\right\}.$$

The energy $\mathcal{E}_\varepsilon$ is called the thin film Thomas-Fermi-von Weizsäcker (TFW) energy (see [7]).

2.2 Mathematical results

The above model (6) was derived in [7] in the particular case of a neutral isolated system, i.e when $E = 0$. Hence the first step of our work is to study it when $E \neq 0$:

Theorem 2.1 (Crystal Ionized by the Electric Field)
Assume that $0 \leq E < \frac{1}{\varepsilon}$. *Then, setting*

$$\lambda_c = (1 - \varepsilon E) \left(\frac{1}{\varepsilon^2} \int_{\Gamma_\varepsilon} m \right),$$

we have:

(i) If $\lambda > \lambda_c$, $\inf_{K_\lambda} \mathcal{E}_\varepsilon = -\infty$.

(ii) If $0 \leq \lambda \leq \lambda_c$, $\inf_{K_\lambda} \mathcal{E}_\varepsilon > -\infty$, *and this energy admits a unique minimizer* $\rho_\lambda \in K_\lambda$. *This solution satisfies in particular the following Euler-Lagrange equations on* Γ_ε *with* $u_\lambda = \sqrt{\rho_\lambda}$:

$$\left\{ \begin{array}{l} -\varepsilon^4 \Delta u_\lambda + \frac{5}{3} \varepsilon^2 u_\lambda^{\frac{7}{3}} = \phi_\lambda u_\lambda, \\ \\ \phi_\lambda = G_\varepsilon \star \left(m - u_\lambda^2 \right) - \varepsilon E x_3 - \theta_\lambda, \end{array} \right. \tag{7}$$

where θ_λ *is a constant which is the Lagrange multiplier for the constraint* $\frac{1}{\varepsilon^2} \int_{\Gamma_\varepsilon} \rho = \lambda$.

As in the one-dimensional model this result states that only ionized solutions exist in a constant exterior electric field.

Let us recall the

Theorem 2.2 (I. Catto, Cl. Le Bris, P.-L. Lions [9]; Existence and Uniqueness of a Periodic Solution)
For $m_{per}(x) = \sum_{k \in \mathbf{Z}^3} \delta(x - k)$, *the following system (obtained from (7) for* $\varepsilon = 1$, $N = +\infty$ *and* $E = 0$*)*

$$\left\{ \begin{array}{l} -\Delta u_{per} + \frac{5}{3} u_{per}^{\frac{7}{3}} = \phi_{per} u_{per}, \\ -\Delta \phi_{per} = m_{per} - u_{per}^2, \\ u_{per} \geq 0 \end{array} \right. \tag{8}$$

has one and only one solution $(u_{per}, \phi_{per}) \in L^\infty \left(\mathbf{R}^3 \right) \times L^1_{unif} \left(\mathbf{R}^3 \right)$ *In particular this solution is* $\mathbf{Z}^3$*-periodic. We recall that*

$$L^1_{unif} \left(\mathbf{R}^3 \right) = \left\{ \phi \in L^1_{loc}(\mathbf{R}^3), \ \sup_{x \in \mathbf{R}^3} |\phi|_{L^1(B_1(x))} < +\infty \right\}$$

In the following, we will consider the solution ρ_λ given by theorem 2.1 for $\lambda = \lambda_c$ and we denote it by ρ. For this solution we prove the

Theorem 2.3 (Exponential Decay of the Electric Field Inside the Crystal)
Let $0 \leq E < \frac{1}{\varepsilon}$ *and* $\lambda = \lambda_c$. *Then there exist two positive constants* C_1, C_2 *(which only*

depend on a bound on E and not on ε) such that the minimizing density ρ and the total electric field E_{tot} (given by equation (5)) satisfy with $\rho_{per}(x) = u_{per}^2(x)$:

$$\left.\begin{array}{l} \left|\rho(x) - \rho_{per}\left(\frac{x}{\varepsilon}\right)\right| \\ \left|E_{tot}(x) + (\nabla\phi_{per})\left(\frac{x}{\varepsilon}\right)\right| \end{array}\right\} \quad \leq \quad C_1 e^{-C_2\frac{d(x)}{\varepsilon}},$$

where $d(x) = d\left(x_3, [-1,1]^c\right)$ is the distance of a point x in the crystal to the boundary of the crystal.

Here again, as in the one-dimensional version (section 1.1), this result states that in the limit $\varepsilon \to 0$, the electric field has no effect inside the crystal, giving an estimate of the penetration length with respect to ε.

2.3 Relation with the physical model before renormalization

In this section we recall the physical model. We will denote with a tilde some physical quantities to avoid every ambiguity with the corresponding renormalized quantities.

We consider a crystal which is a collection of nuclei on a lattice

$$\mu\tilde{\varepsilon}\mathbf{Z}^3 \cap \left(\mathbf{R}^2 \times [-\tilde{L}, \tilde{L}]\right),$$

where $2\tilde{L}$ is the thickness of the crystal and $2\pi\tilde{\varepsilon}$ is Bohr's radius:

$$\tilde{\varepsilon} = \frac{\left(\dfrac{\hbar^2}{2m_e}\right)}{\left(\dfrac{e^2}{\varepsilon_0}\right)}.$$

The parameter μ is adimensional and is only useful to fix the size of the lattice cell. The lattice cell is denoted by

$$\tilde{\Gamma} = \left[-\frac{\mu\tilde{\varepsilon}}{2}, \frac{\mu\tilde{\varepsilon}}{2}\right)^2 \times \mathbf{R}.$$

Each nucleus is assumed to carry a charge $\tilde{z}e$ where e is the electron charge and $\tilde{z}$ is an integer. On a cell, the physical charge density of the nuclei is

$$\tilde{m}(\tilde{x}) = \sum_{k\in[-N,N]} \tilde{z}e\delta(\tilde{x} - k\mu\tilde{\varepsilon}e_3),$$

where $2N+1$ is the total number of nuclei in each cell $\tilde{\Gamma}$, and the integer N is defined by $N + \frac{1}{2} = \frac{\tilde{L}}{\mu\tilde{\varepsilon}}$.

If we denote by $\tilde{\rho}$ the electronic density, we get for a neutral crystal $\int_{\tilde{\Gamma}} \tilde{\rho} = (2N+1)\tilde{z}$ and for a ionized crystal we have

$$\int_{\tilde{\Gamma}} \tilde{\rho} = (2N+1)\tilde{z} - I,$$

where I is the positive ionization.

Then the Thomas-Fermi-von Weizsäcker energy is

$$\tilde{\mathcal{E}}(\tilde{\rho}) = \int_{\tilde{\Gamma}} \frac{\hbar^2}{2m_e} \left|\nabla\sqrt{\tilde{\rho}}\right|^2 + C_{TF}\frac{\hbar^2}{2m_e}\tilde{\rho}^{\frac{5}{3}} + e\tilde{\rho}\cdot\tilde{G}\star\left(\frac{1}{2}e\tilde{\rho}-\tilde{m}\right) + e\tilde{E}\tilde{x}_3\tilde{\rho},$$

where $\tilde{E}$ is the exterior electric field, C_{TF} is an adimensional constant, and the convolution is defined by $\tilde{G}\star\tilde{\sigma}(\tilde{x}) = \int_{\tilde{\Gamma}} d\tilde{y} \quad \tilde{G}(\tilde{x}-\tilde{y})\tilde{\sigma}(\tilde{y})$, and

$$\varepsilon_0\tilde{G}(\tilde{x}) = -\frac{1}{2(\mu\tilde{\varepsilon})^2}|\tilde{x}_3| + \frac{1}{4\pi}\sum_{\tilde{k}\in\mu\tilde{\varepsilon}\mathbf{Z}^2\times\{0\}}\left(\frac{1}{|\tilde{x}-\tilde{k}|} - \frac{1}{(\mu\tilde{\varepsilon})^2}\int_{[-\frac{\mu\tilde{\varepsilon}}{2},\frac{\mu\tilde{\varepsilon}}{2}[\times\{0\}}\frac{d\tilde{y}}{|\tilde{x}-\tilde{y}-\tilde{k}|}\right) + \frac{M}{\mu\tilde{\varepsilon}},$$

where M is the adimensional constant previously introduced in (4).

Now, if we set

$$x = \frac{\tilde{x}}{\tilde{L}} \qquad \text{and} \qquad \varepsilon = \frac{\tilde{\varepsilon}}{\tilde{L}}(C_{TF})^{\frac{3}{2}},$$

we get a model similar to our renormalized model but with nuclei on a lattice $\nu\varepsilon\mathbf{Z}^3$ with a modified charge z, where these quantities are given by

$$z = (C_{TF})^{\frac{3}{2}}\tilde{z} \qquad \text{and} \qquad \nu = \frac{\mu}{(C_{TF})^{\frac{3}{2}}}.$$

In our model, to simplify the presentation, we make the following assumptions

$$z = 1 \qquad \text{and} \qquad \nu = 1.$$

As a consequence, on the renormalized cell $\Gamma_\varepsilon = \left[-\frac{\varepsilon}{2},\frac{\varepsilon}{2}\right)^2\times\mathbf{R}$, we define the renormalized densities by

$$\rho(x) = \varepsilon^3\tilde{L}^3(C_{TF})^{\frac{3}{2}}\tilde{\rho}(\tilde{x}) \quad \text{and} \quad m(x) = \varepsilon^3\tilde{L}^3(C_{TF})^{\frac{3}{2}}\tilde{m}(\tilde{x})$$

and the renormalized energy $\mathcal{E}_\varepsilon$ and the exterior electric field E are chosen proportional to the corresponding physical quantities $\tilde{\mathcal{E}}$ and $\tilde{E}$. We then get exactly the model presented in subsection 2.1 with the renormalized energy (6).

3 Proof of Theorem 2.1

3.1 Preliminaries

Before proving Theorem 2.1 let us present the following straightforward but useful lemma:

Lemma 3.1 *Let*

$$\mathcal{E}_\varepsilon(\rho,m,E) = \int_{\Gamma_\varepsilon}\varepsilon^4\left|\nabla\sqrt{\rho}\right|^2 + \varepsilon^2\rho^{\frac{5}{3}} + \rho\cdot G_\varepsilon\star\left(\frac{1}{2}\rho-m\right) + \varepsilon E x_3\rho$$

and

$$K^\varepsilon_\lambda = \left\{\rho\geq 0, \quad \sqrt{\rho}\in H^1(\Gamma_\varepsilon), \quad |x_3|\rho\in L^1(\Gamma_\varepsilon), \qquad \frac{1}{\varepsilon^2}\int_{\Gamma_\varepsilon}\rho = \lambda > 0\right\}.$$

Let us define

$$\overline{x} = \frac{x}{\varepsilon}$$

and $\overline{\rho}(\overline{x}) = \rho(x)$, $\overline{m}(\overline{x}) = m(x)$. *Then*

$$\rho(x) \quad \textit{minimizes} \quad \mathcal{E}_\varepsilon(\rho, m, E) \quad \textit{on} \quad K_\lambda^\varepsilon$$

if and only if

$$\overline{\rho}(\overline{x}) \quad \text{minimizes} \quad \mathcal{E}_1(\overline{\rho}, \overline{m}, E) \quad \text{on} \quad K_{\frac{\lambda}{\varepsilon}}^1$$

Notations
When $\varepsilon = 1$, we simply drop the index ε and use the notations:

$$\mathcal{E}(\rho) = \int_\Gamma |\nabla\sqrt{\rho}|^2 + \rho^{\frac{5}{3}} + \rho \cdot G \star \left(\frac{1}{2}\rho - m\right) + Ex_3\rho$$

with

$$\Gamma = \left[-\frac{1}{2}, \frac{1}{2}\right)^2 \times \mathbf{R}$$

$$G = G_1$$

$$m(x) = \sum_{k=-N}^{N} \delta(x - ke_3) \quad \text{on} \quad \Gamma$$

and

$$K_\lambda = \left\{\rho \geq 0, \quad \sqrt{\rho} \in H^1(\Gamma), \quad |x_3|\rho \in L^1(\Gamma), \qquad \int_\Gamma \rho = \lambda > 0\right\}.$$

Here $\lambda_c = \left(1 - E\right)\left(\int_\Gamma m\right)$ and $\int_\Gamma m = 2N + 1$.

3.2 Main proof

Let us first say that the proof of theorem 2.1 is essentially an adaptation of the original proof of R. Benguria, H. Brézis, E. H. Lieb [5]. >From Lemma 3.1, this proof reduces to the case $\varepsilon = 1$.

Step 1 : $\mathcal{E}$ is well defined on K_λ

We will check that the energy $\mathcal{E}$ is well defined on K_λ. To do this we need to rewrite the Green function G as

Lemma 3.2

$$G = -\frac{1}{2}|x_3| + \frac{\zeta(x)}{|x|} + \tilde{G}(x)$$

where $\zeta \in C_0^\infty(\Gamma)$ *satisfies* $\frac{1}{4\pi} \geq \zeta \geq 0$ *and for* $\delta > 0$ *small enough*

$$\zeta = \begin{cases} \frac{1}{4\pi} & \textit{on} \quad B_\delta(0) \\ 0 & \textit{on} \quad (B_{2\delta}(0))^c \end{cases}$$

Here $\tilde{G}$ *satisfies*

$$\begin{cases} \tilde{G}(x) \longrightarrow 0 \quad as \quad x \longrightarrow 0 \\ \tilde{G}(x) - \frac{1}{2}|x_3| \in C^\infty(\Gamma) \\ \tilde{G}(x) = 0\left(|x_3|^{-\alpha}\right) \quad as \quad x \longrightarrow +\infty \\ \nabla\tilde{G}(x) = 0\left(|x_3|^{-(1+\alpha)}\right) \quad as \quad x \longrightarrow +\infty \end{cases}$$

for every $0 < \alpha < 1$.

Proof: See [7] Proposition 3.2, Lemma 3.1. $\Diamond$

We now remark that the only possible singular terms in the energy are

$$\begin{array}{l} I_1 = \int_\Gamma \rho^{\frac{5}{3}} \\ I_2 = \int_\Gamma \rho G = \int_\Gamma \rho\left(\tilde{G} - \frac{1}{2}|x_3|\right) + I_2' \quad \text{with} \quad I_2' = \int_\Gamma \rho\frac{\zeta}{|x|} \\ I_3 = \int_\Gamma \rho\,(G \star \rho) = I_3' + I_3'' + I_3''' \end{array}$$

with

$$\begin{array}{l} I_3' = \int_\Gamma \rho\left(\tilde{G} \star \rho\right) \\ I_3'' = -\frac{1}{2}\int\int \rho(x)|x_3 - y_3|\rho(y) \\ I_3''' = \int\int \rho(x)\frac{\zeta(x-y)}{|x-y|}\rho(y) \end{array}$$

Considering

$$\tilde{\rho}(x) = \eta(x_1, x_2)\rho(x)$$

where $\eta \in C_0^\infty(\mathbf{R}^2)$ and

$$\begin{cases} \eta = 1 \quad \text{on} \quad \left[-\frac{1}{2}, \frac{1}{2}\right)^2 \\ \eta \geq 0 \end{cases}$$

Using as in [5] the Sobolev injection

$$\exists C > 0, \forall u \in H^1(\mathbf{R}^3), |u|_{L^6(\mathbf{R}^3)} \leq C|\nabla u|_{L^2(\mathbf{R}^3)}$$

we deduce that $\tilde{\rho} \in L^3(\mathbf{R}^3)$. Because $\rho \in L^1(\Gamma)$ we deduce by Hölder inequality that

$$I_1 < +\infty$$

Using again $\tilde{\rho}$ in place of ρ we bound I_2' by Hölder inequality because $\frac{\zeta(x)}{|x|} \in L^{\frac{5}{2}}(\Gamma)$, and we bound I_3''' using the fact that $\frac{\zeta(x)}{|x|} \star \tilde{\rho} \in L^\infty(\Gamma)$ by Young inequality. To finish, I_3' is bounded because $\tilde{G} \in L^\infty(\Gamma)$ and $|I_3''| < +\infty$ is a consequence of $|x_3 - y_3| \leq |x_3| + |y_3|$ and $|x_3|\rho \in L^1(\Gamma)$.

