A study of heat and mass transfer in enclosures by phase-shifting interferometry and bifurcation analysis

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A STUDY OF HEAT AND MASS TRANSFER IN ENCLOSURES BY PHASE-SHIFTING INTERFEROMETRY AND BIFURCATION ANALYSIS

Oral defence publicly presented on January 16th 2014

by

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Fundamental questions concerning the mass diffusion properties of biological systems under isothermal and non-isothermal conditions still remain due to the lack of experimental techniques capable of visualizing and measuring mass diffusion phenomena with a high accuracy. As a consequence, there is a need to develop new experimental techniques that can deepen our understanding of mass diffusion. Moreover, steady natural convection in a tilted three-dimensional rectangular enclosure has not yet been studied. This tilt can be a slight defect of the experimental device or can be imposed on purpose. In this dissertation, heat and mass transfer phenomena in parallelepipeds are studied focusing on convectionless thermodiffusion and on natural convection of pure fluids (without thermodiffusion). Mass diffusion is studied with a novel optical technique, while steady natural convection is first studied in detail with an improved numerical analysis and then with the same optical technique initially developed for diffusion measurements.

A construction of a precise optical interferometer to visualize and measure mass diffusion is described. The interferometer comprises a polarizing Mach–Zehnder interferometer, a rotating polariser, a CCD camera, and an original image-processing algorithm. A method to determine the isothermal diffusion coefficient as a function of concentration is proposed. This method uses an inverse analysis coupled with a numerical calculation in order to determine the diffusion coefficients from the transient concentration profiles measured with the optical system. Furthermore, thermodiffusion of protein molecules is visualized for the first time. The proposed method has three main advantages in comparison to similar methods: (i) reduced volume sample, (ii) short measurement time, and (iii) increased hydrodynamic stability of the system. These methods are validated by determining the thermophysical properties of benchmark solutions.

The optical technique is first applied to study isothermal diffusion of protein solutions in: (a) dilute binary solutions, (b) binary solutions with a wide concentration range, and (c) dilute ternary solutions. The results show that (a) the isothermal diffusion coefficient in dilute systems decreases with molecular mass, as roughly predicted by the Stokes-Einstein equation; (b) BSA protein has a hard-sphere-like diffusion behaviour and lysozyme protein a soft sphere characteristic; and (c) the cross-term effect between the diffusion species in a dilute ternary system is negligible. The optical technique is then applied to (d) non-isothermal dilute binary solutions, revealing that that the aprotinin (6.5 kDa) and lysozyme (14.3 kDa) molecules are thermophilic and thermophobic, respectively, when using water as solvent at room temperature. Finally, the optical technique is applied to study Rayleigh-Bénard convection in a horizontal cubical cavity. Since natural convection can be studied in more depth by solving the Navier-Stokes equations, a bifurcation analysis is proposed to conduct a thorough study of natural convection in three-dimensional parallelepipeds cavities. Here, a continuation method is developed from a three-dimensional spectral finite element code.

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The proposed numerical method is particularly well suited for the studies involving complex bifurcation diagrams of three-dimensional convection in rectangular parallelepipeds cavities. This continuation method allows the calculation of solution branches, the stability analysis of the solutions along these branches, the detection and precise direct calculation of the bifurcation points, and the jump to newly detected stable or unstable branches, all this being managed by a simple continuation algorithm. This can be used to calculate the bifurcation diagrams describing the convection in tilted cavities. The code for calculating the solution branches and bifurcation points is then validated by reproducing a complex bifurcation diagram reported in the literature for Rayleigh-Bénard convection inside a horizontal cubical cavity.

The stability of the solutions is first studied for a tilted truncated square duct with its length two times longer than the side of its square cross-section. The finite-length duct is tilted around its longest axis. A precise bifurcation diagram is obtained for the horizontal case featuring all the different branches. The calculations
for the square duct are then extended from the Rayleigh-Bénard situation (horizontal case) to the case where a tilt is imposed. In the tilted square duct, three types of stable solutions are found: the leading longitudinal roll $L^-$ solutions, the longitudinal roll $L^+$ solutions, and the oblique roll $O^\pm$ solutions. The domains of existence of these different stable solutions are determined as a function of the Rayleigh number, $Ra$, and inclination angle, $\theta$. Interesting comparisons with previous studies dealing with convection in inclined ducts are obtained. Furthermore, a thorough bifurcation analysis in a tilted cubical cavity is conducted. The steady solutions are studied from their initiation at low $Ra$ to their transition to periodic states for the Prandtl number range $0.71 \leq Pr \leq 130$ (silicone oil). For this cubical cavity, the pitchfork bifurcation obtained for $\theta = 0^\circ$ at the first primary bifurcation (where four stable and four unstable solutions simultaneously emerge) is broken, resulting in a leading branch, three disconnected branches emerging at saddle-node bifurcations, and a secondary branch. It is shown that there is a shift in the $Ra$ domain for all these secondary bifurcations when the cubical cavity is slightly tilted. A thorough stability diagram in the $Ra-\theta$ domain is presented. This bifurcation analysis study is the first of its kind to fully address the influence of a tilt on the stability of three-dimensional convective flows inside rectangular enclosures, and is a motivation to conduct further experiments with the optical tools described in this dissertation.

**Keywords:** Mass transfer, natural convection, bifurcation analysis, Fickian diffusion, thermodiffusion, Soret effect, thermophoresis, phase-shifting interferometry.

**Résumé**

Des questions fondamentales concernant les propriétés de diffusion des systèmes biologiques dans des conditions isothermes et non-isothermes restent en suspens en raison de l’absence de techniques expérimentales capables de visualiser et de mesurer les phénomènes de diffusion avec une très bonne précision. Il existe en conséquence un besoin de développer de nouvelles techniques expérimentales permettant d’approfondir notre compréhension des phénomènes de diffusion. La convection naturelle en cavité tridimensionnelle inclinée est elle-aussi très peu étudiée. Cette inclinaison de la cavité peut correspondre à un léger défaut expérimental ou être imposée volontairement. Dans cette thèse, nous étudions les phénomènes de transport de chaleur et de masse en cavité parallélipipédique, nous intéressant particulièrement à la thermodiffusion en situation sans convection et à la convection naturelle en fluide pur (sans thermodiffusion). La diffusion de masse est étudiée à l’aide d’une nouvelle technique optique, tandis que la convection naturelle est tout d’abord étudiée en détails avec une méthode numérique sophistiquée, puis visualisée expérimentalement à l’aide du même système optique que pour les mesures de diffusion.

Nous présentons l’interféromètre optique de haute précision développé pour les mesures de diffusion. Cet interféromètre comprend un interféromètre polarisé de Mach–Zehnder, un polariseur tournant, une caméra CCD et un algorithme de traitement d’images original. Nous proposons aussi une méthode pour déterminer le coefficient de diffusion isotherme en fonction de la concentration. Cette méthode, basée sur une analyse inverse couplée à un calcul numérique, permet de déterminer les coefficients de diffusion à partir des profils de concentration transitoires obtenus par le système optique. Mentionnons de plus que c’est la première fois que la thermodiffusion est visualisée dans des solutions aqueuses de protéines. La méthode optique proposée présente trois avantages principaux par rapport aux autres méthodes similaires : (i) un volume d’échantillon réduit, (ii) un temps de mesure court, (iii) une stabilité hydrodynamique améliorée. Toutes ces méthodes ont été validées par des mesures sur des systèmes de référence.
La technique optique est d’abord utilisée pour étudier la diffusion isotherme dans des solutions de protéines : (a) dans des solutions binaires diluées, (b) dans des solutions binaires sur un large domaine de concentration, (c) dans des solutions ternaires diluées. Les résultats montrent que (a) le coefficient de diffusion isotherme dans les systèmes dilués décroît avec la masse moléculaire, comme prévu grossièrement par l’équation de Stokes-Einstein ; (b) la protéine BSA a un comportement diffusif de type sphère dure et la protéine lysozyme de type sphère molle ; (c) l’effet de diffusion croisée est négligeable dans les systèmes ternaires dilués. La technique optique est aussi utilisée (d) dans des solutions binaires diluées non-isothermes, révélant que les molécules d’aprotinin (6.5 kDa) et de lysozyme (14.3 kDa) sont, respectivement, thermophiles et thermo-phobiques, quand elles sont en solutions aqueuses à température ambiante. Enfin, la technique optique est utilisée pour l’étude de la convection de Rayleigh-Bénard en cavité cubique horizontale. Puisque la convection peut aussi être étudiée de façon réaliste en utilisant les équations de Navier-Stokes, une analyse numérique de bifurcation est proposée, permettant une étude approfondie de la convection naturelle dans des cavités tridimensionnelles parallélépipédiques. Pour cela, une méthode de continuation a été développée à partir d’un code aux éléments finis spectraux.

La méthode numérique proposée est particulièrement bien adaptée aux études de convection correspondant à des diagrammes de bifurcation complexes. Cette méthode de continuation permet le calcul des branches de solutions, l’analyse de stabilité de ces solutions, la détection et le calcul précis des points de bifurcation, ainsi que le saut vers de nouvelles branches stables ou instables, tout cela étant géré par un simple algorithme de continuation. Cette méthode peut être utilisée pour calculer les diagrammes de bifurcation correspondant à la convection en cavité inclinée. Ce code de continuation a été validé par un calcul où nous avons reproduit le diagramme de bifurcation complexe présenté dans la littérature en rapport avec la convection de Rayleigh-Bénard dans une cavité cubique horizontale.

La convection est tout d’abord étudiée dans un conduit tronqué incliné de section carrée ayant sa longueur égale à deux fois le coté de sa section carrée. Ce conduit est incliné autour de son axe le plus long. Un diagramme de bifurcation précis détaillant toutes les différentes branches est obtenu dans le cas horizontal. Les calculs sont alors étendus au cas où la cavité est inclinée. Dans ce cas incliné, trois types de solutions stables sont obtenus : la solution principale $L^-$ correspondant à des rouleaux longitudinaux dans le sens de l’inclinaison, la solution $L^+$ correspondant à des rouleaux longitudinaux dans le sens opposé, et la solution $O^\pm$ correspondant à des rouleaux obliques. Les domaines d’existence de ces solutions sont déterminés en fonction du nombre de Rayleigh $Ra$ et de l’angle d’inclinaison $\theta$. De bonnes comparaisons avec des études antérieures portant sur la convection en conduite inclinée sont obtenues. Une deuxième étude portant sur le cas d’une cavité cubique inclinée est ensuite présentée. Dans cette étude approfondie, les solutions stationnaires stables sont déterminées à partir de leur initiation à bas $Ra$ jusqu’à leur transition vers un état périodique sur un large domaine de nombre de Prandtl $0.71 \leq Pr \leq 130$ (huile de silicone). Pour cette cavité cubique, la bifurcation fourche, obtenue pour $\theta = 0^\circ$ au premier point de bifurcation primaire et où quatre branches stables et quatre branches instables émergent simultanément, est brisée, donnant une branche principale, trois branches déconnectées émergent à des points nœud-col et une branche secondaire. Nous montrons que toutes ces bifurcations secondaires se déplacent dans le domaine de $Ra$ quand la cavité est inclinée. Un diagramme de stabilité complet est obtenu dans le domaine $Ra-\theta$. Cette étude de bifurcation est la première à analyser de façon approfondie l’influence d’une inclinaison de la cavité sur la stabilité des écoulements convectifs tridimensionnels en cavité parallélépipédique. Les résultats obtenus constituent une motivation pour poursuivre l’étude expérimentale sur ce sujet en utilisant les outils optiques présentés précédemment.

**Mots Clés:** Transfert de masse, convection naturelle, analyse des bifurcations, diffusion massique, thermomodiffusion, effet Soret, thermophorèse, interféromètre à décalage de phase.
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# NOMENCLATURE

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<td>$A$</td>
<td>Amplitude of light</td>
<td>$[V \cdot m^{-1}]$</td>
</tr>
<tr>
<td>$A_o$</td>
<td>Amplitude of the test beam</td>
<td>$[V \cdot m^{-1}]$</td>
</tr>
<tr>
<td>$A_r$</td>
<td>Amplitude of reference beam</td>
<td>$[V \cdot m^{-1}]$</td>
</tr>
<tr>
<td>$A_y$</td>
<td>Aspect ratio in the $y$ direction</td>
<td>[-]</td>
</tr>
<tr>
<td>$A_z$</td>
<td>Aspect ratio in the $z$ direction</td>
<td>[-]</td>
</tr>
<tr>
<td>$C$</td>
<td>Concentration</td>
<td>[wt%] or [mg⋅ml$^{-1}$]</td>
</tr>
<tr>
<td>$C_0$</td>
<td>Local concentration</td>
<td>[wt%]</td>
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<td>$D$</td>
<td>Mass diffusion coefficient</td>
<td>$[m^2 \cdot s^{-1}]$</td>
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<tr>
<td>$D_{opt}$</td>
<td>Minimized numerical diffusion coefficient</td>
<td>$[m^2 \cdot s^{-1}]$</td>
</tr>
<tr>
<td>$D_T$</td>
<td>Thermodiffusion coefficient</td>
<td>$[m^2 \cdot K^{-1} \cdot s^{-1}]$</td>
</tr>
<tr>
<td>$f$</td>
<td>Friction coefficient</td>
<td>[-]</td>
</tr>
<tr>
<td>$g$</td>
<td>Acceleration of gravity</td>
<td>$[m^2 \cdot s^{-1}]$</td>
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<tr>
<td>$h$</td>
<td>Height of the parallelepiped cavity</td>
<td>[m]</td>
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<tr>
<td>$h$</td>
<td>Eigenvector</td>
<td>[-]</td>
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<tr>
<td>$I$</td>
<td>Intensity of light</td>
<td>$[W \cdot m^{-2}]$ or [bits]</td>
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NOMENCLATURE

$I_{\text{max}}$ Maximum electric current, [A]

$j$ Mass flux, [mg · m$^{-2}$ · s$^{-1}$]

$J$ Mass flux rate, [mg · s$^{-1}$]

$k_B$ Boltzmann constant, $1.38065 \times 10^{-23}$ [m$^2$ · kg · s$^{-2}$ · K$^{-1}$]

$K_d$ Derivative gain, [s]

$K_i$ Integral gain, [s$^{-1}$]

$K_p$ Proportional gain, [-]

$k_T$ Thermal conductivity, [W · m$^{-1}$ · K$^{-1}$]

$l$ Width of the cavity, [m]

$L$ Optical path or length of the duct, [m] or [mm] or [-]

$M$ Molecular mass, [Da]

$n$ Refractive index, [-]

$P$ Period of polarized light, [s]

$p$ Pressure, [-]

$P_{\text{max}}$ Maximum electric power, [W]

$q$ Heat flux, [W · m$^{-2}$]

$q$ Normalisation parameter, [-]

$Q$ Dimensionless flow rate, [-]

$r_0$ Molecular radius, [m]

$S_T$ Soret coefficient, [K$^{-1}$]

$T$ Temperature, [°C]

$t$ time, [s]

$T_{\text{room}}$ Room temperature, [°C]
Velocity field in the cavity \( u = (u,v,w), [-] \)

Component of the velocity vector in the \( x, y, z \) directions, [-]

Spatially discritised fields \( X = (u,v,w,T), [-] \)

**GREEK**

\( \alpha \)  
Inclination angle, [deg.]

