Soft matter in confinement and at interfaces
Thomas Salez

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THESIS FOR THE ACCREDITATION TO DIRECT RESEARCH

presented by

Thomas SALEZ

Soft matter in confinement and at interfaces

Defended on June the 4th 2020 at University of Bordeaux
in front of the following jury:

Françoise Brochard-Wyart  President
Elisabeth Charlaix  Reviewer
Jean-François Joanny  Reviewer
Hamid Kellay  Examiner
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Introduction

Soft matter in a nutshell

We live at a time of complexity, in science and physics in particular. Indeed, while classical science focused on “simple” systems and idealised categories, we are now left with the hard but exciting task of exploring the rest: i.e. the vast majority of complex systems and phenomena constituting the world, or involved within our advancing technologies. The ultimate targets are problems as important philosophically as the origins of universe, life, and consciousness – eventually artificial. Every novel system of study along these lines seems to involve complexity through: strong interactions, non-linearities, intricate topology and architecture, disorder, out-of-equilibrium dynamics, and deep information processing.

Soft matter is emblematic in such a context. First, it is interdisciplinary, and thus it transcends by essence the old categories. It stands at the crossroads between chemistry and physics with motivations shifted more and more towards biology. Secondly, it deals with materials that are not simple liquids, nor simple crystalline solids, but all the “in between” in the condensed matter that surrounds our everyday life: cells, tissues, plastics, cosmetic and food gels, emulsions, granular piles, concrete, liquid-crystal displays, paints, lubricants, etc. Thirdly, while classical condensed matter exhibits only two main length scales – the microscopic atomic element and the macroscopic sample size – soft matter is characterized by the addition of a third mesoscopic one. This can be the size of a macromolecular polymer coil, a cell, an ink particle or a pollen colloid, to name a few. Such an apparently-minor addition has in fact profound consequences. Indeed, size and energy are typically inversely related, and, thus, the introduced mesoscopic structure is accompanied with a novel energy scale, that lies in between the molecular and macroscopic ones – which then cannot be too far from thermal energy $k_B T$. It follows that the associated materials are: i) disordered and amorphous; highly deformable and fluctuating; iii) prone to self-assembly. In a sense, soft matter embodies for condensed matter what jazz is to classical music: dirty, messy, lively, active, evolving, spontaneous. For all these reasons, the field has been flourishing, with a number of important fundamental and practical issues.

Moving beyond the bulk, the above mesoscopic feature has two important effects as far as interfaces and confinement are concerned. First, large fluctuations and softness make the interfaces of soft materials highly deformable. A weak perturbation at the surface can induce large changes. Secondly, at a time of miniaturisation and nanotechnology, the developed fabrication and observation tools allow one to study samples whose sizes are comparable to (and even smaller than) their intermediate supramolecular constituents. Therefore, anomalies with respect to the bulk and novel nanophysical
behaviours are expected. This is the reason why soft matter in confinement and at interfaces is a modern research field, that has continuously been raising fundamental and applied questions since its beginning [1]. In a nutshell, this domain is characterised by soft, liquid or amorphous solid objects whose typical size becomes comparable to the one of their inner constituents, or whose surface effects dominate the volume ones. If the devil hides at interfaces, as Pauli once said, those are then a perfect location for practicing the jazzy physics.

Outline of the manuscript

I was lucky enough to enter these lively field and community, right after my PhD, making a $h \to 0$ shift with respect to my previous research topics. During nine exciting years, and within a fruitful international collaborative network, I have been thinking about a collection of different problems and phenomena related to interfacial and confined soft matter. These could tentatively be re-cast formally into five main axes, corresponding to the five chapters of the present manuscript: thin liquid polymer films, glass transition in confinement, soft wetting, soft lubrication and friction in complex assemblies. For each chapter, after some elements of motivation, I made the choice of selecting and presenting only two illustrative results – because I found them a bit more fun or important relatively to other possible topics. Nevertheless, at the end of each chapter I list all our relevant publications, before proposing an outlook on possible novel avenues for exploration. Finally, after the concluding section of the manuscript, I provide through a final appendix a list of miscellaneous works: other articles, patent, books and PhD thesis.
Chapter 1

Thin liquid polymer films

1.1 Context

1.1.1 Polymers in Flatland

Microfilms and nanofilms of polymers are of tremendous interest in a broad variety of interdisciplinary fields, such as physical chemistry, physiology, biophysics, microelectronics or surface science. Besides their fundamental importance, such films are frequently involved in industrial processes, optical, mechanical or chemical, through nanolithography, lubrication, paints, surface treatments, and elastic membranes. Future development of molecular electronics, organic multimedia displays, biomimetic devices, superadhesive or self-cleaning surfaces may even increase the importance of such materials. As an example, thin polymer films are potential candidates for massive data storage, through the IBM Millipede project [2]. The idea is to indent the film surface at the nanoscale, in order to mechanically imprint information, and by this means to increase considerably the surface storage density with respect to microelectronic standards.

Through these practical applications, one easily recognises that a detailed understanding of the fundamental physics at play behind the stability and dynamics of these systems is necessary. When the average thickness (10-100 nm) of polymer nanofilms is comparable to the typical macromolecular size – the average coil radius, i.e. the radius of gyration $R_g$ – the effects of confinement may drastically alter their properties. Indeed, at this nanometric scale, material structure and dynamics are expected to change with respect to their bulk counterparts, as discrete molecular effects start to impose deviations to the classical continuum description. Several questions thus arise, such as the following ones for instance.

First, what is the effect of confinement on molecular mobility, and does the standard hydrodynamic theories still work [4, 5, 6, 7]? Indeed, recent studies have shown that the polymer mobility is increased in confinement for a liquid film [3, 8] (Fig. 1.1). This may be related to the alteration of the entanglement density near boundaries [9, 10, 11, 12, 13], but could also be an artefact due to residual stresses during the sample-preparation step [14, 15]. This link between structure and dynamics remains controversial in the community and there is a lack of quantitative proof of those phenomenological laws.

Secondly, what is the role of the interactions with the boundaries? We could for
instance cite the van der Waals interactions \cite{16}: the influence of a disjoining pressure is expected to be crucial in nanometric films \cite{17}, may modify the classical wetting laws \cite{18,19,20,21}, and may impose severe limits on the stability of confined polymeric devices. Finally, surface instabilities \cite{22,23,24} may be modified drastically by the above phenomena, which deserves dedicated studies.

### 1.1.2 Interfacial slippage

Fluid flow at the macroscale, as in water through a pipe, is typically dominated by physical processes in the bulk of the fluid. What goes on at the surfaces confining the material is normally of little interest and is hidden inside a simple boundary condition that assumes no flow.

Near an interface and at the nanoscale, however, where the surface-to-volume ratio is much larger than commonly encountered, the story is not always so simple. What is the boundary condition that should be assumed? In 1823, Navier postulated that the stress at the solid-liquid boundary should be continuous, with the stress in the liquid at the interface being equal to that on the solid. Writing down the stresses there, Navier introduced a so-called slip length which characterises in terms of a length scale the strength of flow at the surface through a typical ratio: that of the viscosity and the friction coefficient \cite{6,25,27}. Putting in typical numbers, it is found that slip lengths are normally just a couple of nanometers for simple fluids and interfaces \cite{28,29}. So, for large scale flows, the slip length is so small that we can normally consider that there is no fluid velocity at the boundary. This was then the condition that was assumed for about a century and a half.
Figure 1.2: Measurement of the slip length $b$ of polystyrene by dewetting of a thin film on a teflon (AF1600) substrate, as a function of molecular weight $M_w$ [13], and comparison to the Navier-de Gennes prediction [25, 26] (dashed line).

In the mid-twentieth century, polymer materials were industrialised and device miniaturisation became more and more important and lucrative. Polymer molecules are extended in space and tend to overlap strongly with one another in a material, as with long, tangled spaghetti noodles after they are cooked. In the 60’s and 70’s, Edwards and de Gennes determined that, as a result of this molecular entanglement, polymer liquids could have comparatively huge viscosities. A striking example is the pitch-drop experiment at the University of Queensland, Australia. This experiment has been running since 1927, and the flowing polymeric liquid therein has been shown to have a viscosity 100 billion times that of water.

Given that Navier’s stress balance is dependent on the viscosity, the slip length clearly needed to be reconsidered for polymer melts. Inspired by industrial polymer flows involving surfaces, de Gennes noted indeed that Navier’s stress balance could lead to slip lengths as large as a few hundred micrometers, orders of magnitude larger than the smaller, nanometric slip lengths expected for simple liquids [26, 30]. This would be the case for so-called ideal surfaces. Modern surface science has allowed for the creation of such surfaces, which are atomically smooth and typically hydrophobic. In 2009, Bäumchen and co-workers employed experiments in which liquid polymer films dewetting from ideal substrates were shown to exhibit the huge slip lengths predicted by de Gennes a couple of decades earlier [13] (Fig. 1.2). The typical stresses involved in these experiments were large, approaching the atmospheric pressure.
1.2 Main results

1.2.1 Capillary levelling as a nanorheological probe

In order to understand the above anomalies in thin films, and more generally their rheology, a fine and robust nanoprobe is needed. Such a tool is a device or method enabling the measurement of physical quantities at the nanoscale. For instance, in order to know if a material flows and to quantify this flow, the free interface of the sample can be deformed and the resulting evolution observed. This is what we instinctively realise when perturbing the surface of honey in a pot with a spoon: the deformation progressively vanishes under the action of gravity. That relaxation operates over a time scale that increases as the honey is cooled, which is directly related to the viscosity of the material.