Step 2 : Proof of i)

As one may expect, the energy reaches $-\infty$ when some of the electrons are driven away by the electric field. In order to mathematically account for that, we introduce a non-negative function $\chi \in C_0^\infty(\Gamma)$ such that $\int_\Gamma \chi = 1$, and define

$$\rho_n(x) = \frac{\lambda + \lambda_c}{2}\chi + \frac{\lambda - \lambda_c}{2}\chi(x + ne_3),$$

ρ_n being periodically repeated along $\mathbf{Z}^2 \times \{0\}$. Here $\lambda_c = 2N + 1 - 2E = (1 - \varepsilon E) \int m$ with $\varepsilon = \frac{1}{N+\frac{1}{2}}$. If n is large enough to ensure that $\mathrm{supp}(\chi) \cap \mathrm{supp}(\chi(\cdot + ne_3)) = \emptyset$, then $\int_\Gamma \rho_n = \lambda$ and ρ_n is a test-function for the energy. We compute:

$$\begin{aligned}\mathcal{E}(\rho_n) &= \mathcal{E}\left(\frac{\lambda+\lambda_c}{2}\chi\right) + \frac{\lambda-\lambda_c}{2}\int_\Gamma |\nabla\sqrt{\chi}|^2 + \left(\frac{\lambda-\lambda_c}{2}\right)^{5/3}\int_\Gamma \chi^{5/3} \\ &+ \frac{(\lambda-\lambda_c)^2}{8}\int_{\Gamma\times\Gamma} \chi(x)G(x-y)\chi(y)dxdy \\ &+ \frac{\lambda-\lambda_c}{2}\int_\Gamma \chi(x+ne_3)V(x)dx.\end{aligned}$$

where $V(x) = \frac{\lambda+\lambda_c}{2}\chi \star G - \sum_{|j|\le N} G(x - je_3) + Ex_3$, (with the convolution taken over Γ).

Since only the last term in the energy depends on n, and since by lemma 3.2 we have

$$V(x) = -\frac{(\lambda-\lambda_c)}{4}|x_3| + 2Ex_3^+ + r(x)$$

where $r \in L^\infty(\Gamma)$, we deduce when $\lambda > \lambda_c$ that

$$\lim_{n\to+\infty} \mathcal{E}(\rho_n) = -\infty$$

Step 3 : Convexity of the energy $\mathcal{E}$ on K_λ

For $\rho \in K_\lambda$, we can rewrite the energy as

$$\mathcal{E}(\rho) = \int_\Gamma |\nabla\sqrt{\rho}|^2 + \rho^{\frac{5}{3}} + v\rho + w\rho + \frac{1}{2}D_G(\rho - \lambda\chi, \rho - \lambda\chi) - C_\lambda \tag{9}$$

where $v \in L^{\frac{5}{2}}(\Gamma)$, $w \in L^\infty_{loc}(\Gamma)$ with $C(1 + |x_3|) \ge w \ge 1$, D_G is a positive symmetric bilinear form on $K_\lambda - \lambda\chi$ and C_λ is a constant. More precisely we have

$$v(x) = -\sum_{|j|\le N} \frac{\zeta(x - je_3)}{|x - je_3|}$$

$$w(x) = A(x) + 2Ex_3^+ + \frac{(\lambda-\lambda_c)}{2}|x_3| \tag{10}$$

where

$$A(x) = -\sum_{|j|\le N}\left(\tilde{G}(x - je_3) - \frac{1}{2}\left(|x_3 - j| - |x_3|\right)\right) - \lambda\left(G\star\chi - \frac{1}{2}|x_3|\right) + A_0$$

where A_0 is constant such that $A \ge 1$. And the constant C_λ is then given by

$$C_\lambda = A_0 - \frac{\lambda^2}{2}\int_\Gamma \chi(G\star\chi)$$

Moreover the bilinear form D_G is given by the following property

Lemma 3.3 *The following symmetric bilinear form*

$$D_G(f,g) := \int_{\Gamma\times\Gamma} f(x)G(x-y)g(y)$$

is continuous on the Banach space $Y = \left\{ f \in L^1(\Gamma) \cap L^{\frac{5}{3}}(\Gamma), |x_3| f \in L^1(\Gamma) \right\}$. *Moreover for*

$$Y_0 = \left\{ f \in Y, \quad \int_\Gamma f = 0 \right\}$$

we have

$$\forall f \in Y_0, \quad \nabla\left(G \star f\right) \in L^2(\Gamma) \tag{11}$$

and

$$\forall f,g \in Y_0, \quad D_G(f,g) = \int_\Gamma \nabla\left(G\star f\right)\cdot\nabla\left(G\star g\right)$$

In particular D_G *is positive on* Y_0.

Remark 3.4 *Let us point out that the convexity of the bilinear form* D_G *is subjected to the constraint* $f \in Y_0$. *In other words,* $\mathcal{E}$ *is strictly convex on the hyperplanes* $\{\int_\Gamma \rho = \lambda\}$, *for each* λ, *but not on the whole space. This accounts for the existence of* λ_c, *which would not possibly exist if* $\mathcal{E}$ *was convex on the whole space.*

The first two terms of the energy are strictly convex with respect to ρ (see [5]). Because every positive quadratic form is convex, the map $f \longmapsto D_G(f,f)$ is convex on $Y_0 \supset (K_\lambda - \lambda\chi)$, and we deduce in particular that $\mathcal{E}$ is strictly convex on K_λ.

>From the expression (9), we see that $\mathcal{E}$ is naturally defined and strictly convex on

$$K'_\lambda = \left\{\rho \geq 0, \quad \sqrt{\rho} \in H^1(\Gamma)\cap L^2(w), \quad \nabla\left(G\star(\rho-\lambda_c\chi)\right) \in L^2(\Gamma)\right\} \supset K_\lambda \quad \forall 0 \leq \lambda \leq \lambda_c$$

where w is defined in (10) and

$$L^2(w) = \left\{ u \in L^2(\Gamma), \quad \int_\Gamma u^2 w < +\infty \right\}$$

with the norm $|u|_{L^2(w)} = \left(\int_\Gamma u^2 w\right)^{\frac{1}{2}}$. The fact that $K'_{\lambda_c} \supset K_{\lambda_c}$ and $K'_\lambda = K_\lambda$ for $\lambda < \lambda_c$, is a consequence of (11) and the fact that

$$\forall \lambda \in [0,\lambda_c], \quad \left(\rho \in K'_\lambda\right) \Longrightarrow \left(\int_\Gamma \rho = \lambda\right)$$

This is proved by the lemma

Lemma 3.5 *If* $f \in L^1(\Gamma)$, *then* $\nabla\left(G\star f\right)$ *is defined in* $\mathcal{D}'(\Gamma)$. *Moreover*

$$\left(\nabla\left(G\star f\right) \in L^2(\Gamma)\right) \Longrightarrow \left(\int_\Gamma f = 0\right)$$

Step 4 : Minimizing sequences on K'_λ

We first remark that for $\lambda \leq \lambda_c$ and $\rho \in K'_\lambda$, we have (following the bounds on I'_2):

$$\mathcal{E}(\rho) \geq -C + |\rho|_{\frac{5}{3}}^{\frac{5}{3}} - C\,|\rho|_{\frac{5}{3}} \tag{12}$$

We then consider a minimizing sequence $(\rho_n)_n$ in K'_λ. From (12) and the expression of the energy (9) we deduce

$$\left\{\begin{array}{lll} |\sqrt{\rho_n}|_{H^1} & \leq & C \\ |\rho_n|_{L^{\frac{5}{3}}} & \leq & C \\ |\sqrt{\rho_n}|_{L^2(w)} & \leq & C \\ |\nabla\,(G \star (\rho_n - \lambda\chi)|_{L^2} & \leq & C \end{array}\right.$$

Up to extracting a subsequence we have $\sqrt{\rho_n} \to \sqrt{\rho_\infty}$ in L^2_{loc}, i.e.

$$\rho_n \to \rho_\infty \quad \text{in} \quad L^1_{loc}$$

Moreover

$$\left\{\begin{array}{lllll} \sqrt{\rho_n} & \rightharpoonup & \sqrt{\rho_\infty} & \text{in} & H^1_{weak} \\ \rho_n & \rightharpoonup & \rho_\infty & \text{in} & L^{\frac{5}{3}}_{weak} \\ \sqrt{\rho_n} & \rightharpoonup & \sqrt{\rho_\infty} & \text{in} & L^2(w)_{weak} \\ \nabla\,(G \star (\rho_n - \lambda\chi) & \rightharpoonup & F_\infty & \text{in} & L^2_{weak} \end{array}\right.$$

where the limits are identified using the convergence in the sense of distributions. Moreover we have the

Lemma 3.6 $F_\infty = \nabla\,(G \star (\rho_\infty - \lambda\chi)$

By continuity of each convex term Φ of the energy on each corresponding reflexive Banach space, we get

$$\Phi(\rho_\infty) \leq \liminf_{n \to +\infty} \Phi(\rho_n)$$

and then

$$\mathcal{E}(\rho_\infty) \leq \liminf_{n \to +\infty} \mathcal{E}(\rho_n) = \inf_{K'_\lambda} \mathcal{E}$$

In particular, by construction we get $\rho_\infty \in K'_\lambda$. The uniqueness of the solution in K'_λ (and then in K_λ) is a consequence of the strict convexity of the energy on K'_λ.

Step 5 : Euler-Lagrange equation and $\rho_\infty \in K_\lambda$

Let

$$D_\lambda = \left\{\zeta \in H^1(\Gamma), \zeta^2 \in K'_\lambda\right\}$$

Using the fact that for $\rho = \zeta^2$ (note that we do not assume $\zeta \geq 0$):

$$\nabla\sqrt{\rho} = \nabla\zeta\,(\mathrm{sgn}(\zeta))$$

we see that

$$\mathcal{E}(\rho) = \Phi(|\zeta|) = \Phi(\zeta)$$

where

$$\Phi(\zeta) := \int_\Gamma |\nabla\zeta|^2 + |\zeta|^{\frac{10}{3}} + \zeta^2 \cdot G \star \left(\frac{1}{2}\zeta^2 - m\right) + Ex_3\zeta^2$$

Because $\inf_{K'_\lambda} \mathcal{E} = \inf_{D_\lambda} \Phi = \Phi(\sqrt{\rho_\infty})$, we then write down the Euler-Lagrange equation satisfied by $u = \sqrt{\rho_\infty}$,

$$-\Delta u + \frac{5}{3}u^{7/3} = \phi u \tag{13}$$

with

$$\phi = G \star \left(m - u^2\right) - Ex_3 - \theta$$

where θ is the Lagrange multiplier associated with the mass constraint $\int_\Gamma u^2 = \lambda$. This implies in particular that

$$-\Delta\phi = m - u^2 \tag{14}$$

We then use the following lemma which is proved in the following section:

Lemma 3.7 *If $(u, \phi) \in$ is solution of (13)-(14) with $u \geq 0$, then there exists a constant $C > 0$ such that*

$$u(x) \leq \frac{C}{1 + |x_3|^{\frac{3}{2}}}$$

For $\lambda < \lambda_c$, we have $K'_\lambda = K_\lambda$, but for $\lambda = \lambda_c$ we only know that $\rho_\infty \in K'_{\lambda_c} \supset K_{\lambda_c}$. Then lemma 3.7 implies that $\rho_\infty = u^2$ satisfies $x_3\rho_\infty \in L^1(\Gamma)$, which implies $\rho_\infty \in K_\lambda$ for every $\lambda \in [0, \lambda_c]$. This ends the proof of theorem 2.1.$\Diamond$

3.3 Proofs of the lemmata

Proof of lemma 3.3: Following the proof of the bounds on the term I_3, we get for $f, g \in Y$

$$|D_G(f, g)| \leq C|f|_Y|g|_Y$$

where

$$|f|_Y = |(1 + |x_3|)f|_{L^1} + |f|_{L^{\frac{5}{3}}}$$

which proves the continuity of D_G on Y.
For $f \in Y$, we have

$$-\Delta(G \star f) = f \tag{15}$$

Then by elliptic estimates and Sobolev injections, we have $G \star f \in C^0(\Gamma)$ and

$$G \star f = -\frac{1}{2}\left(\int_\Gamma f\right)|x_3| + \frac{1}{2}\mathrm{sgn}(x_3)\left(\int_\Gamma x_3 f\right) + o(1) \quad \text{as} \quad |x_3| \to +\infty \tag{16}$$

Now for $f \in Y_0 \cap C_0^\infty(\Gamma)$, multiplying equation (15) by $G \star f$ and integrating by part, we get

$$\int_\Gamma |\nabla (G \star f)|^2 = \int_\Gamma f\,(G \star f)$$

Using the density of $Y_0 \cap C_0^\infty(\Gamma)$ in Y_0, we get for all $f \in Y_0$:

$$\begin{aligned} D_G(f,f) &= \lim_{f_n \to f, f_n \in Y_0 \cap C_0^\infty(\Gamma)} \int_\Gamma |\nabla (G \star f_n)|^2 \\ &\geq \int_\Gamma \left| \lim_n (\nabla (G \star f_n)) \right|^2 \\ &= \int_\Gamma |\nabla (G \star f)|^2 \end{aligned}$$

which implies in particular (11). Here we have used the

Lemma 3.8 *If $f_n \to f$ in Y, then $\nabla (G \star f_n) \to \nabla (G \star f)$ in $\mathcal{D}'(\Gamma)$.*

Now the bilinear form defined by

$$B(f,g) = \int_\Gamma \nabla (G \star f) \cdot \nabla (G \star g)$$

is well defined on Y_0 and and satisfies the Cauchy-Schwarz inequality

$$|B(f,g)| \leq (B(f,f))^{\frac{1}{2}} (B(g,g))^{\frac{1}{2}}$$

which proves that B is continuous on Y_0. Because B is equal to D_G on $Y_0 \cap C_0^\infty(\Gamma)$ which dense in Y_0, we deduce that $D_G = B$ on Y_0. This ends the proof of the lemma.

Proof of lemma 3.8

Let us consider $\phi = (\phi_1, \phi_2, \phi_3) \in (C_0^\infty(\Gamma))^3$ and $f \in Y$. Then we can write

$$< \nabla (G \star f), \phi >= \int_\Gamma \tilde{v} f + \tilde{w} f - \tilde{C} f \tag{17}$$

where $\tilde{v} \in L^{\frac{5}{2}}(\Gamma) = \left(L^{\frac{5}{3}}(\Gamma)\right)'$, $\tilde{w} \in L^\infty(\Gamma)$ and satisfies $\tilde{w} \geq 0$, and $\tilde{C}$ depends only on ϕ. We take $-\tilde{v} = -G \star (\nabla \cdot \phi) + \frac{1}{2} \left(\int_\Gamma \phi_3\right) \operatorname{sgn}(x_3)$, $\tilde{w} = \frac{1}{2} \left(\int_\Gamma \phi_3\right) \left(\operatorname{sgn}(x_3) + \operatorname{sgn}\left(\int_\Gamma \phi_3\right)\right)$, and $\tilde{C} = -\frac{1}{2} \left|\int_\Gamma \phi_3\right|$. The fact that the second member of (17) is continuous on Y proves the lemma.