\( \beta \)  
Volumetric expansion coefficient, [K\(^{-1}\)]

\( \gamma \)  
Dummy variable, [-]

\( \Gamma \)  
Dufour coefficient, [W \cdot m\(^2\) \cdot kg\(^{-1}\)]

\( \delta \)  
Objective function, [mm \cdot mg \cdot ml\(^{-1}\)] or [mm]

\( \delta C \)  
Concentration difference in ternary experiments, [mg \cdot ml\(^{-1}\)]

\( \Delta C \)  
Concentration difference, [wt\%] or [mg \cdot ml\(^{-1}\)]

\( \Delta t \)  
Time difference between interferograms, [s]

\( \Delta T \)  
Temperature difference, [K]

\( \varepsilon \)  
Convergence criterion, [m\(^2\) \cdot s\(^{-1}\)]

\( \zeta \)  
Dimensionless symbol, [-]

\( \eta \)  
Contrast factor, [wt\%\(^{-1}\) \cdot mm\(^{-1}\)]

\( \theta_c \)  
Critical angle, [deg.]

\( \theta_r \)  
Transmission angle of rotating polarizer, [rad] or [deg.]

\( \theta_{\pm ycri} \)  
Critical angle for the \( \pm y \)-rolls, [deg.]

\( \theta_z \)  
Critical angle for the \( z \)-rolls, [deg.]

\( \Theta \)  
Inclination vector corresponding to \( \theta \), [deg.]
NOMENCLATURE

\( \kappa \)  
Thermal diffusivity, \([\text{m}^2 \cdot \text{s}^{-1}]\)

\( \lambda \)  
Eigenvalue, [-]

\( \lambda_{\text{beam}} \)  
Wavelength, [nm]

\( \mu \)  
Dynamic viscosity, \([\text{Pa} \cdot \text{s}]\)

\( \nu \)  
Kinematic viscosity, \([\text{m}^2 \cdot \text{s}^{-1}]\)

\( \nu_i \)  
Concentration ratio of the \(i\)-th component, [-] or [%]

\( \rho \)  
Density, \([\text{kg} \cdot \text{m}^{-3}]\)

\( \xi \)  
Fitting parameter, \([\text{Da}^{-1/3} \cdot \text{m}^{-2} \cdot \text{s}]\)

\( \tau \)  
Characteristic diffusion time, [s]

\( \tau_G \)  
Weight factor for the golden section method, [-]

\( \phi \)  
Phase shift, [rad]

\( \chi \)  
Solution volume, [ml]

\( \psi \)  
Unwrapped phase shift, [rad]

\( \omega \)  
Angular frequency, \([\text{rad} \cdot \text{s}^{-1}]\)

\( \varnothing \)  
Inclination angle of the camera for PIV measurements, [deg.]

\( \Omega \)  
Inclination vector corresponding to \(\alpha\), [deg.]

DIMENSIONLESS NUMBERS

\( Le \)  
Lewis number

\( Nu \)  
Nusselt number

\( Pr \)  
Prandtl number

\( Ra \)  
Rayleigh number

xxviii
$Ra_c$  Critical Rayleigh number

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<td>Average</td>
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<tr>
<td>B</td>
<td>Component B</td>
</tr>
<tr>
<td>$C$</td>
<td>Cold temperature</td>
</tr>
<tr>
<td>$dummy$</td>
<td>Dummy argument</td>
</tr>
<tr>
<td>exp</td>
<td>Experimental</td>
</tr>
<tr>
<td>$H$</td>
<td>Hot temperature</td>
</tr>
<tr>
<td>$high$</td>
<td>High concentration</td>
</tr>
<tr>
<td>ini</td>
<td>Initial value</td>
</tr>
<tr>
<td>L</td>
<td>Lysozyme</td>
</tr>
<tr>
<td>$low$</td>
<td>Low concentration</td>
</tr>
<tr>
<td>$lower$</td>
<td>Lower boundary</td>
</tr>
<tr>
<td>$m$</td>
<td>Mean value</td>
</tr>
<tr>
<td>N</td>
<td>NaCl</td>
</tr>
<tr>
<td>T</td>
<td>Ternary system</td>
</tr>
<tr>
<td>upper</td>
<td>Upper boundary</td>
</tr>
</tbody>
</table>
**MATHEMATICAL CONVENTION**

\( \mathcal{L} \)  
Spatially discretised linear operator

\( n \)  
Iterative number for the Newton method

\( \mathcal{N} \)  
Spatially discretised nonlinear operator

\( \mathcal{N}_X \)  
Jacobian of \( \mathcal{N} \) with respect to \( X \)

\( \mathcal{N}_{Ra} \)  
Jacobian of \( \mathcal{N} \) with respect to \( Ra \)

\( \mathcal{N}_{X,X} \)  
Double Jacobian of \( \mathcal{N} \) with respect to \( X \)

\( \mathcal{N}_{X,Ra} \)  
Jacobian of \( \mathcal{N} \) with respect to both \( X \) and \( Ra \)

\( x, y, z \)  
Cartesian coordinates

\( e_x, e_y, e_z \)  
Unit vectors in the \( x, y, z \) directions

**ABBREVIATIONS**

\( B \)  
Branch

\( C12 \)  
Dodecane

\( S \)  
Secondary bifurcation

\( P \)  
Primary bifurcation

\( C \)  
Saddle-node bifurcation point in a cubical cavity

\( N \)  
Saddle-node point in a truncated duct

\( H \)  
Hopf bifurcation

\( R4 \)  
Four-roll solution

\( S_p \)  
Plane symmetry

xxx
\( S_A \) \( \pi \)-rotational symmetry

\( L^+ \) Longitudinal roll favoured by the inclination

\( L^- \) Longitudinal roll unfavoured by the inclination

**ACRONYMS**

BCGS Bi-conjugate gradient square

BSA Bovine serum albumin

CCD Charge-coupled device

CGM Conjugate gradient method

DPIT/V Digital particle image thermometry/velocimetry

GA Generic algorithm

GMRS Generalized minimal residual method

GSM Golden section method

GUI Grafical user interface

HPLC High-performance liquid chromatography

IBB Isobutylbenzene

IPU Image processing unit

MD Molecular dynamics

ND Neutral density

NFS No-flow solution

NSPCG Non-symmetric preconditioned conjugate gradient

OBD Optical beam deflection
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ODI</td>
<td>Optical digital interferometry</td>
</tr>
<tr>
<td>OP</td>
<td>Optical path</td>
</tr>
<tr>
<td>OPSI</td>
<td>Orthogonal phase-shifting interferometry</td>
</tr>
<tr>
<td>PBS</td>
<td>Polarizing beam splitter</td>
</tr>
<tr>
<td>PID</td>
<td>Proportional-integral-derivative</td>
</tr>
<tr>
<td>PIV</td>
<td>Particle image velocimetry</td>
</tr>
<tr>
<td>PSI</td>
<td>Phase-shifting interferometry</td>
</tr>
<tr>
<td>SDM</td>
<td>Steepest descent method</td>
</tr>
<tr>
<td>SID</td>
<td>Solution injection device</td>
</tr>
<tr>
<td>TDFRS</td>
<td>Thermal diffusion forced Rayleigh scattering</td>
</tr>
<tr>
<td>THN</td>
<td>1,2,3,4 tetrahydronaphthalene</td>
</tr>
</tbody>
</table>
I

**General introduction and background**
Natural convection is one of the most prominent forms of heat and mass transfer in the universe. It is present in the Earth’s atmosphere [139], its oceans [69], and its mantle [16] and, hence, it is a determining factor for life in our planet. Natural convection also plays a vital role in stellar physics [63], where the energy is transported primarily by convection within a given star radius. Moreover, the industrial importance of natural convection ranges from optimizing biomolecular separation processes [32, 213] to enhancement of the heat cooling rate in electronic devices.

Natural convection is a mechanism in which the fluid motion is not generated by an imposed pressure or shear stress at the boundaries, e.g. due to a pump or fan, but rather by an external force field and density gradients within the fluid, which are usually due to other temperature and/or concentration gradients. Convection is the concerted, collective movement of groups or aggregates of molecules within fluids (e.g. liquids, gases), either through advection or through diffusion or as a combination of both of them. Therefore, convective heat and mass transfer takes place both by diffusion and by advection, in which matter and/or heat is transported by the larger-scale motion of currents in the fluid. In other words, the term ”convection” is used to refer to the sum of advective and diffusive heat and mass transfer. This means that the complete description of heat and mass transfer in a fluid, when the radiation effects can be neglected [104], requires separating the contributions of advection and diffusion. These contributions are additive and can be written as

\[
\left( \begin{array}{c}
\text{transport} \\
\text{total}
\end{array} \right) = \left( \begin{array}{c}
\text{transport by}
\text{diffusion}
\end{array} \right) + \left( \begin{array}{c}
\text{transport by}
\text{advection}
\end{array} \right).
\]

Therefore, when there is no advection the heat and mass transport within the fluid is only due to diffusion. In this case, the heat is transferred due to the lattice vibrations (phonons) and mass is transferred due to the Brownian motion of individual particles. In contrast,
when the fluid is pure, i.e. composed of only one species, there are no concentration gradients and, hence, the mass transport (not heat) is only due to advection.

Moreover, the external force that induces natural convection is usually the buoyancy force, i.e. the force caused by density gradients under a gravitational field. However, other forces such as the electromagnetic force or an inertial force (e.g. Coriolis force) may also induce natural convection [17, 61].

1 BRIEF BACKGROUND

The study of heat and mass transfer in parallelepiped enclosures is the first step to understand natural convection at larger scales. In §1.1, a brief background on isothermal diffusion and thermodiffusion is presented. In §1.2, a brief background on natural convection in homogeneous fluids (without mass diffusion) is presented.

1.1 HEAT AND MASS DIFFUSION IN CONVECTIONLESS SYSTEMS

In a real physical situation, it is common that the fluid undergoing natural convection is composed of different species, e.g. convection in oil reservoirs and in biological systems. A mixture composed of different species, i.e. multicomponent system, and subject to a temperature gradient also undergoes other physical processes, such as Fickian diffusion and thermodiffusion. The simplest fluid mixtures are binary fluids, i.e. those composed of two species. Understanding mass diffusion in binary mixtures is essential to clarify mass diffusion processes in more realistic multicomponent systems. Therefore, developing tools to understand the diffusive properties of binary mixtures is essential. This is one of the main topics of this dissertation. In this section, the fundamentals of mass diffusion are presented.

In a convectionless binary system, the heat and mass transfer is described by
where $j$ and $q$ are the local mass and heat fluxes, respectively, $\rho$ is the density, $D$ is the mass diffusion coefficient, $C_0$ is the local concentration (in weight percent, wt%), $D_T$ is the thermodiffusion coefficient, $\Gamma$ is the Dufour coefficient, and $k_T$ is the thermal conductivity of the material. The gradients $\nabla C$ and $\nabla T$ are the local concentration and temperature gradients, respectively.

The first term on the right-hand side (r.h.s.) of Eq. (1.1a) expresses the Fickian diffusion, which is postulated by Fick’s first law of diffusion [60]. It relates the diffusive flux to the concentration under the assumption of steady state, postulating that there is a mass flux from regions of high concentration to regions of low concentration, and the magnitude of this mass flux is proportional to the concentration gradient (spatial derivative). The mass diffusion coefficient $D$ is the constant of proportionality whose measurement is an important subject of this dissertation. The second term on the r.h.s. of Eq. (1.1a) expresses the thermodiffusion, or Soret effect, whose measurement and visualization is another main subject of this dissertation. Thermodiffusion is also commonly called thermophoresis in biochemistry (for biomolecules and aerosols). It is a phenomenon observed in mixtures of mobile particles where the different particle types exhibit different responses to the force of a temperature gradient. Here, the mass flux is directly proportional to the temperature gradient with the constant of proportionality equal to $\rho C_0 (1-C_0) D_T$. Thus, the second term on the r.h.s. of Eq. (1.1a) describes mass separation due to a temperature gradient, whereas the first term describes homogenization by Fickian diffusion. These concepts are depicted in Fig. 1.1. Notice that since we have concentration gradients during the diffusive processes described in Figs. 1.1(a) and (b), then there is a contribution of Fickian diffusion in both cases. However, in the case of isothermal diffusion ($\nabla T = 0$ K), there is
I General introduction and background

Figure 1.1: Mixing and separation in mass diffusion processes. (a) Isothermal diffusion process ($\nabla T = 0$), it is equivalent to Fickian diffusion ($-\rho D \nabla C$). (b) Thermodiffusion process ($\nabla T \neq 0$), it consists of the contribution from Fickian diffusion and from the Soret effect.

only the contribution of Fickian diffusion ($-\rho D \nabla C$) and, therefore, isothermal diffusion is equivalent to Fickian diffusion (but not the contrary).

The first term on the r.h.s. of Eq. (1.1b) is the Dufour effect. It is the heat flux induced by a concentration gradient. Its contribution in liquid mixtures is very small compared to the Fourier contribution [82], i.e. the second term on the r.h.s. of Eq. (1.1b). Finally, Fourier’s law postulates that the rate of flow of heat energy through a control volume is proportional to the negative temperature gradient across the volume [62]. In this dissertation, the main focus is mass transport in liquid system and, therefore, the Dufour effect can be neglected [82].

The rate of diffusive heat transfer in relation to the mass transport due to Fickian diffusion is described by the Lewis number, which is a dimensionless number defined as the ratio of thermal diffusivity to mass diffusivity and written as

$$Le = \frac{\kappa}{D}. \quad (1.2)$$

In liquids, the thermal diffusivity $\kappa$ is usually two orders of magnitude larger than the
mass diffusivity $D$, i.e. $Le \sim 100$. Hence, the tendency to reach a homogeneous state is stronger for temperature than for concentration. Therefore for large $Le$, the concentration dependence of the thermophysical properties, e.g. $D$ and $D_T$, becomes more relevant than their temperature dependence.

In the following, a brief description of isothermal diffusion and thermodiffusion is presented.

**Isothermal diffusion**

In a binary system, a solvent usually serves as the medium where the solute molecules diffuse. In a micro-scale, the diffusion process occurs due to the Brownian motion of the molecules. The first quantitative measurements of diffusion in binary liquid systems were conducted in 1850 by Graham \[70,71\] with his pioneering infinite slab experiment shown in Fig. 1.2. In these experiments he worked with dilute solutions. He connected two bottles that contained solutions at different concentrations; he waited for several days and then separated the bottles and analysed their content. The results of Graham \[70,71\] were simple and definitive. He showed that diffusion in liquids was at least several thousand times slower than diffusion in gases. He recognized that the diffusion process got still slower as the experiment progressed, that *diffusion must necessarily follow a diminishing*

![Figure 1.2: Diffusion experiment in liquid mixtures conducted by Graham [70] in 1850. This experimental technique is the pioneering method to determine the diffusion rates in a binary mixture. The concentration within the containers is given with respect to the denser component.](image-url)
Table 1.1: Isothermal diffusion coefficients for different species at infinite dilution in water at $T = 25\degree C$ [55]. Most diffusion coefficients $D$ are in the order of $10^{-9} \text{ m}^2/\text{s}$. Notice that for macromolecules, such as ovalbumin (44.3 kDa) and haemoglobin (66 kDa), the isothermal diffusion coefficient is much smaller than for other molecules.