At the nanoscale, the principle is similar, but the dominant driving force is surface tension, rather than gravity. By starting with a non-flat polymer nanofilm supported on a rigid substrate, and by observing its capillary levelling over time, one can thus deduce the internal mobility of the material. More precisely, the developed technique consists of making polystyrene stepped films – by superimposing two flat films with typical thicknesses on the order of several tens of nanometers but with different horizontal
1.2. Main results

extents – and then observing their relaxation using atomic-force microscopy (Fig. 1.3).
The evolution and shape of the profile being well described by fluid mechanics in the
lubrication approximation, one can precisely calibrate this nanoprobe before employing
it to address open questions of nanophysics.

Besides the stepped-film geometry for films supported on a rigid substrate, other
configurations were studied in the same spirit, with a similar degree of accuracy. Exam-
ples include: trenches and holes, or steps on a freestanding film. In addition, blends of
polymers and superimpositions of different layers were investigated, with the molecular-
weight dependency of the extracted viscosity correctly recovered. Other problems, such
as the effects of viscoelasticity, the spreading of a droplet on an artificial precursor film,
the wake generated by a moving perturbation, and multilayer dewetting were also ad-
dressed. Finally, beyond the precise numerical solving of the governing thin-film equa-
tions and the molecular-dynamics simulations of capillary levelling in polymer films,
some interesting mathematical questions arose. Essentially, despite the nonlinear as-
pect of the thin-film equations, key intermediate asymptotic solutions were found to
be universal attractors, i.e. long-term solutions that are stable against variations on
the initial profile. These were demonstrated to depend only on the boundary condi-
tions and initial symmetry of the profile, which was then confirmed experimentally.
All together, the necessary experimental, numerical and theoretical tools have been
calibrated and developed, opening the way for novel, robust nanorheological studies.

1.2.2 Slip effects in polymer melts

Rayleigh-Plateau instability on a slippery fiber

We proposed a new method to study and measure polymeric slippage. The device is
based on a well-known hydrodynamic instability: a liquid film coating a cylindrical
fibre tends to evolve towards a succession of drops in order to minimize its surface
energy. This is the Plateau-Rayleigh instability [31]. Experiments consist in optically
monitoring the development of this instability on microfibres differing from the point of
view of their surface properties. Glass microfibres impose a no-slip condition between
the solid and the liquid, whereas microfibres previously coated with Teflon create a
sliding condition. The significant differences observed in the dynamics of instability
on these two types of fibres and the agreement of the measurements with a thin-film
model make this system an ideal device for measuring sliding robustly (Fig. 1.4).

Slippery dewetting

At first glance, the observation of droplets running down a wind screen seems to be
routine. However, understanding the motion of a meniscus in contact with a solid
surface is still a subtle problem [32]. Strong shear flows inside the liquid near the
solid create a high friction that slows down the motion of the whole liquid. If the
assumption that liquids cannot slide past a solid was entirely true, these friction forces
would become indefinitely large in the meniscus and “not even Herakles could sink a
solid if the [no-slip] model was entirely correct”, as Huh and Scriven wrote in their
publication revealing this paradox [33].
We have shown that slip has a strong influence on the relaxation process of liquid polymer droplets. The observed dynamics exhibits an unexpectedly-rich phenomenology of transient droplet shapes and dynamics. Moreover, slippage between liquid and solid not only controls the speed of the rim but also is responsible for unusual droplet shapes. Rims of large droplets move slow relative to their diameter, giving the liquid sufficient time to form an ideal spherical cap. But for a tiny droplet whose diameter is on the scale of a micron, the situation can be very different. During retraction, a small polystyrene (PS) droplet may form a ridge close to the moving droplet edge, and a dimple can then appear in the center (Fig. 1.5). The octadecyl-trichlorosilane (OTS) coating is a self-assembled monolayer that provides enough slippage with the polymer melt to create a ridge and a dimple in the center before the droplet shape approaches a spherical cap in the end. But the observations on chemically-similar coatings called dodecyl-trichlorosilane (DTS) were at first surprising. Since surfaces covered by DTS are even more slippery for the polymer melt than those coated with OTS, ridges and dimples could have been expected to form. In contrast to OTS, however, the enhanced slippage allows liquid to flow to the center of the droplet, as revealed by boundary-element-method numerical simulations and scaling arguments. Thus, the absence of ridges and dimples can be also an effect of too much slippage. Indeed, droplets in
1.2. Main results

Figure 1.5: (a) Experimental atomic force microscopy data for PS microdroplets dewetting from OTS (top) and DTS (bottom) self-assembled-monolayer substrates; scale bars are 2 µm and the height scales can be seen from the grey lines in (b) and (c). (b) Experimental height profile evolution in time t of the PS droplet dewetting from OTS shown in (a). Time between lines is approximately 10 min. (c) Experimental height profile evolution of the PS droplet dewetting from DTS shown in (a). Time between lines is approximately 4 min. Insets show height profiles, with the radial coordinate r and height profile \( h(r,t) \) scaled by the contact line radius \( R(t) \) and central droplet height \( h(0,t) \).

contact to very slippery surfaces may behave similar to freely-suspended droplets as we have shown.

Beyond the Navier-de Gennes paradigm

We employed the capillary-levelling technique in order to measure the slip length of PS over Teflon substrates. Interestingly, data were found to be at odds with the predictions of de Gennes and the results of dewetting studies (Fig. 1.6). The stresses applied in these new surface relaxation experiments are much weaker, typically two orders of magnitude, than in the dewetting experiments [13] (Fig. 1.2), even while both flows are driven by surface tension. We considered that the surfaces used – even though atomically smooth and well described as ideal for the dewetting experiments – could actually “hang on” to molecules as surface tension drove the films to be flat. This molecular adsorption would cause orders-of-magnitude deviations in the slip lengths measured, which could be understood in the context of a model that assumes few polymer chains transiently attached to the surface. The picture that has emerged is not one of the existence of a simple passive solid, but a solid that responds differently under different experimental conditions. For weak enough driving, these atomically smooth substrates can prevent the adsorbed molecules from flowing; yet a harder push as in a dewetting experiment makes them slide along the substrate easily. The results highlight the importance of a carefully-considered boundary condition when studying fluid motion at the nanoscale.
Chapter 1. Thin liquid polymer films

Figure 1.6: a) Slip length as a function of molecular weight, from capillary-levelling experiments (blue circles) of PS on AF substrates. For comparison, results from PS dewetting experiments (orange squares, data from [13]) on AF substrates are also shown. Two equations with one free parameter (solid lines) describe both sets of experiments: it assumes adsorption of chains in the low-shear-rate levelling experiments and no chain adsorption in the high-shear-rate dewetting experiments. b) The difference in the measured slip length between levelling (blue) and dewetting (orange) experiments is confirmed using a different substrate, a self-assembled monolayer (SAM).

1.3 Publications

- Symmetrization of thin freestanding liquid films via capillary-driven flow
  Physical Review Letters, 124 184502 (2020)

- Influence of outer-layer finite-size effects on the rupture kinetics of a thin polymer film embedded in an immiscible matrix

- Adsorption-induced slip inhibition for polymer melts on ideal substrates
  Nature Communications, 9 1172 (2018)

- Effects of slippage on the dewetting of a droplet
1.3. Publications

T. S. Chan, J. D. McGraw, T. Salez, R. Seemann, and M. Brinkmann

• Existence of a critical layer thickness in PS/PMMA nanolayered films
A. Bironeau, T. Salez, G. Miquelard-Garnier, and C. Sollogoub
Macromolecules, 50 4064 (2017)

• Van der Waals interaction between a moving nano-cylinder and a liquid thin film

• Molecular dynamics simulation of the capillary leveling of viscoelastic polymer films
The Journal of Chemical Physics, 146 203327 (2017) [themed issue on Dynamics of Polymer Materials in Thin Films and Related Geometries]

• Capillary levelling of freestanding liquid nanofilms

• Wake and wave resistance on viscous thin films
R. Ledesma-Alonso, M. Benzaquen, T. Salez, and E. Raphaël
Journal of Fluid Mechanics, 792 829 (2016)

• Slip-mediated dewetting of polymer microdroplets
J. D. McGraw, T. S. Chan, S. Maurer, T. Salez, M. Benzaquen, E. Raphaël, M. Brinkmann, and K. Jacobs
Proceedings of the National Academy of Sciences of the USA, 113 1168 (2016)

• Symmetry plays a key role in the erasing of patterned surface features

• Influence of slip on the Plateau-Rayleigh instability on a fibre
Nature Communications, 6 7409 (2015)

• Approach to universal self-similar attractor for the levelling of thin liquid films
M. Benzaquen, P. Fowler, L. Jubin, T. Salez, K. Dalnoki-Veress, and E. Raphaël
Soft Matter, 10 8608 (2014)

• Viscoelastic effects and anomalous transient levelling exponents in thin films
M. Benzaquen, T. Salez, and E. Raphaël
Europhysics Letters, 106 36003 (2014)
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- **Capillary levelling of a cylindrical hole in a viscous film**  
  M. Backholm, M. Benzaquen, T. Salez, E. Raphaël, and K. Dalnoki-Veress  
  Soft Matter, **10** 2550 (2014)

- **Relaxation and intermediate asymptotics of a rectangular trench in a viscous film**  
  O. Bäumchen, M. Benzaquen, T. Salez, J. D. McGraw, M. Backholm, P. Fowler,  
  E. Raphaël, and K. Dalnoki-Veress  
  Physical Review E, **88** 035001 (2013)