Proof of lemma 3.5

Let us remark that $< \nabla (G \star f), \phi >$ is defined by the second member of (17) for $\phi \in (C_0^\infty(\Gamma))^3$ and $f \in L^1(\Gamma)$. Now we remark that for $s = \operatorname{sgn}\left(\int_\Gamma \phi_3\right)$, we have

$$\begin{aligned} \lim_{n \to +\infty} < \nabla (G \star f), \phi(\cdot + sn) > &= \lim_{n \to +\infty} \int_\Gamma \left(\tilde{v}(\cdot + sn) + \tilde{w}(\cdot + sn) + \tilde{C}\right) f \\ &= \frac{1}{2} \left|\int_\Gamma \phi_3\right| \left(\int_\Gamma f\right) \end{aligned}$$

Now if $\nabla (G \star f) \in L^2(\Gamma)$ we deduce that $\int_\Gamma f = 0$. This ends the proof of the lemma.

Proof of lemma 3.6.

Let $f \in L^1(\Gamma) \cap L^{\frac{5}{3}}(\Gamma)$. Let us recall that for $\phi = (\phi_1, \phi_2, \phi_3) \in (C_0^\infty(\Gamma))^3$ such that $\int_\Gamma \phi_3 = 0$, (17) implies:

$$< \nabla (G \star f), \phi >= \int_\Gamma \tilde{v} f$$

where $\tilde{v} \in L^{\frac{5}{2}}(\Gamma) = \left(L^{\frac{5}{3}}(\Gamma)\right)'$. Because $\rho_n \rightharpoonup \rho_\infty$ in $L^{\frac{5}{3}}_{weak}$, we deduce that for $f_n = \rho_n - \lambda\chi$:

$$\lim_{n\to+\infty} < \nabla\left(G \star f_n\right), \phi > = < \nabla\left(G \star f_\infty\right), \phi >$$

with $f_\infty = \rho_\infty - \lambda\chi$. Because $\nabla\left(G \star f_n\right) \rightharpoonup F_\infty$ in L^2_{weak} we deduce that

$$\forall \phi \in C_0^\infty(\Gamma) \quad \text{with} \quad \int_\Gamma \phi = 0, \quad < \nabla\left(G \star f_\infty\right), \phi > = < F_\infty, \phi >$$

which implies

$$F_\infty = \nabla\left(G \star f_\infty\right) + Ce_3$$

where C is constant and $f_\infty \in L^1(\Gamma) \cap L^{\frac{5}{3}}(\Gamma)$. Using the same argument as in the proof of lemma 3.5 we see in $\pm\infty$ that

$$\frac{1}{2}\int_\Gamma f_\infty \pm C = 0$$

which implies $C = \int_\Gamma f_\infty = 0$. This ends the proof of the lemma.

4 A priori bounds

4.1 First a priori bounds

We are going to need the following bounds:

Proposition 4.1 *Let (u, ϕ) be a solution of*

$$\left\{ \begin{array}{l} -\varepsilon^2\Delta u + \frac{5}{3}u^{\frac{7}{3}} = u\phi \\ \phi = \varepsilon \sum_{|j|\leq N_\varepsilon} G_\varepsilon\left(x - j\varepsilon e_3\right) - \frac{1}{\varepsilon^2}u^2 \star_{\Gamma_\varepsilon} G_\varepsilon - \varepsilon E x_3 - \theta_\varepsilon \end{array} \right. \tag{18}$$

where θ_ε is the associated Lagrange multiplier. Then we have, for some constants C independent of ε:

(i) $\theta_\varepsilon \geq 0$,

(ii) $\phi(x) \leq \frac{C}{|x_3|^2}$ *on* $\{|x_3| > 1\}$,

(iii) $u(x) \leq \frac{C}{|x_3|^{3/2}}$ *on* $\{|x_3| > 1\}$,

(iv) $u(x) \leq C$ *on* $\mathbf{R}^3$,

(v) For all $p < 3$, and for any open bounded set ω of $\mathbf{R}^2$, $\|\phi^+\|_{L^p(\omega\times\mathbf{R})} \leq C|\omega|$,

(vi) $\phi^- \leq C + 2\varepsilon E x_3^+$.

Proof: The proofs of (ii) and (iii) are adaptations of those of [7], which we reproduce here. We introduce the function $e_R(x) = \frac{\sin(\pi|x|/R)}{|x|\sqrt{2\pi R}}$, that is, the ground state of the Laplacian on B_R with homogeneous Dirichlet boundary conditions, and define $g_R = e_R^2$. (Note that $\int_{B_R} g_R = 1$ and $\int |\nabla e_R|^2 = \frac{\pi^2}{R^2}$.) We prolong g_R outside B_R by 0. Then, we have Lemma 2.1 of [7] (see also [6] or [15]), namely:

Lemma 4.2 (Benguria, Lieb, [6]) *Let $\rho = u^2$ be the solution of (18), and ϕ defined by (18). Then, for any $R > 0$, we have:*

$$g_R \star \phi \leq \frac{5}{3} g_R \star u^{4/3} + \frac{\varepsilon^2 \pi^2}{R^2}.$$

And if $|x_3| - R > 1$, $\phi \leq \phi \star g_R$.

The first inequality is due to the fact that u is th ground state of the operator $-\varepsilon^2\Delta + \frac{5}{3}u^{4/3} - \phi$, so that $\varepsilon^2 \int |\nabla e_R(\cdot - y)|^2 + \int (\frac{5}{3}u^{4/3} - \phi) g_R \geq 0$. The second one comes from the fact that on $B_R + x$, ϕ is subharmonic and thus satisfies the mean-value inequality.

Next, denoting by $\tilde{\phi}$ the function $\phi \star g_R - \frac{\varepsilon^2\pi^2}{R^2}$, we have, using Jensen's inequality,

$$\tilde{\phi} \leq \frac{5}{3} g_R \star u^{4/3} \leq \frac{5}{3} (g_R \star u^2)^{2/3}.$$

Noticing that $-\varepsilon^2 \Delta (g_R \star \phi) = 4\pi (m_\varepsilon \star g_R - u^2 \star g_R)$, we infer that

$$-\varepsilon^2 \Delta \tilde{\phi} + \frac{5}{3} (\tilde{\phi})_+^{3/2} \leq 4\pi m_\varepsilon \star g_R.$$

In particular, for $R \geq 1$, $-\varepsilon^2\Delta\tilde{\phi} + \frac{5}{3}(\tilde{\phi})_+^{3/2}$ is bounded from above, since m_ε is a bounded measure. Following the ideas of [8], we infer that $\tilde{\phi}$ is bounded independently of ε, since $C + \frac{\alpha R'^4}{(R'^2 - |x|^2)^4}$ is a supersolution of the above equation as soon as $\alpha \geq 60^2 \varepsilon^4$. Next, we introduce the function $U(x) = \frac{a}{(|x_3|^2 - R^2)^2} + \frac{bR'^4}{(R'^2 - |x_3|^2)^4}$, with $R' > R + 1 > 2$ This is a supersolution in the set $\{|x_3| > R+1\} \cap B_{R'}$ as soon as $a \geq \left(\frac{27\varepsilon^2 R^2}{5(2R+1)}\right)^2$ and $a \geq \frac{\|\tilde{\phi}\|_\infty}{(2R+1)^2}$. This implies in particular that $\tilde{\phi} \leq U$ on $\{|x_3| > R+1\} \cap B_{R'}$. Letting then R' go to infinity, we find that there is a constant independent of R and ε such that

$$\tilde{\phi} \leq \frac{CR^2}{(|x_3|^2 - R^2)^2}$$

on the set $\{|x_3| \geq R+1\}$. This means in particular, using the second point of Lemma 4.2, that $\phi \leq \frac{CR^2}{(|x_3|^2 - R^2)^2} + \frac{\varepsilon^2\pi^2}{R^2}$ if $|x_3| - R \geq 1$. Hence, for any $|x_3| > 2$, taking $R = \frac{|x_3|}{2}$, we have $\phi \leq \frac{C}{|x_3|^2}$. We then conclude that (ii) holds by pointing out that $\tilde{\phi}$ is also bounded, so that if $1 < |x_3| < 2$, taking $R = \frac{1+|x_3|}{2}$ implies $\phi \leq \tilde{\phi} + \frac{4\varepsilon^2\pi^2}{(1+|x_3|)^2} \leq C$. Next, we insert (ii) into (18), getting

$$-\varepsilon^2 \Delta u + \frac{4}{3} u^{7/3} \leq \frac{C}{|x_3|^{7/2}},$$

for some constant C. Hence, using exactly the same technics, but with the supersolution $V(x) = \frac{a}{(|x_3|^2-R^2)^{3/2}} + \frac{bR'^{3/2}}{(R'^2-|x|^2)^{3/2}}$, we show (iii). Then, with (18) and the fact that $G_\varepsilon(x) = \frac{1}{|x|} - \frac{2\pi|x_3|}{\varepsilon^2} + \tilde{G}_\varepsilon(x)$ on Γ_ε, where $\tilde{G}_\varepsilon$ is smooth and goes to 0 as $|x_3| \to \infty$ (see [7]), it is not difficult to show that $\lim_{x_3 \to -\infty} \phi = -\theta_\varepsilon$, so that with (ii), this implies (i).

In order to show (v), we use again that

$$\phi \star g_R \leq C,$$

with C independent of ε. Taking $R = \frac{\varepsilon}{4}$, we infer using the second part of Lemma 4.2 that $\phi(x) \leq C + \frac{\varepsilon^2\pi^2}{R^2} = C + 16\pi^2$ on the set $\mathbf{R}^3 \setminus \bigcup_{i \in \varepsilon\mathbf{Z}^3 \cap \{|x_3|<1\}} B_{\frac{\varepsilon}{4}}(i)$. On the other hand, in each ball $B_{\frac{\varepsilon}{4}}(i)$, ϕ satisfies $-\varepsilon^2\Delta\phi \leq 4\pi\varepsilon^3\delta_i$. Since the function $C + 16\pi^2 + \frac{\varepsilon}{|x-i|}$ is a supersolution of this equation and is greater than ϕ on the boundary of the ball, we deduce that $\phi \leq C + 16\pi^2 + \frac{\varepsilon}{|x-i|}$ in $B_{\frac{\varepsilon}{4}}(i)$. As a consequence, we have

$$\int_{B_{\frac{\varepsilon}{4}}(i)} (\phi_+)^p \leq \varepsilon^3 C + \varepsilon^p \int_{B_{\frac{\varepsilon}{4}}(0)} \frac{dx}{|x|^p} \leq C\varepsilon^3,$$

for any $p < 3$. This implies that for any bounded set Ω, we have $\|\phi^+\|_{L^p(\Omega)} \leq C|\Omega|$. Hence, with the help of (ii), we deduce (v). The last step of the proof is to show the following:

$$u^{4/3} \leq \phi + C - \frac{2\varepsilon^3 E}{2\pi} f_0 \star_{\Gamma_0} (G_\varepsilon - \frac{2\pi}{\varepsilon^2} x_3), \tag{19}$$

for some constant C and some smooth function f_0 having compact support with respect to x_3, and such that $\int_{\Gamma_\varepsilon} f_0 = 1$ (C depends on f_0 in fact.) This inequality will allow to conclude that (iv) and (vi) hold. In order to show (19), we introduce the function $w = u^{4/3} - (\phi + \theta_\varepsilon) + \frac{\varepsilon^3 E}{2\pi} f_0 \star (G_\varepsilon - \frac{2\pi}{\varepsilon^2} x_3) - C_0 - (C_0 - \theta_\varepsilon)^+$, where $C = 2C_0$ will be chosen later on. One easily computes:

$$\varepsilon^2 \Delta w \geq \frac{4}{3} u^{4/3} (\frac{5}{3} u^{4/3} - \phi - 3\pi u^{2/3}),$$

on any set containing no nuclei. Hence, if $S = \{w > 0\}$, which clearly contains no nuclei, we have on S $-\phi \geq \theta_\varepsilon - u^{4/3} + (C_0 - \theta_\varepsilon)^+ + C_0 - \frac{2\varepsilon^3 E}{2\pi} f_0 \star (G_\varepsilon - \frac{2\pi}{\varepsilon^2} x_3)$, which implies $\varepsilon^2 \Delta w \geq \frac{4}{3} u^{4/3} (\frac{2}{3} u^{4/3} - 3\pi u^{2/3} + C_0)$, whenever C_0 is chosen large enough to have $C_0 - \frac{2\varepsilon^3 E}{2\pi} f_0 \star (G_\varepsilon - \frac{2\pi}{\varepsilon^2} x_3) \geq 0$, which is always possible according to the definition of G_ε, and may be done so that C_0 does not depend on ε. Moreover, if we have in addition $C_0 \geq \frac{27\pi^2}{8}$, then the polynomial $\frac{2}{3}t^2 - 3\pi t + C_0$ is non-negative, so that $\varepsilon^2 \Delta w \geq 0$. It is easily seen, using (iii) and the definitions of λ_c and ϕ (18), together with the fact that $G_\varepsilon = -\frac{2\pi}{\varepsilon^2}|x_3| + o(1)$ as $|x_3| \to \infty$, that we have:

$$\phi(x) = -\varepsilon E(x_3 + |x_3|) - \theta_\varepsilon + o(1) \quad \text{as} \quad |x_3| \to \infty,$$

with $o(1)$ possibly depending on ε. Hence, since in addition $\frac{2\varepsilon^3 E}{2\pi} f_0 \star (G_\varepsilon - \frac{2\pi}{\varepsilon^2} x_3) = -2\varepsilon E x_3^+ + o(1)$, $w(x) = -(C_0 - \theta_\varepsilon)^+ - C_0 + o(1)$. Thus, w goes to some negative constant as $|x_3| \to \infty$, so that S is bounded with respect to $|x_3|$. This implies that on

∂S, $w = 0$, so that $w \leq 0$ on S, thanks to the periodicity with respect to x_1 and x_2. Hence, $S = \emptyset$, which implies (19). This shows in particular that u is bounded on the set $\{|x_3| < 1\} \setminus \bigcup_{i \in \varepsilon \mathbf{Z}^3} B_{\frac{\varepsilon}{4}}(i)$. Inside the balls, we use here again supersolution methods, since we have $-\varepsilon^2 \Delta u + \frac{2}{3} u^{7/3} \leq C + C \frac{\varepsilon^{7/4}}{|x-i|^{7/4}}$ on each ball $B_{\frac{\varepsilon}{4}}(i)$, according to the bound $\phi \leq C + \frac{C\varepsilon}{|x-i|}$ on each ball. One easily shows that the function $A + B \frac{|x-i|^{1/4}}{\varepsilon^{1/4}}$ is a supersolution of this problem as soon as A and B are chosen properly, and that they may be chosen independently of ε, so that $u \leq C + C \frac{|x|^{1/4}}{\varepsilon^{1/4}} \leq C$ on $B_{\frac{\varepsilon}{4}}(i)$. This completes the proof of (iv). The proof of (vi) then only amounts, with the help of (19), to point out that $\frac{2\varepsilon^3 E}{2\pi} f_0 \star (G_\varepsilon - \frac{2\pi}{\varepsilon^2} x_3) \geq -C - 2\varepsilon E x_3^+$, which follows from the definition of f_0 and the fact that $G_\varepsilon(x) \geq -\frac{2\pi}{\varepsilon^2}|x_3| - C$. $\Diamond$

We next point out that, integrating the equation $-\Delta v + \frac{5}{3} v^{7/3} - \psi v = 0$ against $v\xi^2$, where $\xi \in \mathcal{D}(\mathbf{R}^3)$ and satisfies $\xi = 1$ in the unit cube Q, $\xi = 0$ in $\mathbf{R}^3 \setminus 2Q$ and $0 \leq \xi \leq 1$, together with $|\nabla \xi| \leq 2$, using the fact that $\int -\Delta v v \xi^2 = \int |\nabla(\xi v)|^2 - \int v^2 |\nabla \xi|^2$,

$$\int_Q |\nabla v|^2 \leq 4 \int_{2Q} v^2 + \int_{2Q} \psi^+ v^2 \leq C + C \int_{2Q} \psi^+ \leq C,$$

where we have used (iv) and (v) of Proposition 4.1. As a consequence, since the same argument is valid with $\xi(\cdot + x_0)$ instead of ξ, v is bounded in H^1_{loc}. Hence, ψ being bounded in $L^p_{unif}(\mathbf{R}^3)$, we may extract from (v, ψ) a subsequence such that v converges strongly in $L^2_{loc}(\mathbf{R}^3)$ and ψ converges weakly in $L^p_{loc}(\mathbf{R}^3)$, for $p < 3$. Moreover, using (v) and (vi) of Proposition 4.1, ψ is bounded in $L^1_{unif}(\{|x_3| < \frac{1}{\varepsilon}\})$, so that its limit is in $L^1_{unif}(\mathbf{R}^3)$. Hence, the limit of (v, ψ), which satisfy (32), must be (u_{per}, ϕ_{per}). We now need the following Lemma, which is an adapted version of Theorem 5.9 of [9].