<table>
<thead>
<tr>
<th>Solute</th>
<th>$D [\text{m}^2/\text{s} \times 10^{-9}]$</th>
<th>Solute</th>
<th>$D [\text{m}^2/\text{s} \times 10^{-9}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>1.21</td>
<td>Glycine</td>
<td>1.06</td>
</tr>
<tr>
<td>Acetone</td>
<td>1.16</td>
<td>Helium</td>
<td>6.28</td>
</tr>
<tr>
<td>Ammonia</td>
<td>1.64</td>
<td>Haemoglobin</td>
<td>0.069</td>
</tr>
<tr>
<td>Agon</td>
<td>2.00</td>
<td>Hydrogen</td>
<td>4.50</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.02</td>
<td>Hydrogen sulfide</td>
<td>1.41</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>1.00</td>
<td>Methane</td>
<td>1.49</td>
</tr>
<tr>
<td>Bromine</td>
<td>1.18</td>
<td>Methanol</td>
<td>0.84</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>1.92</td>
<td>n-Butanol</td>
<td>0.77</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>2.03</td>
<td>Nitrogen</td>
<td>1.88</td>
</tr>
<tr>
<td>Chlorine</td>
<td>1.25</td>
<td>Oxygen</td>
<td>2.10</td>
</tr>
<tr>
<td>Ethane</td>
<td>1.20</td>
<td>Ovalbumin</td>
<td>0.078</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.84</td>
<td>Propane</td>
<td>0.97</td>
</tr>
<tr>
<td>Ethylene</td>
<td>1.87</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

progression. Most importantly, he concluded that the quantities diffused appear to be closely in proportion... to the quantity of salt in the diffusion solutions [70]. In other words, the flux caused by diffusion is proportional to the concentration difference.

These important experimental results were later analysed by Fick [60] in 1855 and a mathematical model that predicts accurately the diffusion process in dilute solutions was first proposed. Fick [60] stated, in analogy with the already successful Fourier’s Law [62], that a total one-dimensional mass flux rate $J$ is proportional to the concentration gradient multiplied by the cross-section area $S$, i.e. $J = Sj = -SpD\nabla C$. The quantity $D$, which Fick called the constant depending of the nature of the substances, is the mass diffusion coefficient.

The knowledge of this coefficient, intrinsic to each substance, is nowadays what is essential in the prediction of all diffusive mass transport phenomena. However, measuring the diffusion coefficient is reputed to be difficult [204]. Table 1.1 shows the diffusion coefficient at infinite dilution in water at $25\degree C$ for different solutes. As shown in this table, most of these values fall close to $10^{-9} \text{ m}^2/\text{s}$. This is true for common organic solvents,
but exceptions occur for large biomolecules such as ovalbumin and haemoglobin where diffusion can be 100 times slower. At 25°C, almost none of these is faster than $10^{-9}$ m$^2$/s. The reason for this narrow range is that the viscosity of simple liquids such as water and hexane varies little, and that the diffusion coefficient is only a weak function of the molecular structure of the solute. The remarkably small range of these values is what makes the measurement of the mass diffusion coefficient in liquid systems a challenging task. Furthermore, if we were to establish a relationship between the diffusion coefficient and the structure of the diffusing molecules, then very high accurate measurements of the mass diffusion coefficient would be required.

Such relationship between the diffusion coefficient and the molecular structure has been proposed in the literature, and is resumed in the well-known Stokes-Einstein equation:

$$D = \frac{k_B T}{f} = \frac{k_B T}{6\pi \mu r_0},$$  \hspace{1cm} (1.3)

where $f$ is the friction coefficient of the solute, $k_B$ is Boltzmann constant, $\mu$ is the dynamic viscosity of the solvent, and $r_0$ is the radius of the solute molecules. Equation (1.3) and its variations have been widely used to estimate the size of solutes [55]. This equation is derived from assuming a continuum medium (solvent) where rigid solute sphere molecules are moving, as shown in Fig. 1.3(a). Therefore, the accuracy of Eq. (1.3) drops drastically when the molecular size of the solute is comparable to the molecular size of the solvent, as shown in Fig. 1.3(b). In such a case, a more rigorous approach to estimate the molecular structure and size of the solute must be taken [76]. However, for the case of proteins which usually have a much larger size than the solvent molecules, Eq. (1.3) can be used to roughly estimate the size of the diffusing molecules. This is merely a rough estimate because the molecular structure of large molecules is usually non-spherical and complex. On the other hand, when the size of the molecules is known, diffusion coefficients calculated from Eq. (1.3) are accurate to only about 20% [167]. Unfortunately, these estimates are compromised in two ways. First, if the solute is hydrated, then the ra-
Figure 1.3: Motion of a solute molecule in an ideal (a) and non-ideal (b) solvent. In both cases the molecule is taken as a hard sphere. In (a) the molecules of the surrounding solvent are much smaller than the molecules of the solute; this diffusion can be modelled with Eq. (1.3). In (b) the molecules of the solvent and solute have similar size and, hence, the model of diffusion is more complex than in (a).

dius \( r_0 \) will refer to the solute-water complex, not to the solute itself. Second, if the solute is not spherical, then \( r_0 \) will represent some average shape. Concerning the shape of the molecule, Perrin [157] has proposed variations of Eq. (1.3) assuming a prolate ellipsoid for the molecular shape of the solute.

Other factors that influence the diffusion coefficient that are not taken into account by the Stokes-Einstein equation are the pH, ionic strength, concentration of the solution, and other external forces. In particular, transport of molecules in concentrated systems is of fundamental importance in medicine, biology, and chemical engineering (e.g. in the mass transport within cartilaginous tissues, in the release and distribution of encapsulated drugs and transport of reactants within the body, and in the production process of plastic materials [105]). Nevertheless, another important assumption of Eq. (1.3) is that solute molecules that move within the continuum medium do not interact with each other, which is only the case for infinite dilute solutions. In concentrated solutions, the interaction between the solute molecules has to be taken into account, making the Stokes-Einstein equation obsolete when trying to accurately predict mass diffusion coefficients in highly concentrated systems.

The difficulties encountered by different models when predicting mass diffusion coef-
ficients create the need of a direct measurement of mass diffusion coefficients. Here, we usually measure spatio-temporal changes of the concentration and then compare the results with a diffusion model, e.g. Fick’s first law, in order to determine the mass diffusion coefficient. Thus, the determination of the mass diffusion coefficients is always restricted to a theory predicting the diffusion phenomena. Fortunately, for most cases Fick’s law is a very accurate model. However, in highly concentrated solutions where the concentration differences are large, the interaction between the molecules is very strong. In this case, the system response becomes nonlinear and the first term on the r.h.s. of Eq. (1.1a) is no longer accurate [202]. In spite of this nonlinearity, when the concentration difference remains small, even for high concentrated solutions, Fick’s law is accurate enough and can be used to predict mass diffusion.

**THERMODYNAMIC EFFECTS**

Soret [165] discovered in 1879 that a salt solution contained in a tube with the two ends kept at different temperatures did not remain uniform in composition: after a steady state had been reached the salt was more concentrated near the cold end than near the hot end of the tube [188]. Ludwig [110] described in 1856 the same phenomenon in a short report. Therefore, this phenomenon is commonly referred to as the ”Soret effect”, but sometimes it is also called ”Ludwig-Soret effect”. Soret concluded that a flux of salt was generated by a temperature gradient and that the mass diffusion induced by temperature gradients can be described by the second term on the r.h.s. of Eq. (1.1a).

The factor $\rho C_0 (1 - C_0)$ is usually added to $D_T$ since the Soret effect does not exist in pure fluids. Nevertheless, $D_T$ remains concentration dependent, exactly as $D$, even for infinite dilute mixtures. In steady-state conditions, i.e. $j = 0$, the two terms on the r.h.s of Eq. (1.1a) are opposite and have equal intensity. If we consider the convectionless mass diffusion process as one-dimensional in the $z$ direction, Eq. (1.1a) becomes

$$\frac{\partial C}{\partial z} = -\frac{D_T}{D} C_0 (1 - C_0) \frac{\partial T}{\partial z},$$  

(1.4)
and the Soret coefficient is defined as

\[ S_T = \frac{D_T}{D}. \tag{1.5} \]

The Soret coefficient may be positive or negative depending on the sign of \( D_T \) which indicates the sense of migration of the reference component (to the cold or to the hot region). The reason for some molecules to migrate to the hot region (thermophilic behaviour) while others migrate to the cold region (thermophobic behaviour) is still a mystery in science (see Artola et al. [12] for recent progress). In spite of this, there are only two research groups that have been able to visualize thermodiffusion in liquid mixtures with a high-accuracy by using optical digital interferometry (ODI) (see Mialdun et al. [122] and Ahadi et al. [6]). These experimental techniques were developed to study thermodiffusion under micro-gravity conditions in the International Space Station (ISS). However, their measurement time is still long, i.e. more than 10 h for short experiments, and accurate visualization of thermodiffusion in biological systems, such as protein solutions, has never been conducted. Thermodiffusion has a strong potential for drug screening applications as well as basic research [58] and, therefore, the development of new experimental tools that help us understand this phenomenon is essential.

Moreover, according to Eq. (1.4), for a mixture containing 50 wt% of each component, i.e. \( C_0 = 0.5 \), and for a temperature difference \( \Delta T = 4 \) K between hot and cold parts of the system, the difference in mass fraction \( \Delta C \) numerically will be equal to the Soret coefficient. Typically, \( \Delta C \) is of the order of 1% of \( C_0 \), sometimes smaller. An order of magnitude of the Soret coefficient in absolute value for organic mixtures or aqueous solutions is usually \( |S_T| \sim 10^{-3} - 10^{-2} \) K\(^{-1}\). Even if the separation remains small, the Soret effect has a lot of implications, such as in the operation of solar ponds [209], the microstructure of the ocean [72], convection in stars [189], and mass transport across biological membranes induced by small thermal gradients in living matter where thermodiffusion could assume a sizeable magnitude for an ensemble of cells with the dimension of an organ or a tumour [28]. Another important application of the Soret effect is in natural
Table 1.2: The Fontainebleau benchmark values for the Soret coefficient of three organic liquid mixtures. Initial mass fraction: 50 wt% - 50 wt%. C12: dodecane. IBB: isobutybenzene. THN: tetrahydronaphthalene. Here, the denser component is taken as reference component for the concentration difference.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>References, $S_T \left[10^{-3} , \text{K}^{-1}\right]$</th>
<th>Proposed benchmark value, $S_T \left[10^{-3} , \text{K}^{-1}\right]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>THN-C12</td>
<td>[164] [31] [215] [108] [52]</td>
<td>9.5 ± 0.5</td>
</tr>
<tr>
<td>THN-IBB</td>
<td>3.14 3.03 3.46 3.55 3.10</td>
<td>3.3 ± 0.3</td>
</tr>
<tr>
<td>IBB-C12</td>
<td>3.69 3.96 3.95 3.95 —</td>
<td>3.9 ± 0.1</td>
</tr>
</tbody>
</table>

hydrocarbon reservoirs \[130,131\], where one of the challenges is optimizing exploitation. In order to achieve this, it is necessary to have a perfect knowledge of the fluid physics in crude oil reservoirs, where the concentration distribution of the different components in hydrocarbon mixtures is mainly driven by phase separation and diffusion.

**The Fontainebleau benchmark.** The Soret effect has to be quantified by “numbers.” In order to do this, the Fontainebleau benchmark has been proposed by five European research groups during a workshop held at the “École des Mines, Fontainebleau (France)”, so this well-known benchmark is now called “The Fontainebleau benchmark” \[163\]. These groups measure the Soret coefficient for specific mixtures by different methods, such as thermal diffusion forced Rayleigh scattering (TDFRS), optical beam deflection (OBD) technique, and convective coupling in annular thermogravitational columns. This benchmark consists of three binary mixtures composed with dodecane (C12), isobutybenzene (IBB), and 1,2,3,4 tetrahydronaphthalene (THN) at a mean temperature of 25°C and 50 wt% in each component. These components have been chosen, as they are representative of a hydrocarbon reservoir mixture, containing an alkane (C12), a one-ring component (IBB) and a two-ring component (THN). After two years of individual investigations, comparisons between the results produced by each laboratory have been completed and the results published in a common paper accompanied by five individual papers originating from each laboratory \[31, 52, 108, 164, 215\]. The aim of these papers was to propose the benchmark values shown in Table 1.2 to which all future techniques should
In this dissertation, the binary mixture IBB-C12 is used, together with another well-known benchmark mixture (ethanol-water at ethanol concentration 39.12 wt%), in order to validate a novel method to visualize thermodiffusion and measure Soret coefficients.

### 1.2 Natural Convection in Enclosures

Natural convection occurs due to temperature differences which affect the density, and thus the relative buoyancy, of the fluid. Heavier (more dense) components will fall, while lighter (less dense) components rise, leading to advection. Natural convection can only occur, therefore, in a fluid under an external field, e.g. gravitational or magnetic fields. It can be seen in a pot of boiling water in which the hot and less-dense water on the bottom layer moves upwards in plumes, and the cool and more dense water near the top of the pot likewise sinks.

Since the pioneering studies of Bénard [19, 20] and Rayleigh [175], the Rayleigh-Bénard convection has been extensively studied. These studies were focused on characterizing the pattern formation within heated layers, which is an intriguing phenomenon. Rayleigh-Bénard convection involves both fluid mechanics and heat transfer, and it is of great interest in many fields, as for example in crystal growth (see Lappa [102, 103], Wilcox [214], and Tsukada et al. [88, 117, 203]). The first studies of Rayleigh-Bénard convection rather concerned infinitely extended layers for which analytical derivations could be performed, but studies in confined enclosures have also been developed in connection with practical applications and with the progress in numerical computing [120].

Convection within a fluid is characterized by the Rayleigh number

\[
Ra = \frac{g\beta(T_H - T_C)h^3}{\kappa \nu},
\]

where \(g\) is the acceleration of gravity, \(\beta\) is the volumetric expansion coefficient, \(h\) is the distance between the heated boundaries, \(\kappa\) is the thermal diffusivity, \(\nu\) is the kinematic viscosity, \(T_H\) and \(T_C\) are the temperatures of the hot and cold boundaries, respectively.
Rayleigh-Bénard convection is an interesting problem for the dynamics of the flows which develop from the motionless conductive solution [27]. A critical Rayleigh number $Ra_c$ has to be reached for the onset of flows, and subsequent flow bifurcations can occur before a chaotic state is reached. The dynamics are particularly rich in confined situations where geometry effects and boundary conditions play an important role and where symmetry considerations are involved [48].

2 INTERFEROMETRIC METHODS TO STUDY DIFFUSION

Interferometers are the most precise methods for the measurement of diffusion coefficients in binary mixtures [55]. These methods utilize the wave properties of light, combined with the effects that the concentration in a solution has on the refractive index, in order to measure unsteady refractive index profiles. These profiles are related to unsteady concentration profiles and finally compared to models of diffusion, e.g. Fick’s law, in order to determine the mass diffusion coefficient.