- **Intermediate asymptotics of the capillary-driven thin film equation**  
  M. Benzaquen, T. Salez, and E. Raphaël  
  European Physical Journal E, **36** 82 (2013)

- **Capillary leveling of stepped films with inhomogeneous molecular mobility**  
  Soft Matter, **9** 8297 (2013) [themed issue on The Geometry and Topology of Soft Materials]

- **Capillary-driven flow induced by a stepped perturbation atop a viscous film**  
  T. Salez, J. D. McGraw, O. Bäumchen, K. Dalnoki-Veress, and E. Raphaël  
  Physics of Fluids, **24** 102111 (2012)

- **Self-similarity and energy dissipation in stepped polymer films**  
  Physical Review Letters, **109** 128303 (2012)

- **Numerical solutions of thin film equations for polymer flows**  
  European Physical Journal E, **35** 114 (2012)

- **Beyond Tanner’s law: crossover between spreading regimes of a viscous droplet on an identical film**  
  Physical Review Letters, **109** 154501 (2012)

### 1.4 Perspectives

We envision three axes of possible exploration in future. First, we would like to invoke the capillary-levelling technique in order to measure the viscosity of polymer melts in extreme confinement. Thanks to the precision of the technique, we should first confirm the confinement-induced fluidisation previously-reported [3, 8], before exploring novel quantitative models for the effective viscosity as a function film thickness and go beyond the previous empirical trend (Fig. 1.1).

Secondly, at small scales, thermal fluctuations are of tremendous importance [34]. Therefore, we would like to incorporate the effects of Langevin-like random stresses within the thin-film equations [35], and explore situations (e.g. instabilities, spreading, coalescence, breakup, etc.) where those dominate. Critical fluids might be ideal
1.4. Perspectives

experimental models [36], amplifying the thermal effects with respect to the capillary ones at a macroscopic scale.

Finally, exploring further the transient viscoelastic processes in thin polymer films might provide new insights into the highly-debated potential artefacts due to residual stresses from sample preparation.

Preprint

- *Capillary levelling of immiscible bilayer films*
  
  
  ArXiv:2005.01974
Chapter 1. Thin liquid polymer films
Chapter 2

Glass transition in confinement

2.1 Context

2.1.1 The glass-transition enigma

Glassy materials are ubiquitous [37], and discussions about glass transition involve many areas of physics, from molecular and spin glasses to hard-sphere jamming [38, 39, 40, 41, 42, 43, 44]. Furthermore, new promising glassy materials continue to appear, such as ultrastable glasses [45] and vitrimers [46]. In spite of the intense interest in the dynamical slowing that accompanies glass formation, a single microscopic theory has yet to emerge [47, 48, 49, 50, 51].

Nevertheless, the phenomenological approach of free volume [52] and the Doolittle Ansatz [53] have been used to support the Vogel-Fulcher-Tammann (VFT) time-temperature superposition [54, 55, 56], which describes so many of the observed behaviours. Fundamental to glass formation are the suggestions that particles are increasingly crowded, and relaxation requires the cooperative participation of a growing number of particles. The hypothesis of a cooperatively rearranging region, as introduced by Adam and Gibbs [57], is appealing and has been observed in computational studies [58, 59]. However, directly measuring molecular motion in bulk glasses remains a difficult task due to the temporal constraints associated with the peculiar glass transition. Associated to cooperative dynamics is the existence of a length scale $\xi$ for cooperative rearrangement [60]. A natural idea was then to study confined glass formers, as an alternative way to measure $\xi$ [61].

2.1.2 Anomalies in confined glass formers

Perhaps, the most active example of attempts to probe $\xi$ through confinement is the study of low-molecular-weight glassy polymer films [62, 63, 64, 65, 66, 67, 68], where fascinating observations have been made during the last two decades. For the most studied case of polystyrene, diminutions in the measured glass-transition temperature have been almost uniformly reported as the film thickness is reduced (Fig. 2.1), both experimentally [69] and numerically [70]. It has been further suggested that this apparent anomaly could be linked to the observed existence of a more mobile interfacial layer [71, 72, 73, 74, 75] (Fig. 2.2).
Figure 2.1: Effective glass-transition temperature $T_g$ of free-standing polystyrene nanofilms as a function of the thickness $h$ of the film, for different molecular weights $M_w$. For comparison, the two dashed lines indicate the spread and uncertainty for results obtained with substrate-supported nanofilms.

As a consequence, there have been many theoretical and numerical attempts to understand the thin-film glass transition, with varying degrees of complexity and success, but as of today the problem remains unsolved and an important controversy holds. The main debates focus on the distinction between additional surface effects – including potential experimental artefacts – and a real finite-size effect attributed to confinement. Similarly, the distinction between the bulk cooperative length and the thickness of the surface mobile layer, despite their rather similar values of a few nanometers, has fuelled the general confusion.

Even more intriguing is perhaps the existence of a universal behaviour of those glass-transition temperature reductions for free-standing polystyrene films with large molecular weights (Fig. 2.1), that is when the thickness of the sample is comparable to the typical size of one macromolecule – its radius of gyration. This other class of anomalies, most probably related with purely polymeric effects, is still an open question as well. And the existence of a universal $(h^*, T_g^*)$ point (Fig. 2.1) has been a complete mystery for almost twenty years now. One tentative mechanism based on a reptation-like sliding motion has been sketched, and later refined, but could not quantitatively capture the observations.

In addition, other geometries have been experimentally explored in great details. The simplest such case is that of polymer spherical nanoparticles, and their recent colloidal analogues. To our knowledge, the first report of anomalous dynamics in polymer nanoparticles is that of Sasaki et al. In that work,
2.1. Context

Figure 2.2: *Thickness of the liquid-like mobile layer at the free surface of various glassy films as a function of temperature near and below the calorimetric glass-transition temperature, for different thicknesses and cooling rates as indicated.*

Differential-scanning calorimetry of aqueous dispersions of polystyrene nanospheres in the 21-274 nm radius range showed no evidence for a reduced glass-transition temperature, but instead revealed a radius-dependent value of the step in heat capacity at the glass transition. Analysis of the data suggested that this result is consistent with a near-surface region of size $\sim 3.8$ nm not contributing to the transition. Then, Rharby used neutron scattering to measure mechanical deformations of polystyrene nanospheres individually dispersed in cross-linked polybutylmethacrylate matrices, and deduced glass-transition temperatures that were reduced from the bulk value for nanospheres less than $\sim 30$ nm in radius [93]. Later measurements by Zhang et al. [96], and Feng et al. [95], showed reductions in the glass-transition temperature for spheres of larger radii, and with a strong dependence on the sphere coating. The latter fact is reminiscent of the drastic effect even small amounts of residual surfactants can have on the reductions in the glass-transition temperature of thin films, as reported by Chen and Torkelson [101]. The above large disparity in observations may partially result from the much more difficult sample preparation in making dispersed nanospheres, as compared to thin films. Indeed, the presence of surfactants and/or residual monomers, and the uncertainty in final molecular weight could result in large variations between different experiments. Nevertheless, it appears necessary to establish a proper theoretical framework for the description of the glass transition in spherical confinement.

Recently, two glassy and rubbery polymeric slabs were put in close contact with each other, and their local properties were measured in order to probe the extent of the interfacial crossover in terms of glass-transition temperature [102]. Once again,
2.2 Main results

2.2.1 Quantitative measure of surface mobility

Using the calibrated stepped-film technique (Chapter 1), it is then possible to study the capillary relaxation of polystyrene films below their glass-transition temperature \( T_g \). The conclusion is striking: the surface evolves. The evolution occurs over several hours, and is still observed a few tens of degrees below \( T_g \). These observations can be understood using a simple two-layer thin-film model. Below the glass-transition temperature, the dynamics is heterogeneous and the film exhibits a liquid-like mobile layer (Fig. 2.3A) whose thickness increases (Fig. 2.2) and reaches the whole sample size (Fig. 2.3B) at the glass transition. The important result is that the mobility of this surface layer can be extracted quantitatively (Fig. 2.4) from a fit to experimental

the hundred-nanometer-like length scale involved appears to be much bigger than any molecular or structural size, which puzzles the community.
2.2. Main results

Figure 2.4: Poiseuille mobility of a low-$M_w$ polystyrene film (defined by the thickness $H$ and viscosity $\eta$ of the flow region) as a function of the inverse temperature $1/T$. As a characteristic feature of the glass transition, the mobility varies over ten decades near $T_g$. When $T > T_g$ (squares), the flow occurs within the whole film (Fig. 2.3B), with an average thickness $H = h_1 + h_2/2$ and bulk viscosity $\eta_b$. The viscosity satisfies the expected Vogel-Fulcher-Tammann (VFT) law for supercooled liquids. When $T < T_g$ (circles), the flow is localised in a near-surface region (Fig. 2.3A) of thickness $H = h_m$, and viscosity $\eta_m$ which seems to follow an Arrhenius-like law, reminiscent of simple liquids.

data below $T_g$. It appears much higher than the corresponding bulk one, and seems to follow an Arrhenius-like trend – characteristic of simple liquids – instead of the bulk VFT trend of supercooled liquids. We note that we also recovered the features of a surface liquid-like layer using molecular-dynamics simulations of stepped films made from binary Lennard-Jones mixtures. Finally, by varying further the molecular weight experimentally, which is expected to affect mostly the viscosity, we could also disentangle the viscosity and thickness of the mobile layer from the single composite mobility parameter. Having done so, we further revealed new, inhibiting anchoring effects of the surface polymer chains at large molecular weights.