Lemma 4.3 *Let (v_n, ψ_n) be a solution of*

$$\begin{cases} -\Delta v + \frac{5}{3} v^{7/3} - \psi v = 0, \\ -\Delta \psi = \sum_{k \in \mathbf{Z}^3 \cap \{|k_3| < n\}} \delta_k - v^2, \\ v \geq 0, \end{cases}$$

such that $\|v_n\|_{L^\infty(\{|x_3|<n\})} + \|\psi_n\|_{L^1_{unif}(\{|x_3|<n\})}$ is bounded independently of n. Then for any sequence R_n such that $R_n \leq n$, $\frac{R_n}{n} \longrightarrow 1$ and $n - R_n \longrightarrow \infty$ as $n \to \infty$. Then we have:

$$\|u_{per} - v_n\|_{L^\infty(\{|x_3|<R_n\})} \longrightarrow 0 \quad \text{as} \quad n \to \infty, \tag{20}$$

$$\|\phi_{per} - \psi_n\|_{L^\infty(\{|x_3|<R_n\})} \longrightarrow 0 \quad \text{as} \quad n \to \infty, \tag{21}$$

where (u_{per}, ϕ_{per}) is the unique solution of (32).

Proof: We refer the reader to [9] (proof of Theorem 5.9), since this proof may be readily adapted to our case. Note that the norm $\|\phi_{per} - \psi_n\|_{L^\infty(\{|x_3|<R_n\})}$ does make sense since ϕ_{per} and ψ_n have exactly the same singularities (the nuclei), which cancel. $\Diamond$

Remark 4.4 *The above Lemma states, roughly speaking, that, no matter what happens outside the crystal, in the limit* $\frac{1}{n} = \varepsilon \to 0$*, the electronic density inside the crystal (the term "inside" meaning the hypothesis we made on* R_n*) converges towards the density of the true crystal* u_{per}*.*

Looking closely at Lemma 4.3, one easily deduce that following corollary:

Corollary 4.5 *Let* $\rho = u^2$ *be the solution of (18), with* $\lambda = \lambda_c$*, and let* ϕ *be defined by (18). Then, for any sequence* η *such that* $\eta \leq 1, \quad \eta \to 1, \quad \frac{\eta}{\varepsilon} \to \infty$*, we have:*

$$\|u - u_{per}(\frac{x}{\varepsilon})\|_{L^\infty(\{|x_3|<1-\eta\})} \longrightarrow 0,$$

$$\|\phi - \phi_{per}(\frac{x}{\varepsilon})\|_{L^\infty(\{|x_3|<1-\eta\})} \longrightarrow 0$$

as $\varepsilon \to 0$*. Here* u_{per} *and* ϕ_{per} *are the solutions of the system (32).*

4.2 Exponential decay estimates

We prove the following theorem which, with the a priori bounds given in section 3 for $\varepsilon = 1$, implies theorem 2.3.

Theorem 4.6 *Let* (u, ϕ) *a solution on* Γ *of*

$$\begin{cases} -\Delta u + \frac{5}{3}u^{\frac{7}{3}} = \phi u \\ -\Delta\phi = m - u^2 \\ u > 0 \end{cases} \tag{22}$$

with $m(x) = \sum_{|k|\leq N} \delta(x - ke_3)$*. We assume that there exists a constant* $C_0 > 0$ *such that such that*

$$|u(x) - u_p(x)| + |\phi(x) - \phi_p(x)| \leq C_0 \quad on \quad \{-N \leq x_3 \leq N\}$$

where (u_p, ϕ_p) *is the periodic solution. Then there exists two constants* $C_1, C_2 > 0$ *(which only depend on* C_0 *and not on* N*) such that*

$$|u(x) - u_p(x)| + |\phi(x) - \phi_p(x)| \leq C_1 e^{-C_2 d(x)} \quad on \quad \{-N \leq x_3 \leq N\}$$

where $d(x) = d\,(x_3, [-N, N]^c)$*.*

The exponential decay far away from the boundary of the crystal presented in theorem 4.6 is physically significant and seems a new result according to our knowledge. This exponential decay is an illustration of the "strong uniqueness" of the solutions for this model and is a kind of Harnack effect but for a system. The explanation of the "strong uniqueness" is simply contained in the fact that the functional $\mathcal{E}$ is strictly convex which implies good properties of the following system (and also of its linearization):

$$\begin{cases} -\frac{\Delta u}{u} + \frac{5}{3}u^{\frac{4}{3}} = \phi \\ -\Delta\phi = m - u^2 \\ u > 0 \end{cases} \tag{23}$$

These properties are illustrated by the following result:

Lemma 4.7 *Let $(u,\phi),(v,\psi)\in L^\infty(\Gamma)\times L^1_{unif}(\Gamma)$ be two solutions of (23) with the same bounded measure m on Γ. Then, for any $\eta\in C_0^\infty(\Gamma)$ (i.e. having compact support with respect to x_3), we have with $u_1=v-u$, $\phi_1=\psi-\phi$:*

$$Q(u,v)+\frac{1}{2}\int_\Gamma|\nabla(\eta\phi_1)|^2=\int_\Gamma\left(u_1^2+\frac{1}{2}\phi_1^2\right)|\nabla\eta|^2+A((u,\phi),(v,\psi)) \tag{24}$$

where Q is the sum of two positive terms

$$Q(u,v)=\int_\Gamma u^2\left|\nabla\left(\frac{\eta u_1}{u}\right)\right|^2+\eta^2(u+u_1)u_1\frac{5}{3}\left((u+u_1)^{4/3}-u^{4/3}\right)$$

and A is antisymmetric in $(u,\phi),(v,\psi)$:

$$A((u,\phi),(v,\psi))=\frac{1}{2}\int_\Gamma\eta^2\phi_1u_1^2$$

Proof: The equations satisfied by u,v,ϕ,ψ read:

$$\left\{\begin{array}{l}-\frac{\Delta u}{u}+\frac{5}{3}u^{4/3}-\phi=0,\\ -\frac{\Delta v}{v}+\frac{5}{3}v^{4/3}-\psi=0,\\ -\Delta(\psi-\phi)=u^2-v^2.\end{array}\right. \tag{25}$$

Multiplying the last equation by $\phi_1\eta^2$ and integrating, we have:

$$\int_\Gamma-\eta^2\phi_1\Delta\phi_1=-\int_\Gamma u_1(2u+u_1)\phi_1\eta^2,$$

so that, using the fact that $\int_\Gamma-\eta^2\xi\Delta\xi=\int_\Gamma|\nabla(\eta\xi)|^2-\int_\Gamma\xi^2|\nabla\eta|^2$ for any $\eta\in C_0^\infty(\Gamma)$ and any sufficiently regular ξ, we deduce that

$$\frac{1}{2}\int_\Gamma|\nabla(\eta\phi_1)|^2\;=\;\frac{1}{2}\int_\Gamma\phi_1^2|\nabla\eta|^2-\frac{1}{2}\int_\Gamma u_1(2u+u_1)\phi_1\eta^2 \tag{26}$$

Next, we substract the first two equations of (25), multiply the difference by $\eta^2(u+u_1)u_1$ and get:

$$\int_\Gamma\left(\frac{\Delta u}{u}-\frac{\Delta v}{v}\right)(u+u_1)u_1\eta^2+\int_\Gamma\frac{5}{3}\eta^2(u+u_1)u_1((u+u_1)^{4/3}-u^{4/3})-\int_\Gamma\phi_1(u+u_1)u_1\eta^2=0.$$

Integrating by parts, one easily computes:

$$\int_\Gamma\left(\frac{\Delta u}{u}-\frac{\Delta v}{v}\right)(u+u_1)u_1\eta^2=\int_\Gamma u^2\left|\nabla\left(\frac{\eta u_1}{u}\right)\right|^2-\int_\Gamma u_1^2|\nabla\eta|^2.$$

As a consequence, we have

$$\int_\Gamma u^2\left|\nabla\left(\frac{\eta u_1}{u}\right)\right|^2+\frac{5}{3}\eta^2(u+u_1)u_1(v^{4/3}-u^{4/3})-\phi_1(u+u_1)u_1\eta^2=\int_{\Gamma_1}u_1^2|\nabla\eta|^2. \tag{27}$$

Adding (26) and (27), we get (24). ◊

Proof of theorem 4.6

Let us define

$$M(d) = \sup_{d(x_3,[-N,N]^c)\geq d} |u(x) - u_p(x), \phi(x) - \phi_p(x)|$$

It is sufficient to prove that

$$\exists L > 0, \quad \exists \gamma \in (0,1), \quad \forall N > 0, \quad \forall d \leq N, \quad M(d+L) \leq \gamma M(d) \quad \text{if} \quad d + L < N$$

We argue by contradiction, assuming that

$$\forall L > 0, \quad \forall \gamma \in (0,1), \quad \exists N > 0, \quad \exists d \leq N, \quad M(d+L) > \gamma M(d) \quad \text{with} \quad d + L < N$$

Let us take sequence

$$\begin{cases} L_n \to +\infty \quad \text{as} \quad n \to +\infty \\ \gamma_n \to 1 \quad \text{as} \quad n \to +\infty \\ d_n + L_n \leq N_n \\ M(d_n + L_n) > \gamma_n M(d_n) \quad \text{for} \quad (u^n, \phi^n) \end{cases}$$

>From the standard elliptic estimates, we get by compactness (up to extraction of a subsequence) that

$$(u^n, \phi^n) \to (u^\infty, \phi^\infty)$$

where (u^∞, ϕ^∞) is solution of (22) on Γ with $m(x) = \sum_{k\in\mathbf{Z}} \delta(x - ke_3)$. From theorem 2.2 we have

$$(u^\infty, \phi^\infty) = (u_p, \phi_p)$$

where we denote here the periodic solution by (u_p, ϕ_p). As a consequence

$$M(d_n + L_n) \to 0$$

We then consider the renormalized sequence

$$\left(\overline{u}_1^n, \overline{\phi}_1^n\right)(x) = \frac{(u^n - u_p, \phi - \phi_p)}{M(d_n + L_n)}(x + x^n)$$

where x^n is a point such that $d(x_3^n, [-N,N]^c) \geq d_n + L_n$ and

$$\frac{|u^n(x^n) - u_p(x^n)| + |\phi(x^n) - \phi_p(x^n)|}{M(d_n + L_n)} \longrightarrow 1$$

Up to extraction of a subsequence we get

$$\left(\overline{u}_1^n, \overline{\phi}_1^n\right) \to \left(\overline{u}_1^\infty, \overline{\phi}_1^\infty\right)$$

which satisfies

$$\sup_\Gamma |\overline{u}_1^\infty(x)| + |\overline{\phi}_1^\infty(x)| \leq 1 = |\overline{u}_1^\infty(0)| + |\overline{\phi}_1^\infty(0)| \tag{28}$$

Taking the limit in (24) we get (up to translate (u_p, ϕ_p)):

$$\int_\Gamma u_p^2 \left| \nabla \left(\frac{\eta \overline{u}_1^\infty}{u_p} \right) \right|^2 + \frac{20}{9} \eta^2 u_p^{\frac{4}{3}} + \frac{1}{2} \left| \nabla \left(\eta \overline{\phi}_1^\infty \right) \right|^2 = \int_\Gamma \left((\overline{u}_1^\infty)^2 + \frac{1}{2} (\overline{\phi}_1^\infty)^2 \right) |\nabla \eta|^2$$

Then taking $\eta(x) = \eta_1(\lambda x_3)$ with $\lambda \to 0$ and

$$\eta_1 \in C_0^\infty(\Gamma)$$

with $\eta = 1$ for $x_3 \in [-1, 1]$, we get at the limit $\lambda = 0$:

$$\overline{u}_1^\infty = 0, \quad \nabla \overline{\phi}_1^\infty = 0$$

To conclude that $\overline{\phi}_1^\infty = 0$ we remark that the equations imply

$$\phi^n - \phi_p = -\frac{1}{u^n u_p} \nabla \left(u_p^2 \nabla \left(\frac{u^n - u_p}{u_p} \right) \right) + \frac{5}{3} \left((u^n)^{\frac{4}{3}} - u_p^{\frac{4}{3}} \right)$$

This gives at the limit

$$\overline{\phi}_1^\infty = -\frac{1}{u_p^2} \nabla \left(u_p^2 \nabla \left(\frac{\overline{u}_1^\infty}{u_p} \right) \right) + \frac{20}{9} u_p^{\frac{1}{3}} \overline{u}_1^\infty = 0$$

Finally $\overline{u}_1^\infty = \overline{\phi}_1^\infty = 0$ gives a contradiction with (28). This ends the proof of the theorem.