Since the wavelength of visible light is quite small, very small changes in the optical path caused by refractive index variations produce measurable changes in the intensity of an interference pattern. As a result, optical interferometry permits extremely accurate measurements of different physical phenomena which are related to the refractive index. However, a drawback is that the utilization of visible light makes interferometers only applicable to transparent solutions. Fortunately, most of the solutions in biological systems are transparent. Thus, interferometric techniques have the strong potential of becoming a powerful tool to measure the diffusion properties for important biomolecules, such as proteins and DNA.

Optical interferometry has been used as a visualization and measurement technique for more than a hundred years. However, new developments in laser and computing have made interferometers practical for a very wide range of measurements [75]. In the case of mass diffusion coefficients in transparent solutions, it represents the most accurate
measurement method.

2.1 CONVENTIONAL INTERFEROMETRIC TECHNIQUES

As shown in Fig. 1.4, there are different arrangements of optical interferometers. Gouy interferometer, shown in Fig. 1.4(a), is a one-beam interferometer and has been developed to measure mass diffusion coefficients with a precision up to 0.1%. They are much easier to build than two-beam interferometers such as Rayleigh and Mach-Zehnder interferometers shown in Fig. 1.4(b) and (c), respectively. However, the fringes of the Gouy interferometer are quite difficult to interpret. Both the Rayleigh and Gouy interferometers have been utilized to obtain values of binary solution diffusion coefficients with a typical accuracy of about ±0.2% and a precision from ±0.1 to ±0.2%. In some studies, an accuracy of ±0.1% or better and a precision of ±0.03% were reported. Mach-Zehnder interferometry has also been used to estimate mass diffusion coefficients at infinite dilution with an accuracy of 10% [37]. In spite of being less accurate and more difficult to construct than Gouy interferometers, Mach–Zehnder interferometers are a solid alternative to the Gouy interferometer because they give information that is simpler to interpret and have the potential of being used with phase-shifting techniques in order to drastically increase the accuracy of the measurement [96, 123].

In these interferometric methods, fringe patterns are produced by passing monochromatic light through a diffusion field enclosed in a diffusion cell. When adjusted to the infinite fringe condition, the interferogram will give a map of the constant phase line that makes possible to establish precise concentration distribution profiles. Other interferometric methods such as the Jamin interferometer [44], and the holographic interferometer [14] have been used to measure mass diffusion coefficients. The fundamental principles of the last two methods are the same as that of Rayleigh interferometry.

Due to their importance and role in the measurement of mass diffusion coefficients, the principles, advantages and disadvantages of Gouy, Rayleigh, Holographic, and Mach-Zehnder interferometry are described.
Gouy interferometry has been the most widely used technique for the experimental study on mass diffusion coefficients in liquids. The theory of this method was developed by a number of researchers among whom Kegeles & Gosting were pioneers [91]. The advantages of the Gouy interferometer lie in the simple arrangement of the optical device, although the theoretical description of the fringe obtained is quite complicated. Figures 1.4(a) and 1.5 show the schematic of the Gouy interferometer optical system. The basic apparatus for measuring the concentration gradient uses a lens L to send parallel light rays from a light source LS through a diffusion cell C. If there is no refractive index variation within the cell, the light will pass straight through the cell to finally focus on one point.
GENERAL INTRODUCTION AND BACKGROUND

Figure 1.5: Principle of Gouy interferometry. A sketch of the light source (LS), the lenses (L), and the cell (C) is shown together with the derived interference pattern.

However, if this cell contains a refractive index profile as shown in Fig. 1.5, then light passing through the center of the cell is deflected while light passing through the extremes remains straight. This difference in the deflecting angle produces an interference pattern of dark horizontal lines.

The fringe pattern in a Gouy interferometer is sensitive to the refractive index gradient distribution inside the diffusion cell. Unlike the fringes produces by two-beam interferometers, the interpretation of Gouy interference fringes requires an accurate adjustment of the position of the non-deviate image. Because this adjustment of the interference pattern is particularly difficult, it is often established by means of reference to Rayleigh interference fringes.

RAYLEIGH INTERFEROMETRY

The Rayleigh interferometer is a two-beam interferometer which makes use of the interference patterns between the reference beam and the test beam to analyse the refractive index variations within a cell.

The setup is very similar to that of Gouy interferometers, using a light source LS and a lens L to create a wide cylindrical beam. However, instead of passing the entire light beam through the cell as Gouy interferometers, two sections of the collimated beam are isolated by a pair of apertures as shown in Fig. 1.4(b). One of these beams passes though a diffusion cell C, while the other beam remains unaltered to be used as reference. Finally,
another lens L is used to combine both beams. Since the optical path of the test beam, i.e. the beam that passes through the diffusion cell, is different from the optical path of the reference beam, as shown in Fig. 1.6, then interference patterns are obtained. These fringe patterns contain information about the refractive index variations within the cell.

This conventional Rayleigh interferometric technique has been utilized for a number of accurate measurements of mass diffusion coefficients in several studies [109, 191]. For the most accurate measurements, the optical system must be of extremely high quality because aberrations in its elements have an influence on the generation of the fringes and cause distortion of the fringe pattern, even in the absence of concentration gradients within the cell. In particular, the cell windows must be manufactured flat with a very small geometrical tolerance in order to avoid small changes in the optical path that can be detected with the Rayleigh interferometer. For better measurements, corrections to the deviations from an ideal optical arrangement have been developed by Creeth [54].

Holographic Interferometry

Holography was invented in 1948 by Gabor [65]. The conventional holographic interferometer commonly used for measurement of mass diffusion coefficients was described
in 1966 by Heflinger et al. [78]. Among its various advantages, the most important is the means to suppress the defects intrinsic to the optical apparatus, correction that is not taken into account by other conventional interferometers. In fact, interferometers such as the Rayleigh interferometer are very sensitive to such optical defects, e.g. lens aberration and optical defects of the cell, increasing the error in the measurements of mass diffusion coefficients. In holographic interferometry, a single cell (not needing to have a high manufacturing accuracy) is used for the measurements. The first step in the measurement of mass diffusion coefficients with holographic interferometry is the construction of the hologram of the diffusion cell which contains a liquid mixture of uniform composition. This hologram is constructed on a photographic plate, as shown in Fig. 1.7. Parallel light from a laser source, LS, is divided into two beams, the reference beam and the test beam. As in Rayleigh interferometry, the test beam passes through the diffusion cell and the reference beam remains unaltered (see Fig. 1.6). The reference beam is then deviated by a prism (in some cases by a mirror), in order to make it converge on the photographic plate so that it interferes with the test beam. Interference patterns are then produced and recorded onto the photographic plate in order to obtain the interferograms characteristic of the optical apparatus, including the diffusion cell.

The holographic plate is then placed at its original position after having been developed and illuminated with the reference beam only. Then, the hologram shows a virtual three-dimensional image of the diffusion cell in its original position. If the test beam
INTERFEROMETRIC METHODS TO STUDY DIFFUSION

passes through the diffusion cell, and if this beam is not interrupted in the reconstruction of the cell image, the virtual holographic image and the cell will be seen in exact coincidence. Furthermore, if the local refractive index of the liquid in the cell has changed since the formation of the hologram, the optical path length for light passing through the same point of the diffusion cell and its virtual image differs. Therefore, a pattern of interference fringes will appear on the holographic plate. As in conventional two-beam interferometers, the interpretation of the fringes is the same for constructive and destructive interference as shown in Fig. 1.6. If changes of refractive index in the diffusion cell occur due to the process of diffusion following formation of a boundary between two mixtures at different concentration, it is possible to observe fringes identical to those of the conventional Rayleigh interferometry. Thus, they can be photographed and interpreted by the same techniques.

The advantage of holographic interferometry is that the observed interference pattern arises from the interaction of two beams which have passed through the same diffusion cell at different times. The cell has a fixed refractive index distribution, whereas there is a transient refractive index distribution which is characteristic of the diffusion process taking place inside the cell. Consequently, any optical defects in the diffusion cell are automatically and exactly compensated and only the refractive index information due to the diffusion field is obtained. Holographic interferometry can be thought as a sort of filter of optical imperfections in the apparatus. On the other hand, in conventional interferometric techniques, the two interfering beams pass through different paths at the same time and, hence, this filtering cannot be achieved.

Holographic interferometry has been applied to determine mass diffusion coefficients in liquid binary solutions by Bochner & Pipman [26]. The size of the cylindrical diffusion cell was 15 mm in diameter and 3 mm in length. They created the initial concentration difference in a quite unique way. First, the diffusion cell was half filled with the heavy solution, which was then frozen to avoid diffusion with the pure water which was subsequently injected at temperature 0°C on top. Then, the complete cell was frozen until
the start of the experiment when the cell was rapidly warmed with an air blower to approximately 30°C within 10 s. This technique produced a nearly-perfect initial step-wise concentration profile within the cell with practically no disturbances, suitable for the comparison with the analytical solution used to determine the mass diffusion coefficient.

Hattori et al. [77] measured diffusion coefficients of Lithium Bromide in aqueous solutions in 20 minutes by holographic interferometry in a small size diffusion cell, which was 10 mm in width, 10 mm in depth, and 60 mm in height. The transient diffusion field was then formed by use of a shear cell. Their study presents a typical way of measuring mass diffusion coefficients by means of holographic interferometry where a measurement time of more than 10 minutes is required due to the recording of the interference change on the photographic plate.

Colombani & Bert [50] used a holographic interferometer to study diffusion and convection in liquids. They showed that holographic interferometry can be used as a powerful tool to study free diffusion, diffusion through a meniscus, the Soret effect, and natural convection in enclosures. In particular, the investigation of the hydrodynamical behaviour in a confined binary mixture (see Colombani et al. [51]) is of great interest because of its relevance to the techniques and phenomena considered in this dissertation.

**MACH-ZEHNDER INTERFEROMETRY**

The principles of the Mach-Zehnder interferometer, as well as its arrangement, are almost the same as those of the holographic interferometer. The only difference lies in that the Mach-Zehnder interferometer does not make use of a holographic plate in order to obtain the interference patterns. Instead, the Mach-Zehnder interferometer uses two beam splitters and two mirrors to divide and recombine the beams, as shown in Fig. 1.4(c). The fringe spacing is controlled by varying the angle between the beams emerging from the interferometer.

The Mach-Zehnder interferometer has three attractive features. One is that the two paths are widely separated and are traversed only once; another is that the region of lo-
calization of the fringes can be made to coincide with the test object, so that an extended source of high intensity can be used; and the other is that it is suitable for image processing when the two beams are made interfere in a charge-coupled device (CCD) sensor connected to a computer. However, adjustment of the interferometer is not easy.

Caldwell et al. [38] first demonstrated in 1957 that the Mach-Zehnder interferometer, in conjunction with a specially designed single-channel diffusion cell, permits a rapid and accurate determination of binary diffusion coefficients in volatile solutions. More recently, Mialdun & Shevtsova [122] developed a Mach-Zehnder interferometer with a FFT method, proposing a novel optical digital interferometry (ODI) technique that provides highly-accurate phase maps of a diffusion field. They developed ODI to visualize and measure thermodiffusion within a Soret cell [125], and later to study the influence of vibrations on diffusion under microgravity conditions [181]. However, their optical technique cannot be used in real-time and the measurement time is still quite long, i.e. more than 10 h for short experiments.

### 2.2 Disadvantages of Conventional Optical Methods

The utilization of interferometric techniques has a great advantage compared to other methods for measuring mass diffusion coefficients, such as diaphragm-cell method [190], Tylor dispersion [143], and dynamic light scattering [155]. Nevertheless, some problems still remain in these conventional techniques: One is that the required measurement time for mass diffusion coefficients is long, e.g. 10 minutes for short time measurements and even days for conventional ones. It is well known that the diffusion in liquids is a very slow phenomenon, so long time measurements are expected. However, a long measurement time is subject to errors such as fluctuations in the environmental conditions and in the case of proteins and high concentrated solutions, possible coagulation or crystallization. Shortening the measurement time will not only result in more accurate measurements but it would facilitate the measurement of the mass diffusion coefficient of numerous new compounds that are created each year in the pharmaceutical and biochem-
ical industries.

Another disadvantage of traditional methods for measuring mass diffusion coefficients is the large optical equipment used, e.g. a long tube or large breadboard for optical parts is needed to observe the diffusion fields. Increasing the number of optical elements in the interferometer may result in a drop of its accuracy and an increase of the amount of the sample that is required to form the diffusion field. In the case of proteins, the amount of sample that can be used to make the transient diffusion field is very limited due to the high costs of these substances. Hence, not only reducing the size of the measurement instrument but also the size of the diffusion cell is essential to effectively measure mass diffusion coefficients accurately and economically.

3 Numerical approach to study natural convection

Natural convection is fundamental in fluid mechanics, having both great scientific value and industrial importance. Many engineering problems, such as thermal comfort in buildings [129], crystal growth [89, 102], and solar collectors [100], depend on this type of convection. Understanding natural convection of pure fluids (i.e. without Soret effect) in parallelepiped cavities is the first step to address these engineering challenges, as well as many other important scientific problems (such as mantle convection [16] and atmospheric convection [59]). Therefore, natural convection in rectangular parallelepiped enclosures has been extensively studied for different boundary conditions, aspect ratios, and heating configurations. In particular, research has focused on parallelepiped cavities with two types of heating configurations: (i) heating from below, i.e. Rayleigh-Bénard convection, and (ii) heating from the lateral sidewalls.

Early three-dimensional numerical studies of natural convection in rectangular parallelepiped cavities heated from the sides include those conducted by Mallinson & Davis [113]. Three-dimensional numerical studies are necessary given the fact that any realistic
convective flow is three-dimensional in nature. In spite of the high-resolution achieved by direct numerical calculations [64,208], the stability of the flow is not considered and, thus, important information concerning the type of bifurcation (steady, saddle-node, or Hopf bifurcations) and subsequent branching is not obtained. Continuation methods, on the other hand, provide a comprehensive stability description of the convective system [179]. Henry & Ben Hadid [79] applied a continuation method to determine the thresholds corresponding to the first flow transition in a three-dimensional parallelepiped cavity heated from the sides for a wide range of aspect ratios in low-Prandtl-number fluids. An improved version of their continuation method is used in this study.

In contrast, Rayleigh-Bénard convection is a more complex phenomenon than natural convection heated from the sides [66], and is one of the most studied problems in fluid mechanics in both extended layers and confined cavities. It has been extensively studied during the course of a century since the pioneering studies of Bénard [20] and Rayleigh [175] in 1901 and 1916, respectively. In this type of fluid motion, the buoyancy forces must overcome the viscous forces for convection to set in. This occurs at a critical Rayleigh number, after which flow patterns with different symmetry properties usually arise. The critical Rayleigh number as a function of the aspect ratio is well-known [41]. The lateral walls increase the critical Rayleigh number due to the additional shear stress exerted to the system. Depending on the roll orientation with respect to the axes of a non-cubical cavity, these stable solutions are usually called transverse or longitudinal rolls. From the different aspect ratios that have been studied, the cubical cavity is the most fundamental geometry. Pallares et al. [149] conducted experiments that show various convective flow patterns in cubical enclosures.