2.2.2 The cooperative-string model

In order to understand the physical origin of such a liquid-like surface layer atop glassy films, and its possible link with the observed $T_g$ shifts, one needs to develop a microscopic theory. Inside a bulk glass, molecules are in an environment similar to the subway at rush hour. Each molecule is trapped in a cage formed by its nearest neighbours, and has very little free volume to move, to change position, and thus to allow for the material to relax towards equilibrium. Given the impossibility of individual mo-
Chapter 2. Glass transition in confinement

Figure 2.5: Glass-transition temperature $T_g$ of polystyrene films supported on silicon substrates, measured by dilatometry, as a function of film thickness $h$ (closed circles) [103]. For comparison, other literature data is indicated (open circles) [67]. The microscopic hypothesis of the random cooperative strings allows one to quantify the local molecular mobility and thus the glass-transition temperature (solid line).

Then, one can add a free interface to the description above. Doing so, it is possible to address quantitatively the two anomalies introduced previously. The key ingredient lies in the fact that a random cooperative string is truncated at the free interface due to the absence of crowding constraints (Fig. 2.3C). In other words, a passenger of the subway standing close to the exit gate does not require any collective motion to escape the train: the passenger can simply jump outside, as a liquid-like molecule. This type of behaviour fluidises the neighbourhood of the gate. Invoking a Brownian description for the cooperative chains and the first-passage density of probability at the interface, one can quantify the local relaxation time in a thin film, and thus its mobility and glass-transition properties (Fig. 2.5). The agreement with literature data is good and a single free parameter is extracted from the fit: the size of the molecular unit of the
cooperative strings. This size is found to be in the nanometer range, and comparable to the persistence length of polystyrene which is self-consistent.

Finally, using the same model, predictions were made in various other geometries: supported films on attractive substrates, free-standing films, spherical and cylindrical particles, which might trigger novel experiments in future.

## 2.3 Publications

- **Rearrangement of 2D aggregates of droplets under compression: signatures of the energy landscape from crystal to glass**
  Physical Review Research, 2 023070 (2020)

- **Cooperative strings and glassy dynamics in various confined geometries**
  M. Arutkin, E. Raphaël, J. A. Forrest, and T. Salez

- **Using $M_w$ dependence of surface dynamics of glassy polymers to probe the length scale of free surface mobility**
  Y. Chai, T. Salez, and J. A. Forrest
  Macromolecules, 53 1084 (2020)

- **Molecular dynamics simulation of the capillary leveling of a glass-forming liquid**
  I. Tanis, K. Karatasos, and T. Salez

- **Glass transition at interfaces**

- **Cooperative strings in glassy nanoparticles**
  M. Arutkin, E. Raphaël, J. A. Forrest, and T. Salez
  Soft Matter, 13 141 (2017) [Emerging Investigators themed issue]

- **La transition vitreuse aux interfaces**
  T. Salez and E. Raphaël
  Reflets de la Physique, 46 24 (2015)

- **Cooperative strings and glassy interfaces**
  Proceedings of the National Academy of Sciences of the USA, 112 8227 (2015)

- **A direct quantitative measure of surface mobility in a glassy polymer**
  Science, 343 994 (2014)
2.4 Perspectives

One main focus would be to understand the case of high-$M_w$ polymer films, through their intriguing confinement effect \[88, 90\]. At the mesoscopic scale, continuum approaches such as lubrication hydrodynamics and elasticity could be used to describe the flow/strain in glassy capillary levelling experiments. At the microscopic scale, a full statistics of loops and bridges of polymer chains in a finite-size sample should be constructed and used to critically assess existing predictions \[90, 91\].

Glassy capillary leveling could be explored further in other geometries. For instance, a low-$M_w$ glassy droplet in total-wetting condition is expected to spread with a contact radius growing as $\sim t^{1/8}$, due to the surface-localised flow region, rather than the Tanner power law $\sim t^{1/10}$ of simple liquids \[18\]. Instabilities (e.g. Rayleigh-Taylor or Rayleigh-Plateau) would be alternative ways of probing the non-conventional glassy mobility. Nanobubbles could also serve as driving sources in glassy-flow problems, thanks to their high Laplace pressure.

Molecular-dynamics simulations of coarse-grained bead-spring polymer models could be developed for various initial configurations with excess surface energy, and the averaged molecular trajectories could be recorded and compared to lubrication theory. In all these situations, the local mobility should be quantified as a function of distance to the free surface, temperature, and molecular weight, and the distinction between flow or other mobility mechanisms – i.e. mainly surface diffusion \[75, 105, 106\] – should be made clear.

At the microscopic level, in addition to the study of mode-coupling theory in confinement for a binary Lennard-Jones mixture, the preliminary-developed cooperative-string theory should be rendered robust and consistent from the point of view of statistical physics. In particular, fluctuations must be taken into account, and their effects quantified, to go beyond the current mean-field description. Enthalpic contributions and interactions of molecules could be included in the description too, in order to provide a general picture for the bulk glass transition and produce realistic departures from the Vogel-Fulcher-Tammann law. Other fractal dimensions of the cooperative regions may be implemented and critically compared to the 1D mechanism above. Finally, using first-passage time arguments, the cooperative-string model might be applied to different interfacial geometries such as bilayer slabs \[102\] and mixtures. The problem of ageing would be interesting to investigate as well with such tools.

Finally, silica seems to be a very peculiar glass former compared to organic glasses and plastics. In particular, it exhibits an Arrhenius time-temperature behaviour unlike most glasses \[107\]. Besides, individual nanoparticles have never been studied so far. It would thus be interesting to invoke single optically-trapped nanoparticles \[108\] of polystyrene and silica with various radii, and to heat them in situ in order to investigate their glass transition in confinement.

Preprint

- *Soft nanobubbles can deform rigid glasses*
  S. Ren, C. Pedersen, A. Carlson, T. Salez, and Y. Wang
  ArXiv:2001.09031
Chapter 3

Soft wetting

3.1 Context

3.1.1 Capillarity of soft solids

Soft solids are increasingly studied since the rise of soft matter at the end of the XXth century. They can be so soft (e.g. cosmetic and food gels or organic vesicles) that they sometimes start to behave like liquids, as capillarity overcomes elasticity [109, 110, 111, 112, 113, 114] (Fig. 3.1). In particular, new intermediate behaviors at the boundary between solid adhesion and liquid wetting are expected for their contact mechanics.

On the one hand, there is the contact between elastic solids [115, 116]: two grains of sand for example; or between elastic adhesive solids such as latex particles. The description of the shape and size of the contact area is the result of many studies conducted in the past. These include pioneering works by Hertz [117], Johnson, Kendall and Roberts (JKR) [118], as well as Derjaguin, Muller and Toporov (DMT) [119]. In the case of an elastic and adhesive spherical particle, the equilibrium form results from a balance between adhesion, which tends to deform the particle, and elasticity which opposes deformation. This field of research is of great importance through its numerous applications that range from biomechanical characterisation [120] to engineering.

On the other hand, there is the wetting of a solid surface by a liquid: a drop of water on a glass window for instance. Here again there is an abundant literature [19, 20, 21], both on the static and dynamic aspects of the problem, and this field of research continues to be active [32]. In the case of a liquid drop, the equilibrium shape and in particular the Young-Dupré contact angle result from a balance between adhesion, which again tends to deform the drop, and liquid-air surface tension which opposes this deformation [121]. The development of electrowetting techniques and the chemical treatments and patterning of surfaces allow for a remarkably precise control of wettability nowadays.

But what about soft-matter objects, such as soft solids, that by definition are neither solid nor liquid?
Chapter 3. Soft wetting

3.1.2 The Shuttleworth controversy

Echoing the previous point: what controls phenomena as different as the shape of a soap bubble, the spreading of a drop of dew on a tree leaf, the dewetting of a Teflon pan, the tears of wine, the meniscus around a fishing line, or the difficulty in extracting certain oils from soils? Capillarity, which tends to minimize interfaces and whose origin is microscopic. Indeed, the molecules of a liquid have a certain affinity between them and attract each other, thus ensuring the cohesion of the whole. But, add a border – an interface – and the molecules become less surrounded by their fellows, and therefore “frustrated”. The macroscopic consequence is an excess of energy per unit of surface, \( \gamma \), tending to reduce interfaces. If capillarity may seem at first sight to be the prerogative of fluid interfaces, in particular at small scales (where it prevails over other effects like gravity), the interfaces between solids and fluids also have an energy cost. In fact, this is what controls the wettability of a solid material via the Young-Dupré relation \([121]\).

There is however an essential difference between a solid and a liquid: the latter can easily rearrange under external stress (e.g. deformation of its container), unlike a crystalline solid whose atoms are linked to their neighbours by strong bonds. Consequently, if one stretches a crystalline solid, one moves its components relative to each other which can modify the surface energy of the solid – an impossible thing with an
3.1. Context

At this stage, two distinct physical quantities should be introduced: i) the “surface energy”, \( \gamma \), which represents the energy cost associated with the creation of a unit of interfacial area (e.g. by cutting the solid into two parts); and ii) the “surface stress”, \( \Gamma \), which represents the force (scalar here to simplify the point) necessary to increase the interfacial area by a unit of area. Now consider an interfacial area \( A \), and an infinitesimal increase \( dA \) of the latter under the action of the external stress \( \Gamma \). A mechanical energy balance leads to balancing the energy increase \( d(\gamma A) \) of the interface and the external work \( \Gamma dA \) received by it.