5 Appendix: An homogenization approach

We present in this Section an alternative approach using the two-scale convergence [1, 13]. In order to do so, we first re-write the system of PDE satisfied by u and ϕ:

$$\left\{ \begin{array}{l} -\varepsilon^2 \Delta u + \frac{5}{3} u^{7/3} - \phi u = 0, \\ -\varepsilon^2 \Delta \phi = m - u^2. \end{array} \right. \tag{29}$$

5.1 Two-scale convergence

The key to the convergence problem is to postulate the following ansatz for the functions (u, ϕ):

$$\left\{ \begin{array}{l} u = u_0(x, \frac{x}{\varepsilon}) + \varepsilon u_1(x, \frac{x}{\varepsilon}) + \varepsilon^2 u_2(x, \frac{x}{\varepsilon}) + \ldots, \\ \phi = \phi_0(x, \frac{x}{\varepsilon}) + \varepsilon \phi_1(x, \frac{x}{\varepsilon}) + \varepsilon^2 \phi_2(x, \frac{x}{\varepsilon}) + \ldots, \end{array} \right. \tag{30}$$

where the functions $u_i(x, y)$ and $\phi_i(x, y)$ are periodic in the second variable. Inserting this ansatz into (29), and noticing that $-\Delta u_i(x, \frac{x}{\varepsilon}) = -\Delta_x u_i(x, \frac{x}{\varepsilon}) - \frac{2}{\varepsilon} \nabla_x \cdot \nabla_y u_i(x, \frac{x}{\varepsilon}) - \frac{1}{\varepsilon^2} \Delta_y u_i(x, \frac{x}{\varepsilon})$, we have, isolating the term of order 0, and admitting that the two variables x and $y = \frac{x}{\varepsilon}$ decouple:

$$\left\{ \begin{array}{l} -\Delta_y u_0 + \frac{5}{3} u_0^{7/3} - \phi_0 u_0 = 0, \\ -\Delta_y \phi_0 = m_0 - u_0^2, \end{array} \right. \tag{31}$$

where we have implicitly assumed that the nonlinear terms pass to the limit in the same fashion as the linear ones, and where $m_0(x,y) = 1_{\{|x_3|<1\}}(x) \sum_{k\in\mathbf{Z}^3} \delta_k(y)$ is the limit in the sense of two-scale convergence (see below) of m_ε. The above ansatz is justified by the notion of two-scale convergence, that we rapidly introduce, referring to [1, 13] for details.

Definition 5.1 *Let Ω be an open subset of $\mathbf{R}^n$, and Q the unit cube of $\mathbf{R}^n$. Let v_n be a sequence in $L^2(\Omega)$. We say that v_n two-scale converges to $v_\infty \in L^2(\Omega \times Q)$ if, for any function $\psi \in \mathcal{D}(\Omega; C^\infty_{per}(Q))$, we have*

$$\lim_{n\to\infty} \int_\Omega v_n(x)\psi(x, \frac{x}{\varepsilon})dx = \int_{\Omega\times Q} v_\infty(x,y)\psi(x,y)dxdy.$$

Note that in practice, the sequence v_n will be indexed by a continuous variable ε, which will be supposed to go to 0. This of course makes no difference in the above definition. The following theorems are borrowed from [13] and [1], and are a way of making rigorous the above formal results.

Theorem 5.2 (Nguetseng, [13]) *From each bounded sequence v_ε in $L^2(\Omega)$, we can extract a subsequence that two-scale converge to some limit $v_0 \in L^2(\Omega \times Q)$.*

Of course, this is only a weak convergence result, and in order to pass to the limit in the nonlinear terms of (29), the following will be useful:

Theorem 5.3 (Allaire, [1]) *Let v_ε be a sequence of functions in $L^2(\Omega)$ which two-scale converges to $v_0 \in L^2(\Omega \times Q)$. Then*

$$\liminf_{\varepsilon\to 0} \|v_\varepsilon\|_{L^2(\Omega)} \geq \|v_0\|_{L^2(\Omega\times Q)},$$

and if equality is achieved, then

$$\lim_{\varepsilon\to 0} \|v_\varepsilon - v_0(x, \frac{x}{\varepsilon})\|_{L^2(\Omega)} = 0,$$

and, for any sequence w_ε of $L^2(\Omega)$ which two-scale converges to $w_0 \in L^2(\Omega \times Q)$, the sequence $v_\varepsilon w_\varepsilon$ two-scale converges to $v_0 w_0$.

5.2 Convergence at order 0

Setting $L^1_{unif}(\mathbf{R}^3) = \{f \in L^1_{loc}(\mathbf{R}^3), \quad \sup_{x\in\mathbf{R}^3} \|f\|_{L^1(B+x)} < \infty\}$, B being the unit ball of $\mathbf{R}^3$, we are now in position to prove the following:

Theorem 5.4 *Let $\rho = u^2$ be the solution of (18), and let ϕ be defined by (18). Then, up to extracting a subsequence, (u, ϕ) two-scale converges to $(u_0, \phi_0) \in L^2(\Gamma_1 \times Q)$, which are solutions of (31), that is*

$$\begin{cases} -\Delta_y u_0 + \frac{5}{3}u_0^{7/3} - \phi_0 u_0 = 0, \\ -\Delta_y \phi_0 = m_0 - u_0^2, \end{cases}$$

with $m_0(x,y) = 1_{\{|x_3|<1\}}(x) \sum_{k\in\mathbf{Z}^3} \delta_k(y)$. *In addition, denoting by* (u_{per}, ϕ_{per}) *the unique solution (given by theorem 2.2) in* $L^\infty(\mathbf{R}^3) \times L^1_{unif}(\mathbf{R}^3)$ *of the problem*

$$\left\{ \begin{array}{l} -\Delta u_{per} + \frac{5}{3} u_{per}^{7/3} - \phi_{per} u_{per} = 0, \\ -\Delta \phi_{per} = \sum_{k\in\mathbf{Z}^3} \delta_k - u_{per}^2, \\ u \geq 0, \end{array} \right. \tag{32}$$

we have:

$$\left\{ \begin{array}{l} u_0(x,y) = 1_{\{|x_3|<1\}}(x) u_{per}(y), \\ \phi_0(x,y) = \phi_{per}(y) \quad \textit{if} \quad |x_3| < 1 \end{array} \right. \tag{33}$$

Proof: The first point is that (32) has indeed a unique solution. This is insured by Theorem 6.5 of [9]. Thus, the definition of (u_{per}, ϕ_{per}) is clear. using the bounds we have shown in Proposition 4.1, one easily shows that (u, ϕ) two-scale converges to some limit (u_0, ϕ_0). We are now going to show that this limit is indeed equal to $(u_{per}(y), \phi_{per}(y))$ if $|x_3| < 1$. In order to prove this claim, we introduce the following rescaled functions:

$$v(x) = u(\varepsilon x), \quad \psi(x) = \phi(\varepsilon x).$$

These functions satisfy the following system:

$$\left\{ \begin{array}{l} -\Delta v + \frac{5}{3} v^{7/3} - \psi v = 0, \\ -\Delta \psi = \sum_{k\in\mathbf{Z}^3 \cap \{|x_3|<\frac{1}{\varepsilon}\}} \delta_k - v^2. \end{array} \right.$$

Applying Lemma 4.3 to our sequence (v, ψ), one easily shows that if $R = \frac{1}{\varepsilon} - \frac{1}{\sqrt{\varepsilon}}$, then $\|u_{per} - v\|_{L^\infty(\{|x_3|<R)} \longrightarrow 0$ as $\varepsilon \to 0$. Now, denoting by $f(x,y)$ smooth function which is Q-periodic in y and has compact support in x, this support being included in $\{|x_3| < 1\}$. Then, on the one hand,

$$\lim_{\varepsilon\to 0} \int u(x) f(x, \frac{x}{\varepsilon}) = \int_{\mathbf{R}^3} \int_Q u_0(x,y) f(x,y) dy dx, \tag{34}$$

and on the other hand, we have, setting $\Omega = \cup_{y\in Q} \mathrm{supp}(f(\cdot, y))$.:

$$\begin{aligned} \int u(x) f(x, \frac{x}{\varepsilon}) dx &= \varepsilon^3 \int_{\frac{1}{\varepsilon}\Omega} v(y) f(\varepsilon y, y) dy \\ &= \int_{\frac{1}{\varepsilon}\Omega} u_{per}(y) f(\varepsilon y, y) dy + \varepsilon^3 \int_{\frac{1}{\varepsilon}\Omega} (u_{per}(y) - v(y)) f(\varepsilon y, y). \end{aligned}$$

Using the periodicity of u_{per} and of $f(x,\cdot)$, one easily sees that the first term converges towards $\int_{\mathbf{R}^3}\int_Q u_{per}(y)f(x,y)dydx$. The second one is dealt with using (20):

$$\begin{aligned}\left|\varepsilon^3\int_{\frac{1}{\varepsilon}\Omega}(u_{per}(y)-v(y))f(\varepsilon y,y)\right| &\leq \|u_{per}-v\|_{L^\infty(\{|x_3|<\frac{1}{\varepsilon}\})}\int|f(x,\frac{x}{\varepsilon})|dx\\ &\leq (\|u_{per}-v\|_{L^\infty(\{|x_3|<\frac{1}{\varepsilon}-\frac{1}{\sqrt{\varepsilon}}\})})\|f(\cdot,\frac{\cdot}{\varepsilon})\|_{L^1(\mathbf{R}^3)}\\ &+ \varepsilon^3(\|u_{per}\|_{L^\infty(Q)}+\|v\|_{L^\infty})\|f\|_{L^\infty}\left|\frac{1}{\varepsilon}\Omega\setminus(\frac{1}{\varepsilon}-\frac{1}{\sqrt{\varepsilon}})\Omega\right|\\ &\leq C\|u_{per}-v\|_{L^\infty(\{|x_3|<\frac{1}{\varepsilon}-\frac{1}{\sqrt{\varepsilon}}\})}\\ &+ C\varepsilon^3(\frac{1}{\varepsilon^3}-(\frac{1}{\varepsilon}-\frac{1}{\sqrt{\varepsilon}})^3).\end{aligned}$$

These two terms converging to 0 as $\varepsilon\to\infty$, we deduce, using (34):

$$u_0(x,y)=u_{per}(y),\quad \forall|x_3|<1.$$

This implies in particular that $\|u_0\|_{L^2(Q\times\Gamma_1)}\geq 2\|u_{per}\|_{L^2(Q)}=2$. Since $\|u\|_{L^2(\Gamma_1)}=\frac{\lambda_e}{\varepsilon^2}=2-\frac{\varepsilon^3E}{2\pi}\longrightarrow 2$ as $\varepsilon\to 0$, one easily sees that

$$\lim_{\varepsilon\to 0}\|u\|_{L^2(\Gamma_1)}=\|u_0\|_{L^2(Q\times\Gamma_1)}. \tag{35}$$

Using Proposition 5.3, this implies that

$$\|u_0(x,\frac{x}{\varepsilon})-u\|_{L^2(\Gamma_1)}\longrightarrow 0$$

as $\varepsilon\to 0$, so that the nonlinear terms pass to the limit in (18), showing (31), up to the fact that $-\varepsilon^2\Delta u$ two-scale converges to $-\Delta_y u_0$, which is shown by the following integrations by parts:

$$\begin{aligned}\int-\varepsilon^2\Delta u(x)f(x,\frac{x}{\varepsilon})dx &= \int u(x)(-\Delta_y f(x,\frac{x}{\varepsilon}))dx+2\varepsilon\int u(x)\nabla_x\cdot\nabla_y f(x,\frac{x}{\varepsilon})dx\\ &+\varepsilon^2\int u(x)(-\Delta_x f(x,\frac{x}{\varepsilon}))dx.\end{aligned}$$

Equation (35) also shows that $\|u\|_{L^2(\Gamma_1\cap\{|x_3|>1\})}\longrightarrow 0$, so that we have $u_0(x,y)=0$ if $|x_3|>1$. This shows the first line of (33). In order to show the second one, we first point out that according to the uniqueness of the solution of (32) and to the bounds we have on ϕ, $\phi_0(x,y)=\phi_{per}(y)$ as soon as $|x_3|<1$, concluding our proof. $\Diamond$

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Chapitre 8

Méthodes numériques en chimie des solides

Nous présentons dans ce chapitre, publié dans un volume de Lecture Notes in Chemistry [P10], une brève introduction aux méthodes dites *ab initio* de calcul de structure électronique dans les solides.

A mathematical insight into *ab initio* simulations of the solid phase

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Abstract We give here an introduction to the language of *ab initio* solid-state theory. Starting from the intrinseque symmetries of a perfect crystal, we show how it is related to band structure theory and give a brief overview of the techniques in use to simulate such systems.

1 Introduction

This article is concerned with *ab initio* numerical solid-state chemistry, that is, the computation of electronic structure in a solid. We will only consider the case of perfect crystals, i.e an infinite periodic arrangement of nuclei, in which electrons are supposed to satisfy the Schrödinger equation. Of course, some extensions are possible, in particular to treat defects in solids (see [71], chapters 12 and 13 for instance).

We start with some definitions, introducing the standard language of lattice structure. Good complements to this introduction may be found in [2, 51]. See also [32] (or any crystallographic textbook) for a more theoretical work. Some extensions to quasi-crystals may be found in [48, 74] for instance.

Section 3 is devoted to the language of band theory, which accounts for the distinction between metals and insulators, and is based on the Bloch theorem. Here again, standard solid-state textbooks, such as [2, 51] provide a very good overview on the topic. Concerning the corresponding mathematical problems, we refer to [73, 8, 55, 29].

Section 4 presents standard *ab initio* theories, starting from the molecular formulation (which means that it involves only a finite number of nuclei and electrons, [66, 67]), and extending it to the case of an infinite periodic crystal. These theories are presented in [71] and [65]. We also give many references in the course of this section, since many problems and methods are overlooked here.

The last section is devoted to the practical aspects of these theories, pointing out the most important numerical features and limitations.

2 Crystalline structure

We consider a perfect crystal, that is, a system of infinite size consisting of a periodically repeated set of nuclei, together with an associated set of electrons. Assuming that the nuclei are fixed, we may describe their positions by a motif m repeated on the nodes of a lattice $\mathcal{R}$:

$$\mathcal{R} = \{ua + vb + wc, \quad u, v, w \in \mathbf{Z}\}. \tag{1}$$

The vectors a, b, c are assumed to be linearly independent vectors of $\mathbf{R}^3$, and are called a basis of $\mathcal{R}$. Using the approximation of classical nuclei, the motif m represents N point particles of positive charge, that is, mathematically speaking, a set of positive Dirac masses :

$$m = \sum_{i=1}^{N} Z_i \delta_{x_i}, \tag{2}$$

where the vectors x_i may be chosen to be in the set :

$$\Gamma(a, b, c) = \left\{xa + yb + zc, \quad x, y, z \in [-\frac{1}{2}, \frac{1}{2}[\right\} \tag{3}$$

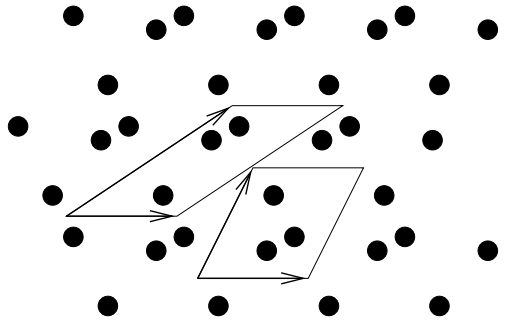

Figure 1: The set of nuclei with two possible unit cells and lattice basis

We call a *unit cell* of the lattice $\mathcal{R}$ any semi-open polyhedron such that its translations along a subset of the vectors of the lattice fills in the whole space $\mathbf{R}^3$ without overlapping. The set $\Gamma(a,b,c)$ defined in (3) is thus a unit cell of $\mathcal{R}$. Many choices of unit cells are possible. If its volume is minimal, which is the case of $\Gamma(a,b,c)$, we call the cell a *primitive* unit cell. Such a cell satisfies the property that, when translated by *all* the vectors of the lattice, it constitutes a partition of $\mathbf{R}^3$. A particular primitive unit cell is the Wigner-Seitz cell, or Dirichlet zone, which is constructed as follows :

(i) The point $0 \in \mathcal{R}$ is jointed to all of its neighbors by segments;

(ii) the mediator planes of these segments are traced;

(iii) each of these planes define a half-space containing 0, and the intersection of these half-spaces is a convex polyhedron, which is the Wigner-Seitz cell.