Puigjaner et al. [168–171] have conducted a thorough bifurcation analysis of Rayleigh-Bénard convection in a cubical cavity filled with air and silicone oil (Prandtl numbers $Pr = 0.71$ and 130, respectively) for perfectly insulating and conducting lateral sidewalls. Their results are summarized in detailed bifurcation diagrams where the different stable and unstable branches are depicted for the Rayleigh number range $Ra \leq 1.5 \times 10^5$. Their
studies yield important results that clarify the stability behaviour of natural convection in a cubical enclosure heated from below. However, in practical applications, it is common that the cavity is tilted. Even when the cavity is intended to be placed horizontally, a very slight inclination exists in a real physical situation. Then, two fundamental questions arise: what is the effect of a slight inclination on the stability of the system?, and for larger inclination angles, what happens during the transition from Rayleigh-Bénard convection to the heated-from-the-sides configuration? In spite of the importance of natural convection in tilted cavities, there is no complete bifurcation analysis that addresses these questions in a realistic three-dimensional configuration.

Concerning the stability analysis in tilted enclosures, the work done by Cliffe & Winters [47, 47] is pioneering. They conducted two-dimensional calculations of natural convection inside a tilted square cavity with adiabatic sidewalls. Their study shows that the symmetric primary pitchfork bifurcation, which is found in the horizontal case, is broken as a result of the tilt. The no-flow solution is then nonexistent and a leading stable branch, consisting of rolls in the same direction as the inclination, takes its place commencing from $Ra \to 0$. Moreover, a disconnected branch corresponding to rolls opposite to the inclination develops from a saddle-node bifurcation. This disconnected branch has initially stable and unstable segments, but the precise bifurcation points over this branch are still unclear. The results of Cliffe & Winters [47] provide a glimpse of the convective phenomenon that unfolds when the cavity is tilted. Namely, the symmetries found in the horizontal case are broken and disconnected branches appear. Nevertheless, their bifurcation analysis fails to predict the effects of the tilt on three-dimensional convection. The extensive experimental work done by Ozoe et al. [145, 147, 148] on tilted ducts indicates that the inclination has a distinctive effect on the various three-dimensional stable solutions. Except for the analysis of Kirchartz & Oertel [92], all bifurcation studies conducted in tilted cavities are based on two-dimensional calculations [1, 8, 133].

Kirchartz & Oertel [92] carried out a thorough study on thermal cellular convection in inclined rectangular boxes, both experimentally and numerically. They limited the anal-
ysis to the case of a turn about the short container axis. They discussed the influence of the shear flows in tilted boxes and the transition to time-dependent oscillatory convection. They used stability diagrams to describe the stable solutions in the system, in which the basic flow, transversal rolls, and longitudinal rolls arise at different Rayleigh numbers and inclination angles. The experimental part of this study yields two important findings: firstly, there are transition angles between cellular convection and a single roll configuration and, secondly, there are critical angles at which some stable solutions cease to exist. Their theoretical model, however, does not predict the critical angles of the multiple stable regimes.

4 REMAINING CHALLENGES

In this chapter, the importance of heat and mass transfer in enclosures was explained. It was described that the study of mass diffusion is more experimental than numerical due to the complex molecular interactions within the mixtures. In contrast, natural convection can be modelled to a good approximation with the Navier-Stokes equations. Nevertheless, there are still several remaining challenges that science and engineering have yet to solve. In this section, the challenges for the experimental techniques focused on the measurement of mass diffusion (isothermal diffusion and thermodiffusion) are discussed in §4.1, and some fundamental natural convection problems that could be solved by numerical techniques are discussed in §4.2.

4.1 EXPERIMENTAL

Cutting edge measurement techniques, such as those recently developed by Mialdun et al. [121–127] and Ahadi et al. [2–6] for diffusion experiments in the International Space Station (ISS) (see detailed explanation in Chapter II §1 and Chapter VI §1) and under normal gravity conditions, still have some significant drawbacks. The most important challenges are mentioned in the following.
1. **Shorten the measurement time.** The measurement of Fickian and Soret coefficients is about 10 h. This is a significantly long measurement time considering the expense of space experiments, as well as the everyday-growing number of biological systems that require accurate measurements of these thermophysical properties. A shorter measurement time is necessary for future industrial and research applications.

2. **Reduce the amount of sample.** For industrial and research applications, reducing the amount of sample might be as important as shortening the measurement time. There are many biological systems that need to be measured, some of which are rare and hence quite expensive to synthesize. Reducing the amount of sample, e.g. to a microgram-level, would make the measurement method more efficient and suitable for determining the Fickian and Soret coefficients of these rare biomolecules.

3. **Conduct accurate and real-time visualization of diffusion fields.** Currently, no research group has developed a method that visualizes concentration profiles in real-time with a high accuracy. Real-time measurements of concentration and temperature fields are desirable in order to ease the measurement process and increase the versatility of the apparatus for further applications. Furthermore, most of the methods mentioned in this chapter cannot conduct accurate measurements of diffusion in multicomponent systems. These methods have low resolution and thus a characterization of multicomponent systems is tedious (with the exception of Maldun et al. [121]). In order to correctly assess the interaction between solutes in multicomponent systems, higher resolutions measurements have to be conducted.

4. **Reduce the bias error by considering initial characteristic conditions.** The methods referenced in this chapter use the analytical solution of the diffusion equation to determine isothermal diffusion coefficients. This results in an increase of the measurement error, specially for short measurement times because the analytical solution does not take into account the initial concentration within the diffusion
cell, which is characteristic of each experiment. Analytical solutions have been used mainly for two reasons: firstly, the resolution of conventional interferometers is very limited, so only low resolution concentration profiles, which are difficult to treat with numerical calculations, are obtained; secondly, it is easy to use an analytical solution in the fitting process of the experimental data. The initial conditions within the cell could be considered by using a numerical solution, instead of an analytical solution, to fit the experimental data and find the Fickian or (and) Soret coefficient(s).

5. **Conduct simultaneous measurements of velocity and temperature fields.** There are currently no established techniques that can simultaneously measure two-dimensional temperature and velocity fields in convective flows. This is of great importance since much of the flows are characterized by temperature and velocity fields.

Solving the problems mentioned above are of utter importance in experimental heat and mass transfer.

### 4.2 Numerical

Cutting edge numerical calculations that address the stability of steady natural convection in three-dimensional enclosures are those conducted by Puigjaner *et al.* [168–171] (see detailed explanation in Chapter V §1). These calculations provide a full characterization of the stable and unstable solutions within a cubical enclosure differentially heated with different boundary conditions. However, there are still some important questions that need to be addressed:

1. **Develop an efficient three-dimensional continuation method to study steady convection in enclosures.** Efforts to clarify natural convection in parallelepiped enclosures have been carried out. However, except for the studies of Puigjaner *et al.* [168–171] conducted for cubical cavities, all the bifurcation analysis performed
have been conducted in two-dimensional cavities. Therefore, there is a need to develop a three-dimensional continuation method that is capable of clarifying the stability of natural convection in a parallelepiped enclosure for a wide range of Rayleigh numbers and aspect ratios.

2. **Clarify the stability of steady natural convection in horizontal parallelepiped (non-cubical) cavities.** Puigjaner et al. [168–171] focused on cubical cavities heated from below. This is an essential case that was worth studying in depth as a first stage. However, in most real applications, the parallelepiped cavity is not cubical, e.g. a heated square duct filled with a fluid [1]. The stability characteristics of natural convection in such three-dimensional cavities is unknown. Addressing this problem would bring us a step closer to explain natural convection in more realistic conditions.

3. **Clarify the stability of natural convection in tilted parallelepiped enclosures.** Little is known concerning the stable solutions that exist in a tilted parallelepiped cavity, both for the cubical and non-cubical cases [47,92]. In a real situation the inclination of the cavity is common and, even in situation where the cavity is intended to be placed horizontal, small defects result in slight tilts. Therefore, clarifying the influence of a tilt on the stability of the solutions for slight inclination angles, as well as for larger angles, is of great importance.

**4.3 Motivation of the Present Study**

The motivation of the present study is twofold:

1. Overcome the challenges and problems stated in §4.1 and §4.2.

2. Unveil possible engineering and research applications after solving such problems. Some applications of the proposed methods could be the following:

   (a) Efficient measurement of isothermal diffusion
(b) Efficient measurement of thermodiffusion
(c) Visualization of biomolecular thermophoresis
(d) Separation of species by controlled thermodiffusion
(e) Analysis of mixtures in multicomponent mixtures
(f) Optimization of heat transfer in a tilted enclosures

5 OBJECTIVES

Following the need to develop better optical techniques to study heat and mass transfer in parallelepiped enclosures, as well as the importance of numerical investigations that address the stability of steady natural convection in such cavities, the main objectives of this study are the following:

- Establish an optical technique capable of conducting real-time measurements of isothermal diffusion and thermodiffusion fields.
- Conduct highly-accurate measurements of isothermal diffusion, thermodiffusion, and natural convection in parallelepiped enclosures.
- Determine the isothermal diffusion coefficients in protein aqueous solutions, clarifying the effects of the molecular weight, molecular structure, and concentration.
- Visualize and measure thermophoresis in protein aqueous solutions for thermophobic and thermophilic biomolecules.
- Develop a three-dimensional continuation method suitable for investigating steady natural convection in parallelepiped enclosures.
- Clarify the influence of a tilt on steady natural convection in a cubical enclosure and a truncated square duct, focusing on the stable solutions for different Rayleigh numbers and Prandtl numbers.
• Establish an experimental setup capable of measuring velocity and temperature fields of natural convection in parallelepiped cavities.

6 CONTENTS OF THIS DISSERTATION

The layout and content of this dissertation is shown in Fig. 1.8.

In Chapter I, a brief introduction of the problem is given. The motivation of this dissertation is presented and the main objectives are stated.

In Chapter II, a novel yet precise technique to visualize isothermal diffusion and thermodiffusion is developed. The construction of a real-time phase-shifting interferometer is described. The principle of the optical technique and the design of the interferometer are explained. The experimental apparatus is validated for the measurement of Soret and Fickian diffusion coefficients by measuring benchmark mixtures.

In Chapter III, the optical system developed in Chapter II is applied to mass diffusion measurements in several biological systems. The importance of Fickian diffusion and thermodiffusion in biological systems is discussed. Biomolecular Fickian diffusion, as well as thermophoresis, in binary and dilute ternary systems is studied. The thermodiffusion field for protein aqueous solutions is visualized for the first time.

In Chapter IV, a continuation method is developed from a three-dimensional spectral finite element code. This method is particularly well suited for the studies involving complex bifurcation diagrams of three-dimensional convection in rectangular parallelepiped cavities. This continuation method allows the calculation of solution branches, the stability analysis of the solutions along these branches, the detection and precise direct calculation of the bifurcation points, and the jump to newly detected stable or unstable branches, all this being managed by a simple continuation algorithm.

In Chapter V, the continuation method developed in Chapter IV is applied to study steady natural convection in a tilted truncated square duct and a tilted cubical cavity. The stability of the solutions in a truncated duct with a square cross-section is studied. The
finite-length square duct is tilted around its longest axis. A thorough bifurcation analysis of steady natural convection in a tilted cubical cavity is also conducted. The solutions are studied from their initiation at low Rayleigh numbers to their transition to periodic states, for a wide range of Prandtl numbers. Finally, the analysis is extended to a cubical cavity slightly tilted in two directions, i.e. without horizontal edges. This study is the first of its kind to accurately describe the stability of the different solutions of convection in tilted parallelepiped enclosures.

In Chapter VI, the phase-shifting interferometer developed in Chapter II is utilized to...
study natural convection in a cubical cavity. A novel technique capable of conducting simultaneous measurements of two-dimensional velocity and temperature fields is presented. Such apparatus is ideal to study the steady flows obtained numerically in Chapter V.

In Chapter VII, the general conclusions and summary of the main findings of this dissertation are presented.
DEVELOPMENT OF PHASE-SHIFTING INTERFEROMETRY FOR MEASUREMENT OF MASS DIFFUSION
OVERVIEW

In this chapter, an optical digital interferometric technique, called phase-shifting interferometry, is proposed for investigating mass diffusion in binary liquid mixtures. The optical technique is developed and validated for convectionless systems where mass diffusion occurs under a quasi-thermal or nonthermal equilibrium state. A well-established experimental method to measure concentration profiles in convectionless systems is also applicable to measure temperature profiles in thermally induced convective systems, since both concentration and temperature are directly related to the physical property measured by the optical interferometer, i.e. the refractive index.

In order to study the mass transport phenomena in liquid mixtures inside rectangular enclosures, the optical system must be able to conduct measurements of transient concentration profiles. The same optical apparatus is used to measure the so-called contrast factors that relate the unwrapped phase and concentration gradients, i.e. the measurement technique is independent and robust. The interferometer has a high-resolution, which is important in order to detect the subtle differences in the diffusion process for similar solutions. This phase-shifting interferometer comprises a polarising Mach–Zehnder interferometer, a rotating polariser, and a CCD camera. An original image-processing program is introduced to determine in real-time the two-dimensional phase maps. The concentration profile within the diffusion field—under isothermal or a linear temperature gradient—is displayed on an external monitor while the diffusion process is taking place.

The Soret and Fickian diffusion coefficients are post-experimentally determined. The Soret coefficient is determined from the concentration and temperature differences between the upper and lower boundaries measured by the interferometer and thermocouples, respectively. The Fickian diffusion coefficient is obtained by fitting a numerical solution to the experimental concentration profile. The optical system is validated by measuring the well-known concentration dependence of the isothermal diffusion coefficient for NaCl-water and sucrose-water in the dilute region at 25°C. The method used to investi-
gate thermodiffusion is also validated through the measurement of Soret coefficients in the well-known liquid pairs of ethanol-water (ethanol 39.12 wt%) and isobutylbenzene-dodecane (50.0 wt%).

In §1, a brief background of the problem, a review of the important literature, and the objectives of this chapter are presented. In §2, the development of phase-shifting interferometry with a rotating polariser is described. In §3, an experimental technique to create isothermal diffusion fields and measure Fickian diffusion coefficients is described and validated. In §4, an experimental technique to create thermodiffusion fields and measure Soret coefficients is described and validated.

1 INTRODUCTION

In Chapter I, the background of the global problem was explained. In this section, a brief background and a more specific literature review is presented. The mass diffusion measurement under quasi-thermal equilibrium (isothermal diffusion) and nonthermal equilibrium (thermodiffusion) is discussed in §1.1 and §1.2, respectively. This review is essential to understand the objectives of the chapter, which are stated in §1.3.

1.1 MEASUREMENT OF ISOThERMAL DIFFUSION

A better understanding of mass transport phenomena is an essential factor in medicine and biochemistry. It also contributes to the investigation of the mechanisms involved in crystal growth or solidification [7,15,49,128]. During the past decades, biochemical engineering has been requiring accurate measurements of the diffusion coefficient of macromolecules in order to properly design new drug formulations [14,138]. However, there is a lack of reliable experimental data due to the measurement difficulties encountered when measuring a process as slow as diffusion. Even though correlations have been proposed to predict the concentration dependence of self-diffusion coefficients [68,195,196], complex solute-solvent interactions and molecular structures have made these correlations a
mere estimation for specific solution conditions, such as for isoelectric point measurements [136]. Therefore, understanding the diffusion phenomena greatly depends on the accuracy of the measurement technique.