In the case of an interface between two fluids, after elongation of the interface, the molecules rearrange freely and are collectively found in an average state similar to that preceding the elongation (Fig. 3.2a). Consequently, the surface energy \( \gamma \) does not depend on the area \( A \) and the previous energy balance leads to \( \Gamma = \gamma \). In other words, “surface energy” or “surface stress” are the same for a fluid. We then understand the classic but ambiguous term “surface tension” and the notation \( \gamma \), invariably used for energy or force balances.

For an interface involving a solid (compressible here to simplify the discussion), things are different. After elongation of the interface, the molecules of the solid are separated from each other in the direction of elongation. They therefore find themselves in a different state from that preceding the elongation (Fig. 3.2b). Consequently, \( \gamma \) now depends on \( A \), and the previous energy balance leads to \( \Gamma = \gamma + A d\gamma/dA \). Finally, by introducing the mechanical deformation, \( \epsilon \), and its link with the increase in area, \( dA = A d\epsilon \), we obtain the Shuttleworth relation [122]: \( \Gamma = \gamma + d\gamma/d\epsilon \). In a nutshell, “Surface energy” and “surface stress” are two different physical quantities, as generally expected for energy or force balances. This Shuttleworth effect was
Chapter 3. Soft wetting

Extensively studied later for crystalline solids [123], but, the crystals not tolerating strong elongations before rupture, it had no major practical implication.

There is, however, another class of solids: non-crystalline solids, called amorphous solids. This terminology essentially gathers two main categories for us: elastomers and glasses. Elastomers are soft solids (e.g. a car tire with an elastic modulus in the MPa range) made of long chains of polymers that are freely entangled but irreversibly connected to each other by a small fraction of crosslinks. Glasses, on the other hand, are rigid solids (e.g. a plastic ruler of elastic modulus in the GPa range) whose constituents are not arranged periodically as in crystals, but in a disordered manner. These two categories of amorphous solids typically tolerate larger deformations than crystals. So it was natural to explore the Shuttleworth effect with them.

In particular, soft elastomers are at the heart of a controversy, following a pioneering experiment carried out at ESPCI Paris on an elastomer (polyvinyl siloxane, PVS) immersed in an ethanol bath [124, 125]. Its results seem to indicate the existence of a Shuttleworth effect – despite the essentially “liquid” microscopic nature of these elastomers.

The debate was largely fuelled by the international workshop on “Capillarity of Soft Interfaces” that took place at the Lorentz center in Leiden, the Netherlands, in 2015. In this emerging community, the existence of a Shuttleworth effect is widely debated. It therefore appeared crucial to test these ideas with new independent experiments. Then, a second team, at ETH Zurich, reported having also detected a Shuttleworth effect on elastomers. This conclusion was based on measurements of the local deformation of crosslinked silicone oils (polydimethylsiloxane, PDMS) wetted by glycerol droplets, and on a new Neumann-like balance of interfacial forces for soft solids [126]. The Swiss team even observed a very significant variation (increase by a factor of $\sim 2.5$ for an elongation $\epsilon = 25\%$) of the surface stress $\Gamma$, which may seem inconsistent with intuition given the microscopic origin of capillarity for homogeneous systems.

Collectively, these results are very intriguing, and several physical chemists immediately invoked possible artefacts linked to the elastomers used: swelling like a sponge by the external liquid, residual presence of free polymer chains in the solid matrix [127, 128], surface properties altered by the presence of a rigid interfacial “crust”, etc. However, these two independent results seem to point in the same direction and no experiment is capable of directly proving the existence of such artefacts within the context of Shuttleworth-like experiments.

3.2 Main results

3.2.1 Adhesion-to-wetting crossover

By an ad-hoc macroscopic approach, we unified the two concepts of adhesion and wetting, recovering similar ideas from the literature [109, 111, 113]. It is based on a calculation of the deformation of an elastic spherical particle placed on a rigid substrate, without external loading, and taking into account a fundamental element: the surface tension of the outer cap. Two forces now oppose adhesion of the particle: its elasticity and its surface tension. The thermodynamic study carried out is divided into two successive parts. At first, the calculation is limited to small deformations for which an
3.2. Main results

Figure 3.3: Deformation of a soft particle, placed on a rigid adhesive substrate, normalized by the Young-Dupré reference [121], as a function of an elastocapillary ratio (increasing with surface tension, and decreasing with both Young modulus and work of adhesion), as calculated from the tenso-elastic-adhesive (TEA) model. The dashed lines correspond to the JKR [118] and Young-Dupré [121] asymptotic regimes, as indicated.

expression of the free energy is provided. The analytical equilibrium solution bridges the gap between adhesion and wetting (Fig. 3.3), and allows for the estimate of typical experimental parameters for observing the new intermediate regime. In a second step, the calculation is extended to the case of large deformations, a relevant framework for comparison with experiments on very soft materials. This numerical study is based on a fruitful analogy with fracture, as suggested by Maugis [116].

As a variation on that topic, we also studied for soft hydrogels the local foot-like feature at the contact line, that was predicted previously [129]. We also performed a rigorous mechanical treatment of the adhesion-to-wetting crossover in the dual case of a rigid particle indenting a soft substrate, which allowed to capture quantitatively the experimental data by Style et al. [113]. Our studies open the way to quantitative experiments on the adhesive contact of various spherical objects relevant to soft matter: biological cells, microgels, nanoparticles of polymers, etc.

3.2.2 Shuttleworth effect in amorphous solids

To contribute to the joint efforts towards solving the Shuttleworth enigma for elastomers, we proposed an alternative approach to the two previous ones [124, 126]. It consists in studying liquid microdroplets placed on stretched amorphous solid films after such a stretching, and measuring the contact angle $\theta_Y$ as a function of the deformation $\epsilon$ in these films – for several solid-liquid pairs.
Figure 3.4: a) Contact angle of a liquid droplet on a glassy substrate at rest (top), and slightly stretched (bottom), measured by adjusting the profile with a spherical cap (red). The scale bar is 50 microns. Note the image of the droplet reflected by the substrate. b) Difference between the surface energies of the solid as a function of substrate’s deformation (black dots), obtained from the measurement of the contact angle and the Young-Dupré law [121]. The results are for four liquid-solid couples involving two liquids, diiodomethane (DIM) and glycerol, and two glasses, polysulfone (PSf) and polycarbonate (PC). The solid black lines come from the theoretical model which simply takes into account the average molecular spacing in the calculation of surface energy. The glassy sample corresponding to each data point is then heated above its glass-transition temperature, then cooled, and a new measurement is carried out (blue points).

Let us focus on glassy solids first. Strikingly, a very small deformation (i.e. a few percents) of the solid substrate is enough to cause a notable variation in the contact angle of a liquid drop placed on it after stretching (Fig. 3.4a). According to Young-Dupré’s law [121], this implies a variation in the difference between the surface energies of the interfaces involving the solid, which is confirmed for four different liquid-solid couples (Fig. 3.4b, black dots). In addition, a simple model involving only the spacing between the molecules of the compressible solid induced by the substrate’s elongation, and therefore the associated change in surface energy, captures the experimental data (Fig. 3.4b, black lines). Finally, by melting the stretched glassy solid above its glass-transition temperature in order to relax elastic stresses, and then cooling it back, before repositioning a droplet on it, allows us to recover the result obtained in the absence of elongation (Fig. 3.4b, blue points). Thus, the existence of the Shuttleworth effect in glasses is established for the first time.
3.2. Main results

Unlike the case of the above glasses, a large deformation (i.e. doubling of the length) of an elastomeric substrate does not cause any measurable variation in the contact angle of a liquid droplet placed on it after stretching (Fig. 3.5). Since six different liquid-solid couples have been tested (Fig. 3.5b), and because there is a priori no physical reason for the dependence in deformation of the surface energy of a solid to have strictly the same numerical value whatever the fluid placed on it, one may be led to conclude that there is no Shuttleworth effect for elastomers. This result seems to contradict those of the two previous experiments [124, 126]. It is however confirmed by molecular-dynamics numerical simulations [130], and agrees well with the intuition on the microscopic structure of an homogeneous elastomer (Fig. 3.5c): i.e. an elastomer is essentially a liquid (i.e. no Shuttleworth effect), but weakly connected by a small fraction of crosslinks.

The controversy on elastomers persists and develops. On the one hand, new theoretical results [131, 132], by the authors of the pioneering experiment [124, 125], seem to indicate that it is in fact expected not to detect a Shuttleworth effect in elastomers (even if it existed) by the Young-Dupré contact-angle method. On the other hand, a separate theoretical result [133] seems to indicate that the Shuttleworth effect is not necessary to explain the experiments at ETH [126]. The difficulty in resolving this controversy probably lies in the fact that the various experiments do not concern exactly
the same physical observables, nor the same materials, and do not rely on the same laws for their modelling.

In summary, the question around the elastomeric Shuttleworth effect is not entirely resolved yet, and one must appreciate the current emulation about capillarity of soft solids. In future, the possible collective resolution of this lively controversy will tell us a little more about the fascinating fundamental properties of glasses and soft matter. Besides, whatever the exact microscopic surface structure of the elastomer (PDMS) prepared and used at ETH [126], it is a fact that it is abundantly used in the world and it exhibits a minima a significant effective Shuttleworth effect. In addition, the existence of a Shuttleworth effect for glasses seems to be proven. We can therefore imagine controlling the wetting properties of a plastic material by simply stretching it. From fog-harvesting nets, to smart textiles and surface treatments, the number of potential applications is very large.