This cell presents the advantage of being unique.

The aim of *ab initio* calculations is to describe the electronic structure of a crystal, the lattice on which the nuclei are set being given. These calculations handle many $\mathcal{R}$-periodic functions, for which treatment a useful tool is the Fourier analysis. This is why we now introduce the notion of reciprocal lattice.

Given a basis (a,b,c) of $\mathcal{R}$, we set :

$$\mathcal{R}^* = \left\{ ua' + vb' + cw', \quad u,v,w \in \mathbf{Z} \right\}, \tag{4}$$

where the basis (a',b',c') is defined as follows :

$$\begin{cases} a \cdot a' = b \cdot b' = c \cdot c' = 2\pi, \\ a \cdot b' = a \cdot c' = b \cdot c' = 0. \end{cases} \tag{5}$$

In other words, the matrices of columns respectively (a,b,c) and $\dfrac{1}{2\pi}(a',b',c')$ are inverse of each other. The point is that this definition of $\mathcal{R}^*$ does not depend on the chosen basis.

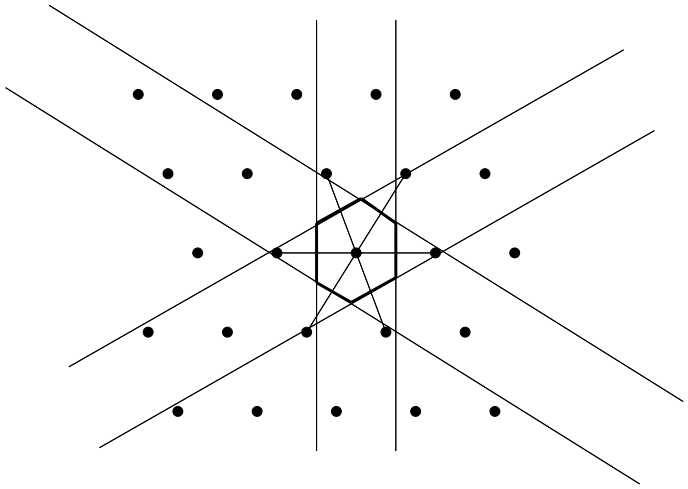

Figure 2: The Wigner-Seitz cell of a lattice

The Wigner-Seitz cell of the reciprocal lattice is called the first Brillouin zone (henceforth abbreviated as BZ) of the crystal.

In many cases, the relevant parameter of the lattice is its invariance group, rather than the lattice itself, especially for optic properties. For definitions of these terms and discussions of related topics, we refer to [51, 2], where one will also find details on the above few assertions, and to [71], chapter 1, for a brief introduction.

3 Band theory

3.1 Band structure

It is a commonly accepted approximation that an electron of a solid experiences a periodic potential. This is why the first step in studying the electronic structure of a solid is the examination of the properties of a Schrödinger operator with periodic potential: let $H = -\Delta + V$ be such an operator, V being $\mathcal{R}$-periodic. The question is, can we find a spectral decomposition of H? This leads us to the following eigenvalue problem, or equivalently to the determination of stationary states of H:

$$-\Delta\psi + V\psi = E\psi. \tag{6}$$

Let us denote by τ_T the operator

$$\psi \longmapsto \psi(\cdot + T), \tag{7}$$

for any $T \in \mathcal{R}$. The point is that H is invariant under such translations, which means, in terms of operators:

$$\tau_T H = H\tau_T, \tag{8}$$

for all $T \in \mathcal{R}$. Since these two operators commute, they have a common diagonalizing basis. In other words, one can find a basis such that each of its element satisfies:

$$\begin{cases} H\psi = E\psi, \\ \tau_T \psi = \gamma(T)\psi, \quad \text{for some} \quad \gamma(T) \in \mathbf{C}. \end{cases} \tag{9}$$

Noticing that $\tau_{T+T'} = \tau_T \tau_{T'} = \tau_{T'} \tau_T$, we infer from (9) that $\gamma(T+T') = \gamma(T)\gamma(T')$. On the other hand, since τ_T is norm-preserving, we necessarily have $|\gamma(T)| = 1$. It follows that there exists a vector k such that:

$$\gamma(T) = e^{ik \cdot T}. \tag{10}$$

From the fact that $T \in \mathcal{R}$, the addition of a vector of the reciprocal lattice $\mathcal{R}^*$ to k does not change $\gamma(T)$, so that we may impose that k is in some primitive unit cell of $\mathcal{R}^*$, for example the first Brillouin zone (BZ). Equation (9) thus becomes:

$$\begin{cases} H\psi = E\psi, \\ \psi(x+T) = e^{ik \cdot T}\psi(x), \quad \text{with} \quad k \in BZ. \end{cases} \tag{11}$$

This leads us to the celebrated Bloch theorem:

Theorem 3.1 *Let $H = -\Delta + V$ be a Schrödinger operator, with $V \in L^2_{loc}$ $\mathcal{R}$-periodic. Then for all $k \in BZ$, there exists an increasing sequence of eigenvalues $\{\lambda_j(k)\}$ and a corresponding sequence of eigenvectors $\{\psi_j^k\}$ of H such that :*

- *$k \mapsto \lambda_j(k)$ is continuous;*
- *$\psi_j^k(x)e^{-ik \cdot x}$ is periodic;*
- *$\sigma(H) = \bigcup_{j \in \mathbf{N}} [\inf_{BZ} \lambda_j, \sup_{BZ} \lambda_j]$.*

($\sigma(H)$ denotes the spectrum of the operator H.)

The above argument is by no means a proof of this result. The interested reader may find more detailed proofs in [73, 55, 29]. The original idea of decomposing the spectrum of this type of Schrödinger operators by looking for solutions which are periodic up to k is due to Bloch [13].

The Bloch theorem gives a spectral decomposition of any Schrödinger operator with periodic potential. In particular, we see that the spectrum of such an operator is constituted of intervals, which are called *bands* of the operator. This gives us an intuition on the behavior of electrons in a crystal: assuming that they are represented by the above eigenstates, preferably the lowest ones, we see that if there are exactly enough electrons to fill in an entire number of bands, we have an energetical gap between the highest non-excited state and the lowest excited one. Conversely, if a band is only partially filled, there is no such a gap. In the first case, one needs a great amount of energy to take an electron from its stationary state to an excited state, and the crystal behaves like an insulator. In the second case, a small amount of energy is sufficient for an electron to reach an excited state: this is a metallic behavior. This is shown in Figure 3.

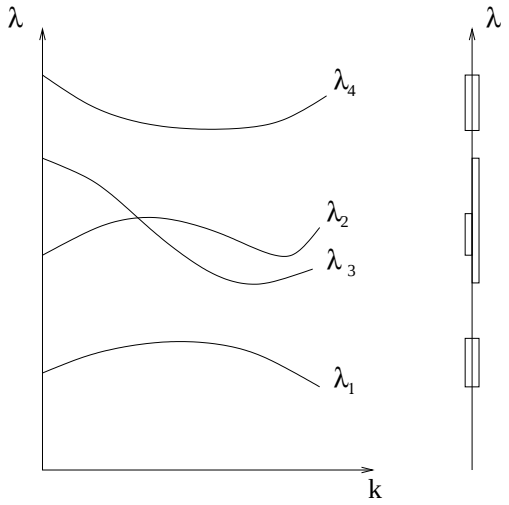

Figure 3: The band structure of a one-dimensional crystal: if there is one electron per cell, only the first band is filled and the crystal is an insulator, whereas if there are two electrons per cell, the second band is only partially filled, so that we have a metal.

3.2 Density of states

If one simulates a crystal at zero-temperature, the above Bloch states are filled in using the *Aufbau* principle, that is, starting from the lowest energy state, then the next lowest, and so on. Of course, this is a much clearer concept in the molecular case, where the are only a numerable quantity of eigenstates, than in the crystal case, where the energy levels are continuously ordered. In this latter case, we know that we have a fixed number of electrons per unit cell, although an electron associated to a precise unit cell need not be localized in this cell. Thus, one eigenstate does not represent an electron by itself, but the set of all similar electrons repeated through the translations by the lattice vectors (physically, this corresponds to delocalized electrons).

Mathematically, this corresponds to defining the following function:

$$n(\lambda) = \frac{2}{|BZ|} \sum_{j \in \mathbf{N}} \int_{BZ} \delta(\lambda - \lambda_j(k)) dk, \tag{12}$$

where $|BZ|$ is the volume of the BZ, and δ a Dirac mass at 0. The function n is called the density of state, and the function f defined by

$$f(\varepsilon) = \int_{-\infty}^{\varepsilon} n(\lambda) d\lambda \tag{13}$$

represents the number of electron states per unit cell with energy lower than ε. The factor 2 in (12) accounts for the fact that we use the closed-shell approximation.[1] The function

[1] The closed-shell approximation corresponds to neglecting the spin of the electrons, and considering two electrons with the same wave function and opposite spin as one particle.

f is non-decreasing, since $n(\lambda) \geq 0$, and we define the Fermi energy ε_F by

$$f(\varepsilon_F) = N, \tag{14}$$

where N is the number of electrons per cell. By doing this, we have filled in entirely the levels lower than the Fermi energy, leaving the higher energy states empty.

In general, when one computes a macroscopic parameter of a crystal, it often appears in the form:

$$S = \frac{2}{|BZ|} \sum_j \int_{BZ} g(j,k) dk, \tag{15}$$

where g is a function of the electronic state labeled by j and k. In many cases, the function g depends only on the energy: $g(j,k) = g(\lambda_j(k))$. Thus, using the definition (12) of n and changing variables in the above definition of S, we have:

$$S = \int_{-\infty}^{\varepsilon_F} g(\lambda) n(\lambda) d\lambda. \tag{16}$$

The density of states thus appears as an important feature of the crystal, in the sense that its values determine those of many of the crystal's macroscopic parameters.

In the case where the temperature T is not 0, one only needs to replace the Heaviside distribution implicitly used above by the Fermi-Dirac distribution $\mu_T(x) = \frac{1}{1+e^{-x/k_B T}}$. Equation (12) would thus become:

$$\begin{aligned} n_T(\lambda) &= \frac{2}{|BZ|} \sum_{j \in \mathbf{N}} \int_{BZ} \mu_T'(\lambda - \lambda_j(k)) dk \\ &= \frac{2}{|BZ|} \sum_{j \in \mathbf{N}} \int_{BZ} \frac{1}{k_B T} \frac{e^{-\frac{\lambda - \lambda_j(k)}{k_B T}}}{1 + e^{-\frac{\lambda - \lambda_j(k)}{k_B T}}} dk. \end{aligned} \tag{17}$$

So that f becomes

$$f_T(\varepsilon) = \frac{2}{|BZ|} \sum_{j \in \mathbf{N}} \int_{BZ} \mu_T(\varepsilon - \lambda_j(k)) dk. \tag{18}$$

Note that in practice, the above integrals over the BZ are replaced by sums over some points of the BZ, according to a prescribed sampling. The most natural sampling is the regular one, in which one distributes M^3 points regularly in the BZ. This in fact corresponds to a periodic boundary condition on a box composed of M^3 unit cells. Indeed, in this case, boundary conditions impose that k takes a finite number of values, namely $(\frac{k_1}{M}a, \frac{k_2}{M}b, \frac{k_3}{M}c)$, with $0 \leq k_i < M$. However, and although this is appealing to justify periodic boundary conditions, this sampling is not optimal, and special points technics [33, 16, 63] need to be used, extensively using the symmetries of the crystal.

4 Electronic calculations: standard approximations

Let us now consider the numerical *ab initio* computations of electronic structure in a crystal, and more specifically the approximations commonly used. So far, we have dealt with the Schrödinger equation satisfied by *one* electron in a periodic potential. Although this is a qualitatively good model, computations have to be more precise.

The approximation of classical nuclei, mentioned in section 2, and which consists in considering that the nuclei are classical point particles, is widely used. It is justified by the fact that the mass of a nucleus is much larger than that of an electron. In the same spirit we will also use the Born Oppenheimer approximation, that is, the nuclei will be supposed to be fixed at their positions, the reason for this being that the electrons move much faster than the nuclei, and their movement will be treated in a second step, considering the electronic energy as an external potential for their movement. Concerning these lattice dynamics treatments, we refer to [71], Chapter 12 and to the references therein.

Another approximation currently made (and used so far) is the non-relativistic treatment of the electrons. This may be a poor one in some cases, especially in heavy nuclei where the speed of the core electrons is of the same order as the velocity of light c ($\frac{v}{c} \simeq 0.58$ in the case of Mercury). But this may be taken into account through relativistic pseudopotentials (see below), or by an *a posteriori* perturbative treatment (see [71]).

Even with these approximations, solving Schrödinger equation is out of reach, in particular because the wave function of the electrons should be a function of NM spatial variables, where N is the number of electrons per cell and M the number of cells. Furthermore, we should rigorously take the limit $M \to \infty$. We thus need to either approximate this wave function (this the case of Hartree-Fock theory, see section 4.1), or use a different way to characterize the electrons state than using their wave function, which is the aim of density functional theory (DFT), reviewed in Section 4.2.

We only give here the equations in a formal way, assuming that they take the same form as in the case of a finite molecule, allowing to state in a more simple way the corresponding theories. We will then point out the difficulties conveyed by the fact that we are studying a solid, particularly the infinity of the number of particles (electrons as well as nuclei), and the periodicity of the system.

4.1 Hartree-Fock formalism

The Hartree-Fock (HF) theory of molecules aims at solving the electronic Schrödinger equation under the assumption that the wave function has the special form of a Slater determinant. It is a way of taking the exclusion principle into account. In this case of a finite number of electrons, say n, the total wave function reads $\phi(x_1, x_2, \ldots, x_n) = \det(\phi_i(x_j))$, and this gives the well-known Hartree-Fock equations:

$$-\frac{1}{2}\Delta\phi_i + V\phi_i + (\rho \star \frac{1}{|x|})\phi_i - \int_{\mathbf{R}^3} \frac{\tau(x,x')}{|x-x'|}\phi_i(x')dx' = -\varepsilon_i\phi_i, \tag{19}$$

with $\tau(x,x') = \sum_{i=1}^{n} \phi_i(x)\phi_i(x')^*$, $\rho(x) = \tau(x,x)$, and V represents the electrostatic potential created by the nuclei[2]; $\star$ denotes the convolution product over $\mathbf{R}^3$.

$$\begin{aligned} E^{HF}(\{\phi_i\}) &= \frac{1}{2}\sum_{i=1}^{n}\int_{\mathbf{R}^3}|\nabla\phi_i|^2 + \int_{\mathbf{R}^3}\rho V + \frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3}\frac{\rho(x)\rho(x')}{|x-x'|}dxdx' \\ &\quad -\frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3}\frac{|\tau(x,x')|^2}{|x-x'|}dxdx' + \frac{1}{2}\sum_{j\neq i}\frac{1}{|X_i - X_j|}, \end{aligned} \tag{20}$$

where the last term accounts for the repulsion of the nuclei, and is added so that the total charge of the system becomes 0, which allows to define its electrostatic interaction (see section 5.3). We see here that although these equations clearly make sense in the case where n is finite, the solid-state case is *not that obvious*. See [20] for the related mathematical problems. Nevertheless, equation (19) does make sense in this case, as soon as the total potential $V_{tot} = V + \rho\star\frac{1}{|x|}$ is not splitted into these two terms, but rather kept together so as to define the potential of a periodic neutral distribution of charge, which does exist.