Among the many methods developed, interferometry is widely recognized as the most accurate method to determine the diffusion coefficients in binary liquid systems [55]. Mach-Zehnder interferometry, for example, has been used as a measurement tool to determine diffusion coefficients in liquids for more than five decades. Caldwell et al. [37,38] demonstrated that Mach-Zehnder interferometry, in conjunction with a specially designed single-channel diffusion cell, permits the determination of binary diffusion coefficients in volatile solutions. Advancements in lasers, Charged Couple Devices (CCD), and image processing techniques in the last decades have permitted digital interferometry to drastically increase the accuracy of the measurement, from the low accurate typical interferograms to high-resolution digital images [42,135]. These digital images usually provide the phase difference between the test beam and reference beam, which in the case of binary solutions, can be related to the concentration in order to obtain spatial concentration profiles [141]. These profiles are later compared to a model of diffusion, generally based on an analytical solution of Fick’s second law, to determine the diffusion coefficient [26,96].

The diffusion coefficient is a thermophysical property known to be dependent on the concentration and the temperature. The most common basis for estimating the temperature dependence of diffusion coefficients in liquids is the Stokes–Einstein equation. Fickian diffusion coefficients calculated from this equation are accurate to only about twenty percent [167]. The concentration dependence, on the other hand, is much more difficult to predict due to the complex molecular interactions at non-diluted concentration levels. Furthermore in a closed system, where the entropy always increases, the concentration dependence of the mass diffusion coefficient is more relevant than the temperature dependence. This is due to the high Lewis number for liquid systems, which is usually in the order of $Le \sim 10^2$, i.e. the system tends to become isothermal faster than homogeneous in concentration. Therefore, a realistic calculation of mass transport, e.g. during crystal
growth, requires accurate measurements of the concentration dependence of the diffusion coefficient.

Conventional methods to determine the concentration dependence of diffusion coefficients create a diffusion field at narrow concentration ranges in order to approximate the diffusion coefficient as constant [26]. The diffusion experiment is then repeated at different mean concentrations to determine a discrete concentration dependence of the diffusion coefficient. Therefore, a measurement technique capable of determining the phase-shift from an interferogram with few fringes (small concentration difference) is required. Moreover, real-time measurements are preferable due to several advantages, such as fast diffusion coefficient determination, high versatility in the data processing, and reliability in the measurement.

Maruyama et al. [116] developed a phase-shifting interferometer that uses a prism and three CCD sensors to obtain real-time phase-shifted data, as shown in Fig. 2.1. This interferometer was used to study crystal growth by measuring concentration profiles around a crystal under gravity and microgravity conditions [115]. Guo et al. [73] applied this op-
tical setup and a shearing test cell to determine isothermal diffusion coefficients in liquid systems for a measurement time of 100 s. Komiya et al. [96] made further improvements by introducing a counter flow cell to generate a nearly ideal step function of the initial concentration profile and determine the diffusion coefficient of salts within 30 s, a very short time compared to conventional methods. An initial step concentration profile is required in conventional determination methods of diffusion coefficients since the experimental concentration profile is compared to an analytical solution, based on Fick’s second law, in which the initial profile is a step function by default. The real-time phase-shifting interferometer previously reported acquires the phase-shifted data from snapshots taken almost simultaneously, an essential element for real-time applications. Nevertheless, the use of different CCD sensors deteriorates the accuracy of the measurement due to the characteristic sensitivity of each sensor and time lag between frames. Therefore, the use of a single CCD sensor is desirable.

1.2 Measurement of Thermodiffusion

Thermodiffusion, also called Soret effect, is the diffusion of molecules under a temperature gradient [110, 188]. This phenomenon induces a separation of species, as opposed to the mixing of species that occurs in Fickian diffusion [60, 70, 71]. Thermodiffusion is of great importance in various fields. In the petroleum industry, for example, thermodiffusion determines the distribution of hydrocarbon mixtures in oil reservoirs [132]. In biotechnology, thermodiffusion (also called thermophoresis [161]) has been proposed as an alternative method to electrophoresis for separation of biomacromolecules, such as proteins and DNA [32]. Thermodiffusion also provides information about proteins concerning their molecular size, charge, and hydration shell [213], i.e. it has a strong potential for drug screening applications as well as basic research [86]. Therefore, various experimental techniques have been developed with the purpose of quantifying the Soret effect [162].

Most of the measuring techniques have been developed focusing on transparent bi-
nary solutions without the presence of biomolecules, such as proteins. Several European research groups established the Fontainebleau benchmark in a concerted effort to provide reference values for Soret, diffusion, and thermodiffusion coefficients \[98,162,163\]. This benchmark accounts for three binary mixtures formed at 50 wt% concentration and 25°C temperature by pairing three organic compounds: 1,2,3,4-tetrahydronaphthalene (THN), isobutylbenzene (IBB), and dodecane (C12). These compounds were chosen based on their relevance in oil reservoirs. Moreover, some recent studies have focused on thermodiffusion in ternary mixtures as a first step to clarify its mechanism in multicomponent systems \[99,121,126\]. Hence, it is necessary to develop a robust experimental technique that is capable of providing insight into macromolecular thermodiffusion in binary systems, with the aim of a further application in more realistic multicomponent environments.

Even though theoretical correlations have been proposed to predict the thermodiffusion phenomenon \[29\], complex molecular interactions have made these approaches a rather ambiguous approximation to specific molecular characteristics. This is another reason to improve the current experimental techniques, so that accurate data is obtained for further theoretical development. All the techniques that have been developed to measure thermodiffusion can be classified according to the heating configuration and the method for measuring concentration. There are two groups regarding the heating configuration: convectionless methods and methods with convective coupling \[162\]. Likewise, there are two groups regarding the concentration measurement method: chemical analysis and refractive index measurement.

The convectionless methods were the first methods to be developed (in fact, one of these methods was used by Soret to discover the thermodiffusion phenomena \[188\]). They consist on placing a binary solution inside a cavity and heating it such that the denser region of the solution resides on the bottom of the cell and, thus, creating a hydrodynamic stable system without convection. Convectionless methods usually make use of a standard Soret cell, which consists of a parallelepiped cavity with two horizontal rigid plates made of a good thermal conductive material, e.g. copper [401 W/(mK)] or aluminium [205
The plates are maintained at different constant temperatures by a thermostatic circulating coolant [95] or Peltier modules [99], the latter becoming the norm in recent years to achieve accurate and fast temperature control. The solution is usually heated from above to avoid natural convection. However, there are ranges of negative Soret coefficients when heating from below has a stabilizing effect [51] in comparison to heating from above with the same temperature difference.

In contrast to convectionless methods, convective coupling methods are those in which the sample is subject to mass transport due to both natural convection and thermodiffusion. The Rayleigh-Bénard configuration has been used to determine the Soret coefficient [166]. Thermogravitational column [30, 58] is another well-known method where a horizontal heat flux is applied to the sample. It is still a matter of debate to know which heating configuration, convectionless or with convective coupling, is the most adequate to measure Soret coefficients. Nevertheless, it is clear that in convectionless binary systems the measurement of the Soret coefficient is straightforward after the steady states for mass and heat have been reached [162].

Concerning the measurement method of the concentration, the optical techniques are regarded as the most accurate [55], providing reliable measurements of the Soret coefficients [127]. All optical techniques use the relation between the refractive index and the concentration—involving the so called contrast factors [178]—in order to conduct temporal measurements of concentration either in a localized point, e.g. in the case of the optical beam deflection (OBD) technique, or in a two-dimensional domain, e.g. in the case of the interferometric techniques. Furthermore, in addition to the probe laser beam used for concentration measurements, Thermal Diffusion Forced Rayleigh Scattering (TDFRS) [94, 211] and thermal lensing [35, 36] make use of a high intensity laser in order to introduce a temperature gradient within the sample. TDFRS has been widely used to determine Soret coefficients in polymers and colloids [57, 93, 212]. Nonetheless, in conventional TDFRS the use of an additive is required to absorb heat in order to increase the temperature of the sample, resulting in an undesired contamination that might
Development of phase-shifting interferometry for measurement of mass diffusion

Affect the transport properties of the species of interest. Therefore, to avoid the drawbacks of using a third component, techniques with in situ optical detection coupled with a boundary temperature control system have been developed, e.g. OBD [98] and interferometric techniques [51] [122]. Even though OBD is one of the most reliable methods currently available to determine Soret coefficients, it is a localized measurement that does not take into account any 2D or 3D characteristics of the thermodiffusion phenomena. In this study, therefore, we have focused on interferometric techniques in order to deepen our understanding of thermodiffusion.

Colombani et al. [51] used holographic interferometry to study hydrodynamic instabilities and the Soret effect in aqueous electrolytes. Mialdun and Shevtsova [122, 124] developed a Mach-Zehnder interferometer coupled with an image processing technique based on a fast Fourier-transform [194] in order to obtain a high-resolution phase diagram instead of the conventional interferogram. This method, termed optical digital interferometry (ODI), has drastically increased the accuracy of the interferometric measurement. ODI was validated with the Fontainebleau benchmark [125]. The technique was subsequently used to measure thermodiffusion in water-isopropanol binary mixtures in the International Space Station [127], study the influence of vibrations on the diffusion in liquids [180, 181], and investigate Fickian diffusion in ternary mixtures [121, 126]. In space, ODI from two perpendicular views was used to follow a component separation $\Delta C$ of less than 1% of its initial mean value. In these experiments, however, the measurement time is rather long, e.g. about 18 h for the space experiments. A shorter measurement time is desirable, mainly for three reasons. First, microgravity experiments are costly; second, conformational changes might occur in biomolecular solutions altering its Soret coefficient value; third, the experimental conditions are more difficult to control. Furthermore, in real applications, a smaller amount of sample is also desirable in order to decrease the measurement costs, which increase drastically for rare biomolecules.
1.3 Objectives

In this chapter, the main objective in this chapter is to develop a phase-shifting interferometer capable of performing highly accurate 2D measurements of the phase difference between the test beam and the reference beam by using a single CCD sensor. In addition, real-time image processing of the phase-shifted data is conducted in order to visualize the concentration profile of transparent solutions inside a diffusion cell or Soret cell. The main objectives are the following:

1. Construct a versatile and highly accurate optical interferometer.

2. Validate the measurement system through the measurement of isothermal diffusion and thermodiffusion in convectionless systems. The measurement system comprises the optical interferometer, the image processing program, and the inverse analysis.

The apparatus is validated for convectionless systems in order to be used in further application, such as Rayleigh-Bénard convection.

2 Phase-shifting Interferometry with Rotating Polariser and Real-time Image Processing

The phase-shifting interferometer comprises a polarising Mach–Zehnder interferometer with a CCD camera, a rotating polariser, and an image-processing program that uses a phase-shifting equation in order to obtain the phase difference between the test beam and reference beam in two-dimensions. In §2.1, the polarising Mach-Zehnder interferometer and the synchronization between the rotating polariser and the CCD camera is described. In §2.2, the principle of the proposed phase-shifting technique is explained by deriving the phase-shifting equation; here, the advantages and disadvantages of the optical system are
**2.1 Polarising Mach–Zehnder Interferometer**

The optical apparatus in this study is a Mach–Zehnder interferometer in which the linear polarisation angles of the test beam and reference beam are orthogonal. This interferometer is termed a polarising Mach–Zehnder interferometer [154]. It has the same measurement principle, advantages, and disadvantages of conventional Mach–Zehnder interferometers. The polarisation angle $\pi/2$ between the test beam and reference beam makes additional image processing possible by introducing a rotating polariser and implementing a phase-shifting algorithm.
Figure 2.3: Photo of the phase-shifting interferometer. It comprises a polarising Mach-Zehnder interferometer and a rotating polariser. The lateral spacing between the holes on the optical table is of 50 mm, which can be used as scale. The sketch of this optical apparatus is shown in Fig. 2.2.

Figure 2.2 shows a schematic diagram of the interferometer and the polarisation of the beams at different segments. Figure 2.3 shows a photo of the phase-shifting interferometer; the holes on the optical table have a lateral spacing of 50 mm and can be used as scale. A Helium–Neon laser beam (1) ($\lambda_{\text{beam}} = 633 \text{ nm, } 5.0 \text{ mW, Newport Corporation R-30991}$) is linearly polarized at an angle of $\pi/4$ with respect to the horizontal plane by a polarising plate (2). The intensity of the beam is adjusted with a ND filter (3). The beam is later amplified by an objective lens (5) and cut by a pinhole (6) so that only the most homogeneous part of the Gaussian intensity distribution is obtained; the objective lens and pinhole are part of the same spatial filter (Sigma-Koki Inc.). Then, the beam is collimated by a convex lens of $f = 500 \text{ mm}$ (7); here, a 35 mm diameter beam is obtained. The beam is then divided by a polarising beam splitter (8) (PBS, Newport Corporation 10BC16PC4) into a test beam and a reference beam with polarisation angles of $\pi/2$ and $0$, respectively. Here, the intensity of the test beam and reference beam is guaranteed to be the same by the polarising plate (2) placed just after the laser. The maximum visualization
Figure 2.4: Circular polarisation of light passing through a rotating polariser. (a) The beam is comprised of a test beam $A_o$, which is clockwise circularly polarized, and a reference beam $A_r$, which is counter-clockwise circularly polarized. It is shown how the phase shift in the wavefront direction is transformed into a phase shift in the polar direction. (b) The combined beam passes through a rotating polariser inclined by $\theta_r$ and rotating at $20\pi$Hz.

After splitting the laser beam into a test beam and reference beam, the test beam is passed through a diffusion cell (9). Light passing through different points of the diffusion cell usually exhibits different optical paths due to spatial refractive index variations caused by concentration or temperature profiles. The wave front of the reference beam remains unaltered so it can be used for comparison with the test beam. The test beam and the reference beam are later combined by another PBS (8) and directed, with a respective polarisation of $\pi/2$ and 0, to a convex lens of $f = 200$ mm (10). At this point, the polarisation angle between these two beams is orthogonal; therefore, no interference between the two beams occurs. For the beams to interfere, a quarter-wave plate (11) is placed after the lens (10) with its extraordinary axis inclined by $\pi/4$ so that the test beam and reference beam become circularly polarized. Since the angle of the extraordinary axis of the quarter-wave plate, i.e. $\pi/4$, is half way between the polarisation angles of the test beam and reference beam, i.e. $\pi/2$ and 0, respectively, the handedness of both polarized beams is opposite, i.e. the test beam is clockwise circularly polarized while the reference beam is counter-clock-wise circularly polarized. Therefore, interference occurs since both beams
are circularly polarized in opposite directions. This is shown in detail in Fig. 2.4(a), where the polarisation state of each beam after the quarter-wave plate (11) is indicated. Nevertheless, only partial interference is achieved because there are still orthogonal components of both beams. In order to guarantee complete interference, a polariser (12) is placed after the quarter-wave plate (11), such that the circularly polarized light is filtered for a single polarisation angle \( \theta_r \), as shown in Fig. 2.4(a). The interferogram can be clearly observed by placing a plate after the polariser (12), as shown in Fig. 2.5.