3.3 Publications

- *Stretching a solid modifies its wettability... or does it?*

- *Déformer un solide modifie sa mouillabilité... ou pas !*
  T. Salez
  L’Actualité Chimique, 451 34 (2020)

- *Elastowetting of soft hydrogel spheres*

- *Surface energy of strained amorphous solids*
  Nature Communications, 9 982 (2018)

- *Liquid droplets act as “compass needles” for the stresses in a deformable membrane*

- *Elastocapillary bending of microfibers around liquid droplets*

- *Solid capillarity: when and how does surface tension deform soft solids?*
  Soft Matter, 12 2993 (2016)
3.4 Perspectives

- **Indentation of a rigid sphere into an elastic substrate with surface tension and adhesion**
  C.-Y. Hui, T. Liu, T. Salez, E. Raphaël, and A. Jagota

- **From adhesion to wetting of a soft particle**
  T. Salez, M. Benzaquen, and E. Raphaël
  Soft Matter, **9** 10699 (2013)

3.4 Perspectives

We envision several possible avenues for exploring further the above questions around solid capillarity. First, new independent experiments are needed to solve the Shuttleworth controversy. Ideally, they would measure the absolute surface energy $\gamma$ of a single solid-fluid interface as a function of the deformation $\epsilon$ of the solid, and for all the solid-liquid couples tested so far. Furthermore, having access to neutron or X-ray sources to obtain a fine characterisation of the surface of the PDMS used at ETH [126] would probably help to close certain questions.

Secondly, by using microfluidics, one could prepare microparticles with controlled elasticity and size, in order to test the adhesion-to-wetting crossover in the case of a deformable spherical particle over a rigid substrate. Indeed, this geometry – despite being a relevant one when considering wetting droplets and biological cells – has never been studied so far.

Thirdly, non-contact AFM experiments near soft (Chapter 4) and potentially-stretched substrates would allow to quantify capillary effects [134] and explore locally, at the nanoscale, both the adhesion-to-wetting crossover and the Shuttleworth effect in amorphous solids.

Finally, on a theoretical standpoint, viscoelastic and plastic extensions – relevant to soft materials – of the Shuttleworth equation should be derived.
Chapter 4

Soft lubrication

4.1 Context

4.1.1 Soft and wet contacts

Soft and wet contacts are widespread in nature and technology. Their rich history in science and engineering involves issues and scales as diverse as the lubrication of roller bearings after the industrial revolution [136] or the catastrophic geological landslides [137]. The properties of these contacts implicate the coupling between the local hydrodynamic pressure – induced by fluid flow – and the deformation of the confining solids.

Recently, such a coupling gained attention in the context of confined, soft and biological matter, where very compliant solids and tiny length scales are common [138]. In fact, this coupling could conceivably play a crucial role in the motion of various physiological and biological entities. Examples are numerous and include e.g.

Figure 4.1: (left) In a surface-forces apparatus (SFA), a flow between an oscillating sphere and an elastic film is created. (right) Real (blue) and imaginary (red) parts of the force-distance response $G_\omega(D)$ obtained for a crosslinked PDMS [135].
the incredible frictional properties of mammalian joints \[139, 140\] through the fine interplay between soft cartilage and viscous synovial fluid, or the crucial influence of vessel boundaries on the motion of deformable red blood cells \[141\]. Furthermore, through surface-forces apparatus (SFA) \[142, 135, 143, 144\] and atomic-force microscopy (AFM) \[145, 146, 147, 148, 120\], the elastohydrodynamic (EHD) coupling offers an alternative strategy for micro and nanorheology of fragile soft materials, with the key advantage of avoiding any solid-solid adhesive contact that could alter their properties (Fig. 4.1).

4.1.2 An emerging elastohydrodynamic lift force

In such a context of confined soft matter, despite the irrelevance of inertia, a novel EHD lift force was theoretically predicted for elastic bodies moving past each other in a fluid \[149\]. Essentially, any symmetric object moving within a viscous fluid and along a nearby soft wall is repelled from the latter by a dynamically-generated emergent normal force (Fig. 4.2). This force intimately arises from a modification in the contact shape and the associated flow, due to the EHD coupling described above. Furthermore, as the gap between the object and the soft wall is reduced, the lift force increases tremendously. This mechanism was further explored and generalised through the motion of vesicles along a wall \[150, 151\], different elastic media and geometries \[152, 153, 154\], added effects of intermolecular interactions \[155\], self-similar properties of the soft-lubricated contact \[156\] and the case of membranes \[157, 158\].

Despite the above theoretical literature, experimental evidence for such a soft EHD lift force is recent and scarce \[159, 160\], including a preliminary qualitative observation reported in the context of smart lubricants and elastic polyelectrolytes \[161\].

4.2 Main results

4.2.1 Inertial-like zoology at low Reynolds number

First, we predicted theoretically a zoology of counter-intuitive low-Reynolds-number behaviours for the unexplored case of an immersed free particle that can simultaneously sediment, slide, or roll near a soft wall: enhanced sedimentation, bouncing, spontaneous rolling, roll reversal and self-sustained long-runout sliding. Those solutions demonstrate that inertial-like effects – usually only relevant for big and fast objects (e.g. aerodynamic lift on a plane’s wing, or Magnus effect in ball sports) – can be triggered at microscopic and biological scales (i.e. at low-Reynolds numbers) by elastic boundaries.

Secondly, we have combined experiments and theory to study the movement of a heavy, lubricated object near a tilted soft wall. The assembly consists of an inclined plane covered with a layer of soft gel, all immersed in an oil of controlled viscosity (Fig. 4.3). We have studied the fall of different cylinders along this surface, varying the elastic modulus and the thickness of the gel coating. In contrast to the case of a rigid surface, we observed that the sliding speed increases significantly along a soft surface, which corresponds to a decrease in effective friction. In addition, the speed of fall, and
Viscous sliding + soft boundary = emergent lift

Integrating (4)–(6) leads to the dimensionless Reynolds equation... EPL 23 113 (1993)

V

Skotheim & Mahadevan, PRL 92 245509 (2004)

µ


4.2. Main results

Figure 4.2: For a non-deformable wall, the classical lubrication pressure \( p(x) \) induced in the viscous fluid by the tangential motion of a sphere at velocity \( V \) is antisymmetric in the transverse direction \( x \), resulting in a null net force (integral of the pressure along \( x \)) in the normal direction \( z \). In contrast, a soft surface is deformed by the pressure field. The latter then loses its symmetry, which results in a finite emergent normal force: the EHD lift force [152].

Therefore the friction, are constant in time, indicating the suppression of any stick-slip feature associated with solid friction. Moreover, when the cylinder slides along the wall, the gel coating is asymmetrically deformed as predicted by soft-lubrication theory (Fig. 4.2). Indeed, the flow under the cylinder generates an overpressure at the front which compresses the gel, and a depression at the back which, conversely, attracts it to the cylinder. This asymmetry of deformation generates a flow asymmetry. Therefore, like the aerodynamic lift created by the asymmetry of air flow around a wing, there emerges here also a lift, but of elastohydrodynamic origin. This self-generated force opposes the weight and explains why the cylinder levitates during its fall, sliding with a constant speed. The experiments are supported by theoretical work in the context of small deformations of the surface. The theory predicts a sliding speed increasing with softness, which has been quantitatively verified for a wide range of parameters. However, when the gels become very soft, \( i.e. \) at large deformation, the theory is no longer verified and the speed decreases again. This suggests the existence of a saturation effect and an optimum rigidity to reduce the effective friction. Our findings pave the way for new design principles to reduce and control friction, and also offer new ways to address phenomena as diverse as the ageing of cartilaginous joints or the origin of landslides.

Subsequently, the optical tracking of the driven motion of a microparticle in a microfluidic channel, decorated with a brush made from a biomimetic polymer, revealed the significance of this force in biological and microscopic settings [162]. By observ-
Chapter 4. Soft lubrication

Figure 4.3: (left) A rigid cylinder immersed in a viscous bath slides along an inclined plane covered with a thin elastic layer. Fluorescent particles embedded in the latter make it possible to observe its deformation using a laser and a camera. (right) Sliding speed $V$ as a function of normalized time $T = t/t_{tot} = tV_{\infty}/L$, for several shear moduli of the elastic coating. Here, $V_{\infty}$ is the time-averaged steady-state sliding speed, $L$ is the total length of the substrate, and $t$ is the time. The dotted line corresponds to the case of a bare glass substrate.

4.2.2 Measuring the lift at the nanoscale

To perform direct quantitative measurement of the EHD lift force, we glued a sphere with a typical size of tens of micrometers to the tip of an AFM cantilever and placed it near a substrate that was oscillated laterally. Doing so, AFM measurements of the lift force were performed in various conditions, including rigid and soft substrates (Fig. 4.4). Near a rigid surface, the force is null. However, a lift force is measured over soft elastomers (PDMS): at a given distance $d$, the softer the wall, the larger the force. In addition, the force follows a power law with the distance with a $-5/2$ exponent – which is a typical feature of the elastohydrodynamic coupling in the thick and incompressible case [153]. Furthermore, the experiments exhibit that the force increases with the substrate’s (and thus fluid’s) velocity and decreases with the wall’s rigidity. The measurements are in agreement with novel quantitative (i.e. beyond scaling [153]) theoretical calculations. Lastly, at very short distance, the observations indicate a saturation of the EHD lift effect.
Figure 4.4: (left) A soft substrate is fixed atop a rigid piezo stage that is transversally oscillated along time $t$, at angular frequency $\omega$ and with amplitude $A$. A rigid sphere is glued to an AFM cantilever and immersed in a viscous liquid lubricant near the substrate. The normal force $F_N$ exerted on the sphere at a given distance from the surface is directly measured from the deflection of the cantilever along $z$. (right) Temporal average $F$ of $F_N$ as a function of the gap distance $d$ to the substrate, for both rigid (silicon wafer) and soft polydimethylsiloxane (PDMS) substrates. The inset shows a log-log representation of the data for the soft substrate where the solid line indicates a $-5/2$ power law characteristic of an EHD lift force in the case of a semi-infinite incompressible elastic substrate [153].