The Fock hamiltonian may be written in the following form:

$$F = -\frac{1}{2}\Delta + V + \rho\star\frac{1}{|x|} - \sum_i \int_{\mathbf{R}^3}\frac{\phi_i(x')^*\,\bullet}{|x-x'|}\phi_i(x)dx', \tag{21}$$

where $V_{tot} = V + \rho\star\frac{1}{|x|}$ is to be understood as a solution of the Poisson equation:

$$-\Delta V_{tot} = 4\pi\left(\sum_{j\in\mathcal{R}} m(\cdot + j) - \rho\right), \tag{22}$$

the measure m defining the nuclei in the primitive unit cell (2). This equation has a periodic solution as soon as $m - \rho$ is neutral over the unit cell of $\mathcal{R}$. A similar treatment is possible for the exchange term (last term in (21)), see [20]. Equation (19) thus reads:

$$F\phi_i = -\varepsilon_i\phi_i. \tag{23}$$

In the case of a solid, the above equations are derived through Bloch's theorem, so that all sums over i are replace by sums over i *and* integrals over the BZ, and the wave functions and energies are labelled by $k \in BZ$. In other words, setting

$$\tau(x,x') = \sum_{j\in\mathbf{N}}\int_{BZ}\phi_j^k(x)\phi_j^{k*}(x')(\varepsilon_F - \varepsilon_j^k)^+ dk, \tag{24}$$

where $t^+ = \max(t,0)$, i.e the term $(\varepsilon_F - \varepsilon_j^k)^+$ selects only the states having lower energy than the Fermi energy ε_F defined in (14), and F being defined by

$$F\phi = -\frac{1}{2}\Delta\phi + V_{tot}\phi - \int_{\mathbf{R}^3}\frac{\tau(x,x')}{|x-x'|}\phi(x')dx', \tag{25}$$

[2] $V(x) = -\sum_{j=1}^{p}\frac{Z_j}{|x-X_j|}$, where p is the number of nuclei, and X_j and Z_j respectively their positions and charges.

with V_{tot} defined by (22), the ϕ_i^k should satisfy

$$F\phi_i^k = -\varepsilon_i^k \phi_i^k. \tag{26}$$

4.2 Density functional theory

Density functional theory (DFT) takes the problem from another standpoint than the one used by HF theory: instead of approximating the wave function, it approximates the total energy, writing it as a function of the electronic density ρ. Its theoretical ground is a theorem by Hohenberg and Kohn [49], which asserts that there exists a functional F of the density, independent of the external potential V, such that the electronic density of the ground state of the n-electrons problem with external potential V is a solution of:

$$\inf\left\{F(\rho) + \int_{\mathbf{R}^3} \rho V, \quad \rho \geq 0, \quad \int_{\mathbf{R}^3} \rho = n\right\}. \tag{27}$$

Kohn and Sham proposed a computational framework in relation with this theorem in [53]. It consists essentially in giving a guess on the functional F. The choice of Kohn and Sham corresponds to:

$$F(\rho) = T(\rho) + \frac{1}{2}\int_{\mathbf{R}^3}\int_{\mathbf{R}^3} \frac{\rho(x)\rho(x')}{|x-x'|}dxdx' + E_x(\rho) + E_c(\rho), \tag{28}$$

where

$$T(\rho) = \inf\left\{\frac{1}{2}\sum_{i=1}^{n}\int_{\mathbf{R}^3} |\nabla\phi_i|^2, \quad \sum_{i=1}^{n}|\phi_i|^2 = \rho\right\}, \tag{29}$$

and E_x and E_c are respectively the exchange and correlation energies. The local density approximation (LDA), currently used, consists in using the exchange energy of a homogeneous electron gas, that is:

$$E_x^{LDA}(\rho) = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int_{\mathbf{R}^3}\rho^{4/3}. \tag{30}$$

Perdew and Zunger proposed in [70] for the correlation energy

$$E_c^{PZ}(\rho) = \int_{\mathbf{R}^3}\rho\epsilon_c\left(\left(\frac{3}{4\pi\rho}\right)^{1/3}\right), \tag{31}$$

with

$$\epsilon_c(r) = \begin{cases} 0.00311\log(r) - 0.0480 + 0.0020r\log(r) - 0.0116r & \text{if} \quad r < 1, \\ -0.1423/(1 + 1.0529\sqrt{r} + 0.3334r) & \text{if} \quad r \geq 1. \end{cases} \tag{32}$$

Many other choices are possible, for example the $X\alpha$ setting [22], where $E_x + E_c = \alpha\int_{\mathbf{R}^3}\rho^{4/3}$, or the generalized gradient approximations (GGA), in which corrections to LDA are brought by terms of the form $G(\nabla\rho, \nabla^2\rho)$. See [10, 56, 69, 67] for instance.

In practice, this way of computing the density is used in the following manner:

$$\begin{cases} -\Delta\phi_i + V_{\text{eff}}\,\phi_i = -\varepsilon_i\phi_i, \quad \forall i, \\ V_{\text{eff}} = V_{\text{nuclei}} + \rho \star \frac{1}{|x|} + \frac{d}{d\rho}E_x + \frac{d}{d\rho}E_c, \\ \rho = \sum_i |\phi_i|^2, \end{cases} \tag{33}$$

where the ε_i are the lowest n eigenvalues of the operator $-\Delta + V_{\text{eff}}$. In the case of a solid, one needs to group the electrostatic terms together so as to be able to compute it through Poisson's equation (22). Moreover, the same dependance on the wave vector k as in HF theory appears here. Therefore, (33) becomes:

$$\begin{cases} -\Delta\phi_i^k + V_{\text{eff}}\,\phi_i^k = -\varepsilon_i^k\phi_i^k, \quad \forall i,k \\ V_{\text{eff}} = V_{tot} + \frac{d}{d\rho}E_x + \frac{d}{d\rho}E_c, \\ \rho = \sum_i \int_{BZ} |\phi_i^k|^2(\varepsilon_F - \varepsilon_j^k)^+ dk. \end{cases} \tag{34}$$

4.3 The use of pseudo-potentials

In many cases, the core electrons are physically almost unaffected by any change of environment. (This is particularly true in the case of low-energy transformations.) Hence, a natural approximation would be to consider them as frozen in some determined state (coming from the computation of a relevent atomic system), and compute only valence electrons. In order to implement this approximation, one introduces pseudo-potentials (PP). We consider here only their application to DFT, although a similar method carries through HF theory.

Consider a case where a number of (core) electrons are modelized by a pseudo-potential V_{ps}. Then, (34) would become:

$$\begin{cases} -\Delta\phi'^k_i + V_{\text{eff}}\,\phi'^k_i = -\varepsilon'^k_i\phi'^k_i, \quad \forall i,k \\ V_{\text{eff}} = V'_{tot} + \frac{d}{d\rho'}E_x + \frac{d}{d\rho'}E_c + V_{ps}, \\ \rho' = \sum_i \int_{BZ} |\phi'^k_i|^2(\varepsilon_F - \varepsilon_j^k)^+ dk, \end{cases} \tag{35}$$

where V'_{tot} accounts for the interaction between core electrons and the remaining electrons, which wave functions are denoted by ϕ'^k_i. The PP operator must reproduce screened nuclear attractions, and account for Pauli exclusion principle, forcing the valence orbitals to be orthogonal to core ones. Moreover, the eigenvalues ε'^k_i should be equal to the corresponding ε_i^k, and the corresponding eigenfunctions as close as possible to the "real" orbitals ϕ_i^k. And in the case of heavy atoms, the relativistic feature of the core electrons should be accounted for in V_{ps}. Above all this, the main feature of V_{ps} should be to simplify the computations, smoothing the Coulombic singalurity of the nucleus and having a usable expression. This gives a set of rules to elaborate PPs.

There exists a wide variety of pseudo-potentials, that we cannot display here. See for instance [6, 43, 76], concerning DFT pseudo-potentials, and [45, 46, 47] in the case of HF theory.

4.4 Self-consistent field algorithms

Solving the Hartree-Fock or the Kohn-Sham equations is done through the self-consistent field (SCF) procedure. It may be summarized as follows:

(i) Guess a first density $\rho = \rho_0$ (in the case of Kohn-Sham formalism), or a set of wave functions ϕ_i^k (in the case of Hartree-Fock setting), for each $k \in BZ$.

(ii) Compute the effective potential V_{eff}:

- in the KS formalism, $V_{\text{eff}} = V + \rho \star \frac{1}{|x|} + \frac{d}{d\rho}E_x + \frac{d}{d\rho}E_c$,[3]
- in the HF formalism, $V_{\text{eff}} = V + \rho \star \frac{1}{|x|} + \sum_j \int_{BZ} \left((\phi_j^k \bullet) \star \frac{1}{|x|}\phi_j^k \right) dk$.[3]

(iii) Compute eigenvalues $-\varepsilon_i^k$ and eigenvectors ϕ_i^k of $H = -\Delta + V_{\text{eff}}$, for each $k \in BZ$, and the Fermi energy ε_F.

(iv) Compute the new density $\rho = \displaystyle\sum_{i=1}^{N} \int_{BZ} |\phi_i^k|^2 (\varepsilon_F - \varepsilon_j^k)^+ dk$.

(v) If the new ϕ_i^k's (in HF theory) or the new ρ (in KS theory) are equal to the preceding one(s), self-consistency is reached. Otherwise, go back to step (ii).

In fact, important convergence problems occur in such an algorithm, and relaxation techniques need to be used to ease the convergence. See [19] for precisions.[4] In particular, when dealing with a metal, the levels near the Fermi surface may very well be alternatively filled and empty, generating oscillations. In this case, one needs, in a smoothing procedure, to partially fill each of them, which corresponds to the physical fact that these orbital behave as a mixing of themselves rather than individually. Another problem is that rigorously, one should at each SCF cycle compute the eigenvalues and eigenvectors $\varepsilon_i^k, \phi_i^k$ for all $k \in BZ$, which means numerically for many of them. In order to overcome this difficulty, one needs to choose these points very cleverly. This is done by special point technics (see Section 5.2 and [71], Chapters 4 and 10, or [63, 33, 62]). These technics usually allow to perform the calculation with only one (in the case of an insulator) to about twenty (in the case of a metal) k-points.

From the fact that the algorithms used are the same in both HF and DF theory, one would think that they are quite similar technics. On the other hand, fundamental differences should be highlighted:

- The use of Kohn-Sham scheme yields an approximation of the kinetic energy that is not present in HF theory.

[3] V denotes the potential generated by the nuclei.

[4] The author is concerned with molecular models there, but convergence problems are in fact exactly the same as in solid-state models, as far as insulators are concerned. The case of metals is much more tricky, because of the Fermi surface.

- In the DFT formalism, the ε_i^k and ϕ_i^k obtained through the SCF algorithm have nothing to do *a priori* with the real electronic energies and orbitals. On the contrary, in the HF theory, they are interpretable in such a way. Furthermore, even the empty eigenstates of HF theory can be viewed in some way as excited states, according to Koopmans' theorem (see [66]).

- On the other hand, the HF theory neglects correlation effects, assuming that each electron interacts with the average field of the others. See [39] and [71], chapter 11 for a discussion of this topic. This problem accounts for large disagreement between HF theory and experiment, since correlation effects are usually important in solids. This may be dealt with through correlation-only energy [68, 39, 21, 3, 4].

- In HF theory, the exact treatment of the exchange energy implies more difficult computations. However, the simplification used in DFT raises inaccuracies. Furthermore, in DFT, the self-interaction of the electrons (second term in (28)) is overestimated since it contains an interaction of each electron with itself. Hence, there is a need for a self-interaction correction (SIC). Several such corrections have been proposed, which roughly consists in substracting from the energy the self-interaction of the computed pseudo-orbitals ϕ_i^k [50, 11, 70].

5 Numerical schemes

Let us now turn to the numerical schemes corresponding to the above theoretical framework. In both DFT and HF formalism, one chooses a basis (χ_j^k) of Bloch functions on which the crystalline orbitals of the electrons are developed, and solves the equations (26) or (34) in this basis, which become:

$$H^k C^k = S^k C^k E^k, \tag{36}$$

where H^k is the matrix of the corresponding Hamiltonian in the considered basis, S^k the overlap matrix, C^k the matrix of the crystalline orbitals and E^k is the diagonal matrix of the energies ε_i^k. In other words, we have:

$$\phi_i^k(x) = \sum_{j=1}^{N} c_{ji}^k \chi_j^k(x), \tag{37}$$

where each χ_j^k is periodic up to k, i.e satisfies the second equation of (11).

$$H_{ij}^k = \langle \chi_i^k | H | \chi_j^k \rangle, \quad S_{ij}^k = \langle \chi_i^k | \chi_j^k \rangle. \tag{38}$$

5.1 Basis sets

Hence, the first crucial choice is the Bloch functions χ_j^k. Let us briefly summarize the most widely used ones:

- Plane waves (PW): they present the advantage of carrying periodicity by themselves, and to be an orthogonal basis. Furthermore, the operator $-\Delta$ is diagonal in such a basis. Nevertheless, crystalline orbitals are usually not fairly regular near the nuclei, presenting cusps. Thus, their Fourier coefficients are not fastly decaying, so that one needs a great amount of plane waves to approximate in a good manner those orbitals.

- Gaussian-type orbitals (GTO): this corresponds to the choice

$$\chi_j^k(x) = \sum_{l \in \mathcal{R}} \chi_j(x-l) e^{ik\cdot l}, \tag{39}$$

  where χ_j is a linear combination of Gaussians multiplied by spherical harmonics. They come from the molecular *ab initio* calculations, in which they are widely used because they make the computation of bielectronic integrals easier, using formulas due to Boys [17]. The point is, those molecular basis cannot be used directly in solid-state computations. In particular, very diffuse Gaussians increase dramatically the number of integrals to be explicitly calculated in the computation of electrostatic interactions.

  In the HF formalism, these kinds of basis facilitate the computation of the exchange term, in the same fashion as in the molecular case [17].

  Another good point concerning GTO is the fact that the Fourier transform of a Gaussian is a Gaussian. Thus, the completion of a GTO basis with PWs is computationally convenient [9]. Indeed, the additional problems raised by the computation of overlap and bielectronic integrals[5] are solved by the fact that (in the case of a PW and a GTO) the first ones are simply the Fourier transforms of Gaussians, and the second ones the Fourier transforms of Gaussians multiplied by the Fourier transform of $\frac{1}{|x|}$, that is, $\frac{1}{|\xi|^2}$. In this case, GTO functions are used to represent core electrons, which are localized near the nuclei, and valence electrons are represented by a mixed combination of PWs and GTOs.