The key point of this interferometer is that the polariser (12) is mounted on a stepper motor (14) so that the transmission angle \( \theta_r \) of the rotating polariser is linearly varied to obtain interferograms with different intensities, as shown in Fig. 2.4(b). The interferometer as a whole was built on high-performance vibration isolation system (Herz Co. TDI-2010LAY) with a shock abortion system, as shown in Fig. 2.3. The whole setup was placed inside an enclosed room environmentally controlled. The room temperature is kept constant within an uncertainty of \( \pm 0.5 \)°C.

In this setup, the phase-shifting technique requires that the incident ray of light charges the same capacitor (sensor) of the CCD array at any rotating angle \( \theta_r \). Therefore, it
is crucial that the rotating polariser is as perpendicular as possible to the incident beam because the displacement $\gamma$ of the exiting beam increases in a non-perpendicularly aligned setup, as shown in Fig. 2.6. Moreover, placing the CCD sensor as close as possible to the rotating polariser is also a crucial factor because it reduces the displacement $\gamma$ in an exiting beam that is tilted. In addition to this optical problem, a poor alignment of the polariser generates undesired vibrations that might affect the highly sensitive optical system. The polariser is circular and its center of mass is then carefully aligned with the axis of the stepper motor to avoid mechanical vibrations. Eliminating all sources of vibration and disturbance is essential considering the sensitivity of the interferometer. Hence, in order to obtain a well-aligned setup that is free of vibrations, it is imperative that the polariser is placed with its center of mass aligned to the axis of the stepper motor while preserving its perpendicularity to the optical axis and closeness to the CCD sensor.

In this study, the interferograms were acquired using a CCD camera (13) (Hamamatsu Inc. C3077-70) at a rate of 30 fps. This camera is an interlaced camera with a $640 \times 480$-pixel resolution. In order to increase the spatial resolution in the direction of the quasi-one-dimensional diffusion field, the camera is placed vertically as shown in Fig. 2.5(a). In the initial setup, the incident beam passes above the stepper motor before passing through the rotating polariser. However, the stepper motor gets quite hot when used for long
periods of time, as shown by the thermoviewer measurement of the surface of the stepper motor in Fig. 2.5(b). This might generate an undesired natural convection above the stepper motor that might have a negative effect on the quality of the measurement. The setup shown in Fig. 2.5 is simple and, therefore, is used in isothermal experiments where the time is short. For long-time measurements, e.g. in the thermodiffusion experiments, the stepper motor is placed next to the incident beam (see Fig. 2.10).

Notice that the CCD camera and the rotating polariser are on a stage that is placed on a rail, as shown in Fig. 2.3 (also see Fig. 2.10(a)). This is important because the visualization range can be adjusted by setting the position of the CCD camera on the rail. For the current interferometer, the height of the visualization field view can be adjusted between 1 mm and 10 mm.

The motivation in modifying the conventional Mach–Zehnder interferometer into the polarising Mach–Zehnder interferometer described above lies in the application of a temporal phase-shifting technique [81]. In this technique, the phase difference between the test beam and reference beam, from 0 to $2\pi$, is obtained at a high spatial resolution by processing the intensity of interferograms taken at different transmission angles $\theta_r$ of the rotating polariser. In this experimental setup, the intensities of the fringe patterns were taken for the angles $\theta_r = 0, \frac{2\pi}{3}, \frac{4\pi}{3}$ (relative to each other), as shown in Fig. 2.4(b). The stepper motor used for rotating the polariser is a five-phase stepper motor controlled by a high precision motor driver (Oriental Motor Co. SG8030J-D). The angular speed of the rotating polariser $\dot{\theta}_r$ was set to $20\pi$ Hz. Consequently, the CCD camera set at 30 fps acquires three interferograms per revolution.

### 2.2 Phase-shifting equation

Temporal phase-shifting techniques have been described by Creath [53] and Schreiber et al. [177]. In this subsection, the phase-shifting equation for three recorded interferograms is derived and briefly explained. The derivation procedure of the phase-shifting equation is important to understand the advantages and disadvantages of the proposed
phase-shifting technique. The resulting phase-shifted data is presented in §2.4, where the accuracy of the proposed method is compared to another phase-shifting techniques reported by Maruyama et al. [116].

In this study, a three-bucket temporal phase-shifting technique [53] was chosen to obtain high-resolution phase-shifted data. A rotating polariser with transmission angle $\theta_r$ is placed before two CCD camera in the polarising Mach-Zehnder interferometer, as shown in Figs. 2.2, 2.3, and 2.4.

The amplitude $A(x,z)$ of the light passing through a rotating polariser with a transmission angle $\theta_r$ is

$$A(x,z) = A_r \cos(\omega t - \theta_r) + A_o \cos(\omega t + \theta_r + \phi),$$  \hspace{1cm} (2.1)

where $\phi$, $\omega$, $A_r$, and $A_o$ are the phase shift, the angular frequency of the circularly polarized light, the amplitudes of the reference beam, and the amplitude of the test (or object) beam, respectively. Here, the $x$ axis is horizontal while the $z$ axis is vertical (see the coordinate system in Fig. 2.7). Note that the amplitude of light passing through a given location $(x_1, z_1)$ can be expressed as a function of $\theta_r$ and $\phi$, i.e. we can write $A(\theta_r, \phi)$. The intensity of light $I(\theta_r, \phi)$ acquired by the CCD sensor at a given location is then equal to the time-averaged absolute value of the amplitude described in Eq. (2.1). Therefore, the intensity acquired at $(x_1, z_1)$ is

$$I(\theta_r, \phi) = \frac{1}{P} \int_0^P |A(\theta_r, \phi)|^2 dt,$$  \hspace{1cm} (2.2)

where $P$ is the period of the polarized light which is defined as $P = 2\pi/\omega$. After expanding arithmetically and simplifying Eq. (2.2), $I(\theta_r, \phi)$ becomes

$$I(\theta_r, \phi) = \frac{1}{2} (A_r^2 + A_o^2) + A_r A_o \cos(\phi + 2\theta_r).$$  \hspace{1cm} (2.3)

Therefore, the spatial intensity $I$ depends on both the transmission angle $\theta_r$ and the phase
shift $\phi$; the former is controlled by a stepper motor and the latter is the physical quantity to be measured. Creath [53] has described the three-bucket phase-shifting with a constant $\Delta \theta_r$ value, in particular for $\Delta \theta_r = \pi/2$ and $2\pi/3$. We consider that $\Delta \theta_r = 2\pi/3$ is the best choice in order to simplify the synchronization procedure of the rotating polariser and the CCD cameras. The phase-shifting interferograms $I_1$, $I_2$, $I_3$ that are acquired at $\theta_r = 0$, $2\pi/3$, $4\pi/3$, respectively, become

\begin{align}
I_1(\phi) &= \frac{1}{2}(A_r^2 + A_o^2) + A_r A_o \cos(\phi), \quad (2.4a) \\
I_2(\phi) &= \frac{1}{2}(A_r^2 + A_o^2) + A_r A_o \cos(\phi + \frac{4\pi}{3}), \quad (2.4b) \\
I_3(\phi) &= \frac{1}{2}(A_r^2 + A_o^2) + A_r A_o \cos(\phi + \frac{8\pi}{3}). \quad (2.4c)
\end{align}

Here, we assume that the phase shift $\phi$ is constant for the three consecutive intensities $I_1$, $I_2$, and $I_3$, i.e., the technique is only applicable for a steady state phenomenon or for phenomena where $\phi$ does not change significantly between $I_1$, $I_2$, and $I_3$. The amplitudes $A_r$ and $A_o$ in Eq. (2.4) can be cancelled by using basic algebraic operations. The phase shift detected by a pixel in the location $(x_1, z_1)$ is then

$$
\phi = \arctan\left(\sqrt{3} \frac{I_2 - I_3}{I_2 - 2I_1 + I_3}\right). \quad (2.5)
$$

The phase-shifted data (phase map) for the whole two-dimensional domain is written as

$$
\phi(x, z) = \arctan\left(\sqrt{3} \frac{I_2(x, z) - I_3(x, z)}{I_2(x, z) - 2I_1(x, z) + I_3(x, z)}\right). \quad (2.6)
$$

This is the phase-shifting equation used in this study to determine the wrapped phase map within a diffusion cell, Soret cell, or Rayleigh-Bénard cell. Because of the nature of the arctangent calculation in Eq. (2.6), the phase calculation is done modulo $\pi$ (between $-\pi/2$ and $+\pi/2$). Hence, the signs of quantities proportional to $\sin \phi$ and $\cos \phi$ must
be examined in order to remove the phase ambiguities and determine the phase modulo $2\pi$ [53].

**ADVANTAGES OF PHASE-SHIFTING INTERFEROMETRY**

The main advantage of this technique compared to conventional interferometry is that the resolution of the phase shift measurement, i.e. the intensity resolution measured by the CCD camera, is increased by $2^8$ ($=256$). The phase difference between fringes in a conventional interferogram, e.g. those shown in Fig. 2.12, is of $2\pi$ by definition. Hence, only the values corresponding to the maximum or minimum intensity in the interferogram are used to determine the phase difference; the phase difference resolution would then be $2\pi$ rad. On the other hand, the phase-shifted data gives a gray scale value of the phase difference, expressed in bytes, from 0 to $2\pi$ (modulo $2\pi$) or from 0 to $\pi$ (modulo $\pi$). Therefore, the resolution of the measurement of the phase difference becomes $2\pi/2^9$ rad (modulo $2\pi$). This is a much higher resolution than that of FFT methods, where the typical resolution is around $2\pi/50$ and can be as high as $2\pi/100$ [81].

Furthermore, the spatial resolution is determined by the size of the CCD sensor (fixed pixel grid) and the focus of the lens (10) (see Fig. 2.2), which is varied depending on the scale of the experiment. In this study, the spatial resolution is in the range of 20-40 $\mu$m. This digitized measurement is far superior than conventional interferometry where it is difficult to precisely locate the maxima or minima of the fringe intensity pattern. A good measurement precision in conventional interferometry occurs for an interferogram highly dense in fringes. However, for a measurement where the variation of the refractive index is small, few fringes (maxima or minima of the intensity) in the interferogram are obtained. This obstacle is overcome by phase-shifting interferometry, where the data between fringes can be retrieved. Notice that the spatial resolution differs from the accuracy of the phase measurement which, in addition to the accuracy of the optical setup, depends on the surrounding state, e.g. isolation of the optical table air disturbances.

Finally, the simplicity of Eq. (2.6) makes this image processing a more straightfor-
ward computation than with FFT methods. Therefore, a real-time image processing is now feasible. This optical system, however, has some drawbacks.

**Disadvantages of Phase-shifting Interferometry**

In Eq. (2.6) we have assumed that the phase shift $\phi(x,z)$ does not depend explicitly on time, i.e. it is only applicable to time-invariant systems. This is because $\phi$ is taken as constant in Eqs. (2.4)(a-c). Hence, the technique is only applicable to systems where $\phi(x,z)$ between three consecutive snapshots is zero (steady state) or negligible (quasi-steady-state). In other words, the measurement principle is no longer valid when $\phi$ varies significantly within $1/10$ s. The suggested phase-shifting technique can only be used to study steady state phenomena [184] or slow unsteady state phenomena, such as mass diffusion.

Another drawback of the proposed phase-shifting interferometer is the complex optical setup in comparison to other optical techniques, such as FFT-based optical digital interferometry (ODI) [125]. This complexity mainly consists in adjusting the polarization state of light in the polarizing phase-shifting interferometer, as shown in Fig. 2.2, and the synchronization of the rotating polariser and the CCD camera, as shown in Fig. 2.4. If high accuracy and measurement time are not an issue, simpler optical methods for determining isothermal diffusion coefficients could be used [39, 152, 173, 174].

In addition, phase-shifting interferometry also has the drawbacks intrinsic to Mach-Zehnder interferometry. For example, only transparent fluids can be studied. Fortunately, most of the liquids in biological systems are transparent and, therefore, can be studied with the proposed setup. Also notice that the refractive index gradient perpendicular to the light beam cannot be too large in order to avoid a strong beam deflection. Finally, if the distance between fringes is in the order of the pixel size, then the phase-shifted data becomes unreadable. FFT methods are more suitable to obtain the phase map when there is a large number of fringes within the interferogram.
2.3 Orthogonal Phase-Shifting Interferometry

The optical system consists of two orthogonally aligned Mach-Zehnder phase-shifting interferometers (see §2.1 for the description of a single interferometer). The technique is then termed orthogonal phase-shifting interferometry (OPSI). Two independent beams with the same wavelength permit different sensitivities, which are determined by the optical path (OP) inside the cell. The sensitivity of the interferometers may also be varied by changing the laser wavelength [99]. A brief description of the modified interferometric layout is presented.

The interferometric layout is shown in Fig. 2.7. This optical device was built on the same high-performance vibration isolation system (Herz Co., TDI-2010LAY) and in the same environmentally controlled room (±0.5°C uncertainty) as the single phase-shifting interferometer described in §2.1. Figure 2.8 shows the initial arrangement of the various optical elements on the optical table. The optical axis of both interferometers is set to 200 mm above the optical table. For a quasi-one-dimensional phenomenon, such as the diffusion or thermodiffusion fields created in this study, only one interferometric view is sufficient. However, the introduction of an additional interferometer provides two different optical paths for the test beams within a cell (diffusion, Soret, or Rayleigh-Bénard cell). Thus, different sensitivities can be selected in order to visualize two different phenomena, such as heat conduction and mass diffusion. In this study, both interferometers are used to measure two-dimensional concentration and temperature profiles. For example, in a thermodiffusion experiment, the interferometer with the laser beam \( L1 \) is used during the thermodiffusion phase (\( \Delta T \neq 0 \)), while the interferometer with the laser beam \( L2 \) is used during the isothermal diffusion phase (\( \Delta T = 0 \) K), where \( \Delta T \) is the temperature difference between the upper and lower boundaries (see §4.2). In a Rayleigh-Bénard experiment, both interferometers can be used to see different temperature profiles from the orthogonal views.

Two Helium-Neon laser beams (\( L1 \) Newport Corp., \( \lambda_{\text{beam}} = 633 \) nm, 5.0 mW, and \( L2 \)
Neoark Corp. \( \lambda_{\text{beam}} = 632.8 \, \text{nm}, 7.0 \, \text{mW} \) are linearly polarized by using polarisers with their transmission angle fixed to \( \pi/2 \) with respect to the horizontal. The intensity of each laser beam is adjusted using ND filters. Here, an independent intensity adjustment for each light source is necessary in the case the interferometers have different magnifying rates, laser power output, or CCD cameras. The beams are then expanded with spatial filters (Sigma-Koki Inc.) and collimated with convex lenses. polarising beam splitters (PBS) (Newport Corp. 10BC16PC.4) are then used to split the beams into a test beam and a reference beam with orthogonal polarisation state. The test beams from lasers 1.
Figure 2.8: Setup of the orthogonal phase-shifting interferometer. The optical axis of both internal interferometers is set 200 mm above the optical table. The crossing of the test beams in the test section is shown in Fig. 2.9.

and L2 have horizontal and vertical linear polarisation, respectively; whereas the reference beams from lasers L1 and L2 have vertical and horizontal linear polarisation, respectively. The polarisation state of light for each segment of the interferometer is indicated by the square insets in Fig. 2.7. The collimated test beams are shown in Figs. 2.9(a,c) just at the test section where they overlap. Figure 2.9(b) shows the unexpanded test beam L2 (the spatial filter and lenses were removed for L2) and the collimated L1 just at the crossing point in the test section.