4.3 Publications

- **Rotation of a submerged finite cylinder moving down a soft incline**
  Soft Matter, 16 4000 (2020)

- **Direct measurement of the elastohydrodynamic lift force at the nanoscale**
  Z. Zhang, V. Bertin, M. Arshad, E. Raphaël, T. Salez, and A. Maali
  Physical Review Letters, 124 054502 (2020)

- **Asymptotic regimes in elastohydrodynamic and stochastic leveling on a viscous film**
  C. Pedersen, J. F. Niven, T. Salez, K. Dahniki-Veress, and A. Carlson
  Physical Review Fluids, 4 124003 (2019)

- **Hydroelastic wake on a thin elastic sheet floating on water**
  Physical Review Fluids, 4 014808 (2019)

- **Microfluidic probing of the complex interfacial rheology of multilayer capsules**
  C. Trégouët, T. Salez, C. Monteux, and M. Reyssat
4.4 Perspectives

First, exploring experimentally the above inertial-like EHD zoology appears to be a relevant task, as well as incorporating viscoelastic and poroelastic features to those. Biomimetic and real cartilages, with their puzzling frictional properties, could be eventually studied this way. Besides, softness put aside, other symmetry-breaking mechanisms within the lubrication framework (Fig. 4.2) could be explored, such as slip inhomogeneities or capillary responses, to name a few.

Secondly, spatially patterning the softness, in the spirit of the droplet-durotaxis experiment, and optimising such patterning might be a way to tune the effective EHD friction, which may perhaps find some practical applications in pistons’ surface treatments or sliding sports.

Thirdly, collective effects such as Cheerio-like interactions near soft interfaces, or shear-thickening of dense suspensions, might be revisited in an EHD context.

Finally, already in the purely deterministic context above, we conclude that there is an important—but-emerging activity, with only recent experimental evidence of some essential effects. Therefore, it becomes evident that addressing further the influence of thermal fluctuations on the latter background is a virgin playground. Indeed, the effects of thermal noise amount to injecting energy from the molecular environment
into the system, and *vice versa*, which could very well trigger the emergent forces mentioned above, thus resulting in a non-trivial and intriguing anomalous-diffusive scenario. While the role of solid (rigid) \cite{170, 171, 172, 173, 174}, fluctuating \cite{34} and liquid \cite{175} boundaries on Brownian motion have been studied experimentally and theoretically, the case of elastic boundaries seems mostly virgin theoretically \cite{176}, and unexplored experimentally.

**Preprint**

- *Lift induced by slip inhomogeneities in lubricated contacts*
  
  
  ArXiv:1912.02617
Chapter 5

Friction in complex assemblies

5.1 Context

5.1.1 The classical laws of friction

We are all familiar with friction, a phenomenon that was first studied by da Vinci [177], and formalised later on by Amontons and Coulomb [178, 179]. Da Vinci established that the traction force $T$, required at the onset of sliding of an object is simply $T = \mu N$, where $N$ is the normal force or load, and the proportionality constant $\mu$ is the coefficient of friction. He suggested that the latter is always 1/4, but later work by Amontons and Coulomb showed that this coefficient is in fact not universal and depends on the nature of the sliding objects. Collectively, the classic Amontons-Coulomb laws tell us that the friction force during sliding is independent of the area of contact, independent of the velocity, and proportional to the load. These laws apply in many cases, and have important implications in engineering, as illustrated for instance by the widespread capstan mechanism [180, 181].

5.1.2 Open questions in tribology

Many aspects of friction remain elusive and have resulted in intense study despite the seemingly classical nature of the field of tribology [183]. Consider for example the rather non-intuitive result that $T$ is independent on the area of contact: this was not resolved until more recent works by Tabor and Bowden [184]. Besides, the role of humidity and capillary adhesion is non-trivial [185, 186]. Further technological advances, like the atomic-force microscope, surface-forces apparatus, and quartz-crystal microbalance, in conjunction with theoretical and computational advances [187] have renewed interest in friction and improved our understanding. Studies have revealed that many systems exhibit much more complex behaviors, especially as we venture down to the nanoscale [188]. Take as an example the experiments on multi-walled nanotubes where inner and outer tubes could be slid apart to study true molecular friction [189, 182]. Such works have shown area dependence as well as vanishing friction (Fig. 5.1), clearly breaking the simple friction laws.

While friction in simple model systems is better understood, friction in complex assemblies remain an open field for investigations. Examples are numerous and include
macroscopic systems, such as the wet granular media used to build up ancient pyramids [190]. In this case, some puzzling relation between friction and effective elasticity has been uncovered (Fig. 5.2). Adding some topological constraints and connectivity, through granular chains [191] or rope and textile knots [192, 193, 194], is also a way to trigger interesting emerging behaviours. Besides, there are as well important biological examples such as the DNA ejection mechanism from a viral capsid that resembles a capstan mechanism [195], or the intricate frictional behaviour between soft protein filaments [196]. Finally, numerically simulating wind-driven hair motion – including friction, humidity, bending softness, twists and curls – is a relevant example of complex problems for applied mathematicians in the animation industry.

5.2 Main results

5.2.1 The phonebook enigma

A classic demonstration of friction is to take two phonebooks, interleave their sheets and attempt to separate them by pulling on their spines: impossible. The accumulated friction between the pages is so high that even lifting a car by the interleaved phonebooks cannot pull them apart (Fig. 5.3).

Less spectacular than lifting a car, but more instructive is to try the following experiments. Let us take two notebooks with a thickness $2M\epsilon$ each, were $2M$ is the total number of sheets in a notebook and $\epsilon$ is the thickness of one sheet. After interleaving the sheets, it is immediately obvious that the thickness in the overlap region is $4M\epsilon$, and that the traction force needed to separate the two books is immense. Now, let us remove every other sheet in each notebook and repeat the experiment. Again,
5.2. Main results

![Graph: Dynamic friction coefficient as a function of effective shear elastic modulus for three sand types, mixed with varying amounts of water][190]

Two things are immediately obvious: the thickness in the overlap region is now the same as that at the spines; and the notebooks can be easily separated. In the latter case, the friction is just the sum of the frictions at each interface. Taken one step further, it is straightforward to set up a simple traction device, either by hanging masses or with a scale, which will reveal the following crucial facts: if alternating sheets are removed and the remaining sheets are all parallel to each other as they approach the overlap region, the traction force scales linearly with the number of sheets, \(T \sim M\). In contrast, if the sheets fan out and make an angle with respect to the central plane as they approach the overlap region, then the traction force is greater and increases dramatically with the number of sheets. In fact, in some circumstances a ten-fold increase in the number of sheets results in a traction force that is increased by four orders of magnitude! Such experiments quickly reveal that the secret to this amplification of friction lies in the angle the sheets make as they approach the overlap region.

In the laboratory, a tensile tester was used (Fig. 5.3). Each booklet was prepared with \(2M\) identical sheets of paper, with width \(w\), thickness \(\epsilon\) and various \(M\) values. The total traction force \(T\) was measured upon pulling in a vertical orientation, at constant velocity and with intermittent stops, at different distances \(d\) from the clamp of each book to the overlap region. The nonlinear effect of the number of sheets was immediately clear. Additionally, the variation with \(d\) was also highly nonlinear.

The mechanism can be understood as follows. Each sheet makes an angle as it goes from the clamp to the overlap region. Therefore, a component of the local traction exerted on one sheet by the operator results in a local normal force exerted on the stack of sheets below it in the contact region. The mechanism is then clear and the role of the angle is crucial. With the application of the Amonton-Coulomb laws [178, 179] at the onset of sliding, the result is a self-amplified friction force that resists the traction:

\[ \text{Friction is still an active research topic} \]

Sliding Friction on Wet and Dry Sand

A. Fall,1 B. Weber,1 M. Pakpour, 1,2 ... Publishers Limited. All rights reserved

the harder the operator pulls, the greater the normal load and thus the frictional resistance – like in the capstan mechanism \[ \text{[180, 181]} \]. Summing over all the local tractions yields the total traction \( T \). One can proceed analytically by using a continuum description at large \( M \) and by introducing the dimensionless variable \( \alpha = 2 \mu \epsilon M^2/d \). Not surprisingly, one also needs a boundary condition on the outermost sheets of the stack, \( T^* \), the source of which may be the elasticity of the paper as it bends, gravity, or any tiny adhesion. Upon integration, we obtain the total traction force \( T \) that essentially behaves as \( \sim 2MT^* \exp(\alpha) \). Remarkably, as \( \alpha \to 0 \), which corresponds to large \( d \), or small angles, we recover the intuitive relation \( T = 2\mu \epsilon M^2/d \): without any angle, the friction force is just due to all the independent interfaces with local friction \( T^* \). This limiting case arises naturally and is analogous to the suggested experiment with alternating sheets removed. In contrast, in the general case, the total traction force depends almost exponentially on one single quantity, \( \alpha \), which has thus been named the “Hercules number” by Mason Porter (Improbable Research). By plotting \( T/(2MT^*) \) as a function of the Hercules number, all the data can be collapsed onto a single master curve (Fig. 5.3).