- Muffin-tin orbitals (MTO): this method is a mixing of the two previous ones. The space is separated into two regions: the first one is a union of (non intersecting) spheres around the nuclei, which are called atomic spheres, and the second one is the remaining region, called the interstitial region. The muffin-tin approximation consists essentially in assuming that the potential and electron density are radially symmetric in the atomic spheres, and using PW expansion in the interstitial region. There exists a wide variety of such methods (APW, LAPW, FLAPW), for which we refer to [1, 35, 12, 5]. The FLAPW is also detailed in [71], chapter 9. As an example of such methods, we describe here the APW method:

As pointed out above, the main approximation of APW method relies on the separation of the space into MT spheres (one around each nucleus), and the remaining region, which

[5] Of the form, respectively: $\int \chi_i^k \chi_j^k$ and $\int\int \frac{\chi_i^k(x)\chi_j^k(y)}{|x-y|} dxdy$.

is called the interstitial region. In the MT spheres, the basis is a combination of solutions of radial Schrödinger equation:

$$\chi_j^k(x) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} A_{lm}(k+R_j) u_l(x-X_s) Y_{lm}\left(\frac{x-X_s}{|x-X_s|}\right), \tag{40}$$

where $R_j \in \mathcal{R}$, X_s is the position of the center of the MT sphere,[6] and Y_{lm} are the spherical harmonics. The function u_l is a solution of the radial Schrödinger equation:

$$-\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{du_l}{dr}\right) + \left[\frac{l(l+1)}{r^2} + V(r)\right] u_l = E u_l. \tag{41}$$

In the interstitial region, the potential is assumed to be constant, and the wave functions are developped on a plane wave basis:

$$\chi_j^k(x) = e^{i(k+R_j)\cdot x}, \quad \text{with } R_j \in \mathcal{R}. \tag{42}$$

In order to have a basis of continuous functions, we need to equate the two values of χ_j^k on the MT spheres. Developping the exponential function on spherical harmonics, one gets:

$$e^{i(k+R_j)\cdot x} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l j_l(|k+R_j||x-X_s|) Y_{lm}\left(\frac{k+R_j}{|k+R_j|}\right)^* Y_{lm}\left(\frac{x-X_s}{|x-X_s|}\right) e^{i(k+R_j)\cdot X_s}, \tag{43}$$

where j_l is the l-th order spherical Bessel function. This implies that the coefficient $A_{lm}(k+R_j)$ is equal to :

$$A_{lm}(k+R_j) = 4\pi e^{i(k+R_j)\cdot X_s} i^l Y_{lm}\left(\frac{k+R_j}{|k+R_j|}\right) \frac{j_l(|k+R_j||R_{MT}^s|)}{u_l(E, R_{MT}^s)}. \tag{44}$$

The radius R_{MT}^s denotes here the radius of the considered MT sphere. This entirely determines our basis functions χ_j^k. Note that χ_j^k is continuous, but not derivable through the MT surface. This must be taken into account in the expression of the energy (hence in that of the hamiltonian) by adding some derivative jump terms [65].

Of course, the above technics are not the only ones. Let us mention the KKR (Korringa-Kohn-Rostoker) method [54, 52], which in some sense is an extension of the muffin-tin approximation, and uses the Green function method. The recursion method also uses Green function methods, but aims at calculating directly the DOS rather than solving the equations satisfied by the wave functions of the electrons. See for instance [40].

5.2 Reciprocal space integration and special point technics

As pointed out in Section 3.2, one frequently needs, in the course of electronic calculations, to compute the average value of some periodic function of the wave vector k over the

[6] Hence the position of a nucleus, and in general the nearest one

Brillouin zone (as for instance in (12)). In the present Section, we explain how the use of special point technics greatly reduces the computational cost of these evaluations.

For example, let f be a function defined on the reciprocal space, sharing the symmetries of the crystal. We want to evaluate

$$F = \int_{BZ} f(k)dk. \tag{45}$$

The first point is to expand f as a Fourier series, on the real space :

$$f(k) = \sum_{T \in \mathcal{R}} \hat{f}(T) e^{ikT}. \tag{46}$$

Next, note that if R is an element of the symmetry group of the crystal, then it is one of the reciprocal lattice, so that $f(Rk) = f(k)$, which implies that $\hat{f}(RT) = \hat{f}(T)$, since R is an orthogonal transformation. Hence, we may reorganize the above sum as follows :

$$f(k) = \sum_{n \in \mathbf{N}} f_n \frac{1}{\sqrt{\sharp C_n}} \sum_{T \in C_n} e^{ikT}, \tag{47}$$

where $(C_n)_{n \in \mathbf{N}}$ is a partition of the lattice vectors into non-symmetrically equivalent sets, n indexing them increasingly with respect to their norms. f_n is equal to $\sqrt{\sharp C_n}\hat{f}(T)$, for some $T \in C_n$. Hence, setting $A_n(k) = \dfrac{1}{\sqrt{\sharp C_n}} \displaystyle\sum_{T \in C_n} e^{ikT}$, which is normalized over the BZ, we have :

$$f(k) = \sum_{n \in \mathbf{N}} f_n A_n(k). \tag{48}$$

Since f_0 is exactly the evarage of f over the BZ, finding a k such that

$$\forall n \in \mathbf{N},\ A_n(k) = 0, \tag{49}$$

would yield :

$$F = \int_{BZ} f(k)dk = f_0 = f(k). \tag{50}$$

Hence the evaluation of f would only require one evaluation of the function f, at a point which is *independent of* f. Of course, such a point does not necessarily exist in general. In particular, the number of integers for which (49) may be satisfied is limited by the compatibility between these equations. One thus needs to generalize this simple observation.

In a more general point of view, we look for a set of points $(k_i)_{1 \le i \le N_p}$ and a set of weights $(w_i)_{1 \le i \le N_p}$ such that

$$\sum_{i=1}^{N_p} w_i = 1, \quad \text{and} \quad \sum_{i=1}^{N_p} w_i A_n(k_i) = 0, \quad n = 1, \dots N_T. \tag{51}$$

Using the Fourier expansion of f, we then have :

$$\sum_{i=1}^{N_p} w_i f(k_i) = f_0 + \sum_{n=N_T+1}^{\infty} f_n \sum_{i=1}^{N_p} w_i A_n(k_i). \tag{52}$$

Thus, provided the last term is small enough, a good approximation to f_0 is $\sum_{i=1}^{N_p} w_i f(k_i)$, the error being

$$\epsilon = - \sum_{n=N_T+1}^{\infty} f_n \sum_{i=1}^{N_p} w_i A_n(k_i). \tag{53}$$

In particular, the importance of this error is determined by that of the Fourier coefficients f_n, which decay very fast in the case of a smooth function. This makes this technic particularly powerful especially in the case of insulators. For metals, where the function f presents discontinuities (because the conduction band is only partially filled), one needs to use smearing technics, which basically consists in approximating f by a smooth function which integral is very close to that of f. See for example [37] or [16].

Hence, the main question is, how can one generate a set of special points? In many cases (see for instance [63, 18, 33, 7]) special points are only the smallest subset of a particular sampling of the BZ which image by symmetries of the crystal reproduce the corresponding sampling.

5.3 Ewald sums

As pointed out in Section 4, an important difficulty consists in giving a sense to the Coulomb potential (and the exchange term in HF theory). Since the second one is in some sense easier to deal with than the first one [28], we only consider here the first one.

In order to define the Coulomb potential V of a periodic distribution of charge $h = \sum_{j\in\mathcal{R}} h_0(\cdot + j)$, the first natural way is to set:

$$V(x) = \sum_{j\in\mathcal{R}} \left(h_0 \star \frac{1}{|x|} \right)(x + j). \tag{54}$$

The problem is that, if $\int h_0 = \int_{\Gamma(\mathcal{R})} h \neq 0$, the above sum, of which each term behaves like $\frac{\int_{\Gamma(\mathcal{R})} h}{|j|}$, is divergent. Thus, the only way to obtain a convergent series is to group the terms so as to have a neutral distribution of charge on each periodic cell. In the case of a neutral crystal, of which we are interested in, this corresponds to compute the potential of the electrons and the nuclei together rather than one at a time. Even in this case, the definition is not that clear[7]. Thus, we need a more efficient definition of V. It is provided

[7] In the case of a cubic unit cell, with h_0 shearing its symmetries, the quadrupole moment cancels, and the sum defined in (54) is convergent. In the general case, it is not.

by the Poisson equation:

$$-\Delta V = 4\pi h. \tag{55}$$

This equation, with f defined as above, admits a unique $\mathcal{R}$-periodic solution up to a constant (as soon as $\int h_0 = 0$). The point is, such a V may be written as:

$$V = G \star_{\Gamma(\mathcal{R})} h, \tag{56}$$

where G is the periodic solution of

$$\begin{cases} -\Delta G = 4\pi\left(\sum_{j\in\mathcal{R}} \delta_j - \frac{1}{|\Gamma(\mathcal{R})|}\right), \\ G \quad \text{is} \quad \mathcal{R}-\text{periodic}, \end{cases} \tag{57}$$

and $\star_{\Gamma(\mathcal{R})}$ denotes the convolution product over $\Gamma(\mathcal{R})$, that is:

$$\left(h \star_{\Gamma(\mathcal{R})} g\right)(x) = \int_{\Gamma(\mathcal{R})} h(y)g(x-y)dy. \tag{58}$$

The potential G, which is uniquely defined up to a constant by (57), is thus the Coulomb potential associated to the lattice $\mathcal{R}$.

In other words, a good knowledge of G would allow to compute any potential arising from a periodic neutral distribution of charge. One straightforward way to compute this potential is to use the Fourier transform. Indeed, using the first equation of (57), one easily proves that:

$$|k|^2 \widehat{G}(k) = 4\pi, \quad \forall k \in \mathcal{R}^* \setminus \{0\}. \tag{59}$$

Here, the Fourier transform is defined by:

$$\widehat{f}(k) = \int_{\Gamma(\mathcal{R})} f(x)e^{-ik\cdot x}dx, \tag{60}$$

for all $k \in \mathcal{R}^*$. Thus, we have the following expression for G:

$$G(x) = C_0 + \frac{4\pi}{|\Gamma(\mathcal{R})|} \sum_{k\in\mathcal{R}^*\setminus\{0\}} \frac{e^{ik\cdot x}}{|k|^2}. \tag{61}$$

Here C_0 is an arbitrary constant, accounting for the fact that (57) defines G up to a constant. A common choice for C_0 is 0, i.e $\int_{\Gamma(\mathcal{R})} G = 0$, but it is not the only possibility. The point is that the above sum is only conditionally convergent, and thus, although useful for theoretical purposes, **not convenient** for computations. Hence, a more suitable expression of G must be obtained. It is obtained through the Ewald potential [34, 26]. It consists in screening G with a Gaussian, i.e in writing:

$$G(x) = G \star_{\Gamma(\mathcal{R})} g + (G - G \star_{\Gamma(\mathcal{R})} g), \tag{62}$$

where g is a periodized Gaussian:

$$g(x) = \frac{4\gamma^{3/2}}{\sqrt{\pi}} \sum_{j \in \mathcal{R}} e^{-\gamma |x-j|^2}, \quad \gamma > 0. \tag{63}$$

The trick is to develop the first term of (62) in Fourier series, because the Fourier transform of a Gaussian is a Gaussian ($\widehat{g}(k) = e^{-\frac{|k|^2|}{4\gamma}}$), and to develop the second one in direct space:

$$G \star_{\Gamma(\mathcal{R})} g(x) = \frac{1}{|\Gamma(\mathcal{R})|} \sum_{k \in \mathcal{R}^*} \widehat{g}(k) \widehat{G}(k) e^{ik \cdot x} = \frac{1}{|\Gamma(\mathcal{R})|} \sum_{k \in \mathcal{R}^*} \frac{4\pi}{|k|^2} e^{-\frac{|k|^2}{4\gamma} + ik \cdot x}, \tag{64}$$

$$(G - G \star_{\Gamma(\mathcal{R})} g)(x) = -\frac{\pi}{\gamma |\Gamma(\mathcal{R})|} + \sum_{j \in \mathcal{R}} \frac{\operatorname{erfc}(\sqrt{\gamma}|x-j|)}{|x-j|}, \tag{65}$$

with

$$\operatorname{erfc}(t) = 1 - \frac{2}{\sqrt{\pi}} \int_0^t e^{-u^2} du = \frac{2}{\sqrt{\pi}} \int_t^\infty e^{-u^2} du, \tag{66}$$

which behaves like $\frac{e^{-t^2}}{\sqrt{\pi} t}$ as $t \to \infty$. Collecting the above equation, we may thus write G as a sum over the direct lattice $\mathcal{R}$ whose terms behave like $\frac{e^{-\gamma |j|^2}}{\sqrt{\pi}|j|^2}$, plus a sum over $\mathcal{R}^*$ whose terms behave like $\frac{e^{-\frac{|k|^2}{4\gamma}}}{|k|^2}$:

$$G(x) = -\frac{\pi}{\gamma |\Gamma(\mathcal{R})|} + \sum_{j \in \mathcal{R}} \frac{\operatorname{erfc}(\sqrt{\gamma}|x-j|)}{|x-j|} + \frac{4\pi}{|\Gamma(\mathcal{R})|} \sum_{k \in \mathcal{R}^* \setminus \{0\}} \frac{e^{-\frac{|k|^2}{4\gamma} + ik \cdot x}}{|k|^2}. \tag{67}$$

(The first term is present to satisfy the normalization $\int_{\Gamma(\mathcal{R})} G = 0$.) The parameter γ is to be set so as to have a good compromise between the convergence of the two sums: the first sum converges better when γ is large, whereas the second one converges better when γ is small. Furthermore, this expression of G allows to assert:

Proposition 5.1 *Let $h(x) = \sum_{j \in \mathcal{R}} h_0(x + j)$ be a periodic distribution of charge, such that:*

(a) g_0 is fast-decaying at infinity (i.e, $|x|^p h_0 \in L^1(\mathbf{R}^3)$, $\quad \forall p \geq 1$);

(b) the multipole moments of order $0, 1, 2$ of f_0 cancel.

Then, defining $F = G \star h_0 = G \star_{\Gamma(\mathcal{R})} h$, F is the Coulombic potential generated by h, i.e satisfies (57). Moreover, F satisfies:

$$F(x) = \sum_{j \in \mathcal{R}} \left(\frac{\operatorname{erfc}(\sqrt{\gamma}|x-j|)}{|x-j|} \star h_0 \right) + \frac{4\pi}{|\Gamma(\mathcal{R})|} \sum_{k \in \mathcal{R}^* \setminus \{0\}} \left(\frac{e^{-\frac{|k|^2}{4\gamma} + ik \cdot x}}{|k|^2} \star h_0 \right), \tag{68}$$

and these two sums are normally convergent.

This gives a way to numerically compute the Coulombic potential of such a distribution, by truncating the above sums, provided one can find such an h_0. A proof of this (provided h is neutral) may be found in [44]. Detailed discussions on these topics may be found in [36], appendix B, or in [26].

Note that the condition (a) is only technical, whereas condition (b) is more important: if (b) is not satisfied, equation (68) computes the Coulombic potential of the projection of h on the subspace of functions satisfying (b).

Of course, this basic formula must be then used in an efficient way, by grouping together terms so that the convergence is increased, and choosing the truncation of the series in a suitable manner. We refer to [28], chapter 2, for an example of these kind of considerations.

In the case of many atoms per cell, the above method should be improved by the use of the Reduced-Cell Multipole Method (RCMM), which consists, roughly speaking, in grouping the particles together into bigger and bigger sets as one goes away from the point at which we compute the potential. See [23, 24] for a description of this method, which is an adaptation to the periodic case of the standard fast-multipole method [41].

6 Conclusion

We have displayed here the roots of numerical solid state quantum chemistry, insisting on periodic-type codes [25, 38, 64, 75]. These methods have experienced lots of advances in the recent years, becoming nowadays in position to reach the same accuracy and speed as the more widely used cluster approachs, which roughly speaking consist in isolating a cluster of matter and treating it through molecular technics, thereby benefitting from these methods, which are much older and more accurate.

The near future will surely give birth to new and more powerful technics, as for example N-scaling methods (see [71], chapter 3 or [57]), or RCMM method [23].

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