5.2.2 Strain-stiffening in entangled granular chains

Particularly unstable, piles of grains usually collapse very quickly under their own weight to form a cone. If a variety of attractive forces (such as capillary interactions and Van der Waals or electrostatic forces) can partially stabilise them, their effect remains limited. We however studied heaps of grains that are very stable. The trick is to connect some grains together in order to form polymeric-like chains.

We performed two series of force-indentation experiments (Fig. 5.4). In the first one, each pile consisted of dense assemblies of chains with the exact same length. The longer the chains, the more stable the pile. In the second one, the chains were mixed at different concentrations together with individual grains: a situation that
mimics the dilution of polymer chains in a solvent. In both cases, we showed that the bonds between the grains of a given chain produce frictional constraints for the other chains. Under external indentation, this triggers a self-amplifying friction mechanism – reminiscent of the phonebook mechanism above – with several locking points that render the system particularly resistant to deformation.

To rationalize the experimental findings, and in addition to the friction ingredient, we invoked the statistical physics of polymers. As such, our results extend Edwards’ conjecture about the fundamental analogy between thermal liquids and athermal granular assemblies [197], to the case of polymeric liquids and granular chains. The surprising robustness of granular-chain piles does not only allow to simulate the behavior of dense polymer media at the macroscopic scale, but also to reconsider the properties of smart complex assemblies, such as textiles, biological fibres or building materials.

5.3 Publications

- *Emergent strain-stiffening in interlocked granular chains*
  D. Dumont, M. Houze, P. Rambach, T. Salez, S. Patinet, and P. Damman
  Physical Review Letters, **120** 088001 (2018)

- *Why can’t you separate interleaved books?*
  K. Dalnoki-Veress, T. Salez, and F. Restagno
  Physics Today, **69** 74 (2016)

- *Self-amplification of solid friction in interleaved assemblies*
  Physical Review Letters, **116** 015502 (2016)
5.4 Perspectives

While the phonebook study started as a compelling popular enigma to solve, the same effect can be seen in many other systems with the common theme being that a pulling force results in an orthogonal load, which enhances friction. An example is a toy known as the Chinese finger trap, where fingers inserted into a rubber or braided tube cannot be pulled out as the tension tightens the tube. In fact, this finger-trap system is also used in medicine [192]. Likewise, the mooring of a ship around a capstan is possible because the windings of a rope tighten around the capstan, thereby increasing friction [180, 181]. The uncovered mechanism also bears resemblance to catch bonds – molecular links which strengthen as a result of a tensile stress and facilitate cell adhesion. Therefore, in addition to elucidating the longstanding and fun phonebook enigma, and to exploring it further with e.g. soft and lubricated sheets, one could address the mechanical behavior of more complex and fundamental interleaved systems, involving textiles, brushes, muscular fibres, or nanoscale mechanical devices such as graphene sheets or thin polymer films. A smart nanomechanical transistor could perhaps be designed with such knowledge. Besides, electrostatic forces could be added and explored by the use of conductive sheets.

While granular-chain assemblies have been studied in statics, their dynamics is intriguing. First, one should recover the state of the art with driven simple granular assemblies. Then, one could vibrate single granular chains in order to investigate further the polymeric analogy for the individual dynamics. Entropic forces, confinement effects, DNA-like translocation, and suction mechanisms might be studied this way. Finally, assembling several granular chains together might allow to simulate the levelling of thin polymer films (Chapter 1), under the action of gravity instead of capillarity, and to probe some effective glass transition and surface localisation of the dynamics (Chapter 2). This type of studies would be in the direct spirit of the jamming of simple granular media in order to simulate the glass transition, but with new and fundamental polymeric effects now being at the core.

Preprints

- **Nonlinear amplification of adhesion forces in interleaved books**
  ArXiv:2004.01520

- **A microscopic picture of erosion and sedimentation processes in dense granular flows**
  P. Soulard, D. Dumont, T. Salez, E. Raphaël, and P. Damman
  ArXiv:1912.10873
Conclusion

Summary of the manuscript

I presented a collection of different problems and phenomena related to interfacial and confined soft matter, that were studied during the nine years following my PhD. These works were organised into five distinct axes, and thus chapters. In a first axis on thin liquid polymer films, I described our robust capillary-levelling technique that allowed us to perform precise nanorheological measurements and, in particular, to address slip effects in polymer nanofilms. Then, in a second axis, the same method applied to thin glassy films was employed to address the glass transition in confinement, and motivated the development of a microscopic cooperative-string theory for glassy dynamics at interfaces. The two next axes dealt with soft boundaries, first through wetting on those and secondly for lubrication flows nearby. In the case of wetting, a novel adhesion-to-wetting crossover was theoretically introduced as surface capillary effects start to dominate over bulk elastic ones. Besides, the Shuttleworth controversy was addressed, with in particular a first demonstration of the existence of strain-dependent surface energies for polymer glasses, but apparently not for elastomers. As far as the soft-lubrication axis is concerned, an emergent elastohydrodynamic lift force (among other inertial-like features at low Reynolds numbers) was revealed and measured at both the macroscopic and microscopic scales. Finally, a fifth research axis about friction in complex assemblies was introduced, with two main results being the solving of the popular phonebook enigma, and a novel realization of Edwards’ conjecture through the demonstration that statistical polymer physics holds for athermal granular-chain assemblies. Together with a frictional ingredient, this last fact allowed us to explain the striking strain-stiffening property of dense granular-chain media. In addition to the few highlighted results, possible novel avenues for future research were drawn for each axis, some of them being currently under preliminary exploration.

Towards a mesoscopic physics of amorphous matter

In soft matter physics, there is still a largely unexplored area between microscopic physics, governed by quantum effects and orbital interactions on the one hand, and that, more macroscopic, of so-called continuous media, described by the theories of hydrodynamics and elasticity on the other hand. Given the progress in nanofabrication (lithography, self-assembly, etc.) and nano-observation (AFM, SFA, nonlinear spectroscopy, etc.), it is now possible to experimentally access these intermediate sizes, where thermal fluctuations and molecular interactions largely dominate. At these length scales, a rich phenomenology of new effects appears. Let us cite as examples: the flow in nanotubes and their abnormal, gigantic hydraulic conductance [198], the
strong sliding of polymers on substrates assembled in molecular monolayers [199], the
atomic friction between carbon sheets [189, 182], the nanowetting of graphene [200], the
capillary meniscus around a carbon nanotube [201], or chemical reactions in nanocon-
finement [202]. Such examples have been multiplying recently, and might even reach
the quantum frontier ultimately, with important practical implications ranging from
energy conversion to biolubrication. In summary, the soft matter of the XXIst century
might pursue a trend similar to that previously followed by hard condensed matter, via
the so-called mesoscopic physics, through the emergence of a new mesoscopic physics
of amorphous matter.
Appendix A

Miscellaneous works

A.1 Other articles

A.1.1 Soft contact patterns

- Shearing-induced contact pattern formation in hydrogels sliding in polymer solution
  S. Yashima, S. Hirayama, T. Kurokawa, T. Salez, H. Takefuji, W. Hong, and J. P. Gong

- Adhesion-induced fingering instabilities in thin elastic films under strain
  B. Davis-Purcell, P. Soulard, T. Salez, E. Raphaël, and K. Dalnoki-Veress

A.1.2 Polymer microshells

- Probing the adsorption/desorption of amphiphilic polymers at the air-water interface during large interfacial deformations
  C. Trégouët, T. Salez, N. Pantoustier, P. Perrin, M. Reyssat, and C. Monteux

- Adsorption dynamics of hydrophobically modified polymers at an air-water interface
  C. Trégouët, A. Mikhailovskaya, T. Salez, N. Pantoustier, P. Perrin, M. Reyssat, and C. Monteux

- One-step fabrication of pH-responsive membranes and microcapsules through interfacial H-bond polymer complexation
  J. Dupré de Baubigny, C. Trégouët, T. Salez, N. Pantoustier, P. Perrin, M. Reyssat, and C. Monteux
  Scientific Reports, 7 1265 (2017)
A.1.3 Porous reactors

- *Two-phase flow in a chemically active porous medium*
  A. Darmon, M. Benzaquen, T. Salez, and O. Dauchot
  The Journal of Chemical Physics, 141 244704 (2014)

A.1.4 Cold atoms and molecules

- *Photoassociative creation of ultracold heteronuclear $^6$Li $^{40}$K* molecules*
  Europhysics Letters, 96 33001 (2011)

- *Large atom number dual-species magneto-optical trap for fermionic $^6$Li and $^{40}$K atoms*
  European Physical Journal D, 65 223 (2011)

A.2 Patent

- *Method and system for making microcoils and product thereof*
  P. D. Fowler, R. D. Schulman, T. Salez, E. Raphaël, and K. Dalnoki-Veress
  U.S. Patent No. 0102674 (2020)

A.3 Books

- *A quantum simulator*
  T. Salez

- *Petits problèmes de physique, du quotidien au laboratoire*
  F. Graner, R. Kaiser, A. Marchand et T. Salez
  Dunod, Paris (2011)

A.4 PhD thesis

- *Towards quantum degenerate atomic Fermi mixtures*
  T. Salez
  Ecole Normale Supérieure, Paris (2011)
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