The test and reference beams of each interferometer are then combined by another PBS and focused on a CCD camera (Hamamatsu Inc. C3077-70) by convex lenses. The combined beams for each interferometer are shown in Fig. 2.9(d). These areas correspond to the maximum visualization area for L1 and L2. This is more than enough for diffusion experiments where the visualization scale is small (less than 3 and 8 mm for thermodiffusion and isothermal diffusion experiments, respectively). However, for experiments dealing with natural convection, this size of the collimated light is the limiting factor since it limits the Rayleigh number (proportional to the characteristic length to the power three). At this point (after the second PBS), the relative polarisation angle between
the reference and test beams is $\pi/2$. Then, the quarter-wave plates are placed after each focusing lens to change the polarisation state of light. Here, the beams are circularly polarized with opposite handedness, i.e. for $L1$ ($L2$), the reference (test) beam is clockwise circularly polarized, while the test (reference) beam is counter-clockwise circularly polarized, as shown in the detailed circular polarisation state in Fig. 2.7. The light is filtered with the polariser in the direction of its extraordinary axis which is tilted by $\theta_r$, allowing a complete interference. The CCD cameras acquire an image similar to that of a typical interferogram (see Fig. 2.12). A single polariser in disk-form with diameter of 130 mm was used to polarize both interferometric beams.
Figure 2.10: Photos of the orthogonal phase-shifting interferometer. The sketch of this interferometer is shown in Fig. 2.7. (a) Orthogonal phase-shifting interferometer. (b) Upper view of the rotating polariser and surrounding elements.
2.4 IMAGE PROCESSING

Two types of image processing are conducted: real-time image processing and post-experimental image processing. The real-time image processing accounts for the phase-shifting, the one-dimensional unwrapping of the phase-map, and the display of the concentration profile. The post-experimental image processing accounts for the background subtraction and the two-dimensional unwrapping of the phase map.

The image processing programs were written in Processing programming language, which is a free integrated development environment easily accessible in the internet. The Processing language project was initiated in 2001 by Casey Reas and Benjamin Fry [176]. The language builds on the Java language, but uses a simplified syntax and graphics programming model. The advantages of Processing is that the program is compiled and executed with the same command, and that the results are immediately displayed on the monitor of the computer while allowing interaction with its peripherals. In addition to this, there are many libraries created by third parties which are available. In this study, the JMyron library [183] was used for acquiring the video feed and transform the frames into matrices that can be processed with an original code. The images from the CCD camera are directly acquired by connecting the video output to a computer using a standard USB-Video conversion cable.

REAL-TIME PHASE-SHIFTING PROCESSING

The program acquires three consecutive frames of $640 \times 240$ pixels at intervals of $1/30$ s, and store them in a memory address. Each pixel has an 8-bit value (0 to 255 brightness in decimal value) and represents the light intensity $I_1$, $I_2$, and $I_3$ in Eqs. (2.4)(a-c). In order to obtain the phase difference at the discrete positions $(y, z)$ each pixel value for three consecutive images is substituted in Eq. (2.6). As a result the phase map in radians is obtained. In this process, the interlace protocol of the CCD camera must also be taken into account, since the rows of pixels change from odd to even between consecutive frames.
Fig. 2.11: Results for the phase-shifting processing modulo $\pi$. The phase-shifting processing results are displayed in real-time. The timer that is used to register the measurement time is displayed in the lower right corner.

due to the interlace protocol. Figure 2.11 shows the display window with the phase-shifted data just at the beginning of an isothermal diffusion experiment. The upper half region covered with equidistant lines is that of air; the lower half region with the quasi-isothermal value corresponds to a homogeneous solution (see §3 for more details on the isothermal experiment). The green box at the lower right indicates the timer displayed in $10^{-1}$ s. This timer is important to accurately measure the phenomena in $\Delta t$ intervals. Automated measurements eliminate bias error due to manual operation.

Fig. 2.12 shows the raw interferogram intensities $I_1$, $I_2$, and $I_3$ and the derived phase-shifted data $\phi(y, z)$ modulo $\pi$. These raw interferograms are taken at a transmission angle $\theta_r = \theta_{ini}, \theta_{ini} + 2\pi/3,$ and $\theta_{ini} + 4\pi/3$ of the polariser. $\theta_{ini}$ is the initial angle of the rotating polariser and does not affect the phase-shifting results. The derived phase-shifted data, which is also termed phase map, shows two fringes for every fringe in the interferogram, revealing the modulo $\pi$ characteristic. Moreover, notice that the Cartesian coordinates in Fig. 2.12 are those of the phase-shifting interferometer that uses the light source $L2$, as indicated in Fig. 2.7. The equidistant and parallel lines in the phase-shifted data suggest that the wavefront of the test beam is planar. Furthermore, the tilt of the mirrors $M1$ and $M4$ can be adjusted to achieve the isophase condition, which corresponds
Fig. 2.12: Phase-shifted data $\phi(y, z)$ acquired from three consecutive interferograms at the transmission angles $\theta = \theta_{ini}, \theta_{ini} + 2\pi/3,$ and $\theta_{ini} + 4\pi/3$. The phase-shifting equation, i.e. Eq. (2.6), is used to obtain the phase-shifted data modulo $\pi$ by using the interferometer with the laser beam $L2$ (see Fig. 2.7). An additional adjustment of the reference mirror—$M1$ and $M4$ for $L1$ and $L2$, respectively—creates the isophase condition.

Figure 2.13 shows the results of the Processing program that is used to display the intensity of the phase-shifted data on a vertical line. This program is particularly useful to adjust the ND filter of each interferometer in order to achieve a linear intensity profile (see Fig. 2.13), and also to adjust the reference mirrors in order to obtain the isophase or infinite fringe conditions (see Fig. 2.12). The obtained phase-shifted data may also be transformed into modulo $2\pi$ data, as shown in Fig. 2.14(a). The phase-shifted data quality is largely improved in comparison to that obtained with the phase-shifting interferometer previously reported by Maruyama et al. [115, 116] shown in Fig. 2.14(b). This is mainly due to the use of a single CCD sensor. When measuring intensity, i.e. the most
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Figure 2.13: Phase-shifted data modulo $\pi$ for equidistant fringes in absence of a refractive index gradient. The profile indicates a quasi-linear distribution of the wrapped phase shift. The phase-shifted data and the intensity profile are shown in real-time for the adjustment of the optical apparatus.

Figure 2.14: Comparison of the quality of phase-shifted data (modulo $2\pi$) between that obtained by (a) the system proposed in Fig. 2.2, and (b) the configuration proposed by Maruyama et al. [116] and shown in Fig. 2.1. It is evident that the current system is more accurate and reliable.
Figure 2.15: Phase-shifted data results in an isothermal diffusion experiment. The phase-shifted data are visualized in real-time and are output every $\Delta t = 100$ s. This value is set in the program. A lower density solution is placed over a higher density solution inside a diffusion cell (see §3).

...important direct measurement in this study, the use of a single CCD sensor eliminates the bias error caused by different sensitivity and time lag between sensors. Therefore, a single CCD sensor provides snapshots with the exact same sensitivity taken at same time intervals. Moreover, the data is further processed in real-time while continuing the spatial phase difference acquisition. In this study, the processing performance was optimized by conducting the phase-shifted data acquisition and data analysis separately with two computers in parallel.

Figure 2.15 shows an example of the phase-shifted data that is obtained during a diffusion experiment. Here, the program was set to automatically output the phase-shifted data every $\Delta t = 100$ s. Furthermore, in order to reduce the computational load of calculating the arctangent in Eq. (2.6) for 153600 pixels, the calculation range was reduced to approximately one third of the total domain. In this experiment, a higher density solution is first injected in a diffusion cell and then a lower density solution is placed on top in order to create the concentration gradient and initiate the diffusion process. A detailed
The phase-shifted data is a wrapped phase map between 0 and \(2\pi\) for a modulo \(2\pi\) measurement (likewise, when expressed as modulo \(\pi\) it is between 0 and \(\pi\)). The first step to relate this wrapped phase map with the concentration and temperature profiles within the cell is to unwrap this phase map, i.e. connect all its discontinuities. The simplest case for unwrapping a phase map is when the fringes in the phase-shifted data are parallel, such as in the isothermal diffusion case shown in Fig. 2.15.

Here, the determination of mass diffusion coefficients is done by fitting a numerical calculation of the concentration distribution to the experimental concentration profile (this step is explained in detail in §3.4). Therefore, an accurate measurement of the transient concentration profiles is required. This measurement is conducted by calculating the phase-shifted data \(\phi(x,z)\), process it to obtain the unwrapped phase difference \(\psi(x,z)\), and then apply the proper boundary conditions to obtain the concentration profile. In an isothermal diffusion experiment, the phase difference, the refractive index, the density of the fluid, and the concentration are all directly proportional to each other and, hence, we can obtain the concentration difference \(C(x,z)\) from the phase difference \(\psi(x,z)\). If the boundary conditions for the concentration are unknown, such as in the case of a thermodiffusion experiment, then the appropriate contrast factors are required.

The process of acquiring the concentration profile from the phase-shifted data is shown in Fig. 2.16. Figure 2.16(a) shows a typical phase-shifted data of a free diffusion isothermal experiment obtained by using Eq. (2.6); Fig. 2.16(b) indicates the distribution of the phase difference, from 0 to \(2\pi\), along the segment \(\overline{ab}\); Fig. 2.16(c) shows the absolute phase difference obtained by connecting the phase-shifted data at discontinuous points beginning from the first pixel. This unwrapped phase shift is directly proportional to the concentration, since the refractive index is also directly proportional to concentration. The change of the unwrapped phase shift \(\Delta \psi\) is linearly related to the change of the refractive index \(\Delta n\) as follows:
\[
\Delta n(x, z) = \frac{\lambda_{\text{beam}}}{2\pi L} \Delta \psi(x, z),
\]

where \( L \) is the length of the optical path (OP) and \( \lambda_{\text{beam}} \) is the wavelength of the laser beam (fixed to \( \lambda_{\text{beam}} = 632.8 \text{ nm} \) in the current optical setup). The variation of the refractive index \( \Delta n \) in Eq. (2.7) might include the contributions from both temperature and concentration [125] when neither contribution is optically suppressed. The contribution of pressure is neglected since the pressure inside the cell is constant. Therefore, the concentration or temperature distribution can be obtained from Fig. 2.16(c) by applying the proper boundary conditions. Figure 2.17(a) shows the concentration profile derived in an isothermal diffusion experiment.

Finally, in order to increase the accuracy of the measurement, the concentration profile for a given domain is averaged, as shown in Fig. 2.17(b). In an isothermal diffusion experiment, the average is only taken after the initial disturbance due to the injection process has disappeared and the diffusion process within the cell has become quasi-one-dimensional. In a thermodiffusion experiment, the average is taken after a linear temperature profile
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Figure 2.17: Average of unwrapped phase shift in a one-dimensional diffusion experiment. (a) The unwrapped two-dimensional concentration distribution. (b) The average along y (horizontal direction) as a function of the position $z$. This profile is smoother than the profile obtained from a single line.

within the Soret cell has been reached.

The unwrapping procedure described in Fig. 2.16 is conducted while the phase-shifted data is being acquired. The concentration or temperature profile within a cell is displayed on a monitor in real-time. Since the phase-shifted data is already available as matrices inside the computer memory, this data can be processed and analysed while the diffusion process is taking place, for example, to determine the mass diffusion coefficients by inverse analysis (explained in §3.4). If the time required to complete the image processing is fast enough to ensure the same refractive index between frames at intervals of $1/30$ s, then a real-time image processing is possible (see the drawbacks of the apparatus in §2.2).

A screen shot of the program written in Processing language is shown in Fig. 2.18. This program is named Emerald. The entire graphical user interface (GUI) was built from scratch with an original design. The operation of the program is fast and user-friendly, while keeping its main functionality, i.e. displaying and save the experimental information. The operation panel with its buttons and timer are shown in the 4th quadrant. For a more detailed explanation of each button see Fig. 2.19. Important functionalities of these buttons include: initiate the phase-shifting processing, select the average area, unwrap

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This program displays: the phase-shifted data $\phi(x/y,z)$ computed with Eq. (2.6) for the whole pixel domain with the unwrapped phase shift $\psi(x/y,z)$ displayed in blue tone (2\textsuperscript{nd} quadrant), the unwrapped and averaged phase shift $\psi_{ave}(z)$ or the concentration profile within the cell $C(z)$ (3\textsuperscript{rd} quadrant), the temporal variation of the concentration for an equidistant grid (1\textsuperscript{st} quadrant), and the operation panel with its buttons and timer (4\textsuperscript{th} quadrant). $x/y$ indicates that the horizontal axis can be either $x$ or $y$, as shown in the test section in Fig. 2.7.
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Figure 2.19: A more detailed explanation of the panel of the real-time processing program (4th quadrant in Fig. 2.18). The function of the different buttons is indicated.

(link) the discontinuous phase-shifted data, apply the boundary conditions, and save the experimental data which are displayed. Useful functions, such as reading, recording, and displaying the scale are also included (see 2nd quadrant; the parentheses under the scale indicate the number of pixels per mm). The most important function is the processing of the phase-shifted data \( \phi(y, z) \), which is computed with Eq. (2.6) for the whole pixel domain. These real-time phase-shifted data are displayed in the 2nd quadrant. Moreover, as explained in Fig. 2.17(a), the one-dimensional unwrapping is conducted for all the lines perpendicular to the isophase lines. These results are displayed in the 2nd quadrant in blue tone, with the darker tone indicating a higher concentration. The 1st quadrant shows the temporal variation of the averaged phase shift \( \psi_{\text{ave}}(t) \) for each grid. If the grids are too dense, then \( \psi_{\text{ave}}(t) \) is shown for grid intervals.

The unwrapped and averaged phase shift profile \( \psi_{\text{ave}}(z) \) is displayed in the 3rd quadrant. If the contrast factor is positive, this profile is then identical to the concentration profile within the cell \( C(z) \), whereas for a negative contrast factor the profiles are opposite (see §4.3 for the explanation on the contrast factors). With Emerald, we can also follow the temporal variation of the concentration \( C(t) \), which is related to \( \psi_{\text{ave}}(t) \), for a grid.
applied on the unwrapped phase shift. The equidistant grid is shown within the blue tone rectangle in the 2nd quadrant in Fig. 2.18.

Notice that the smoothness of the spatial profiles (3rd quadrant) and temporal profiles (1st quadrant) indicates that the spatial measurement is more precise than the temporal measurement. This might be due to an accumulative error in the synchronization of the rotating polariser and CCD camera. The smoothness (precision) of the spatial profiles can be further improved by adjusting the ND filter in the interferometer and by adjusting the sensitivity of the CCD sensors. The smoothness (precision) of the temporal profiles can be improved by avoiding any kind of vibration of the optical table or disturbance due to the surrounding air, and also by improving the synchronization of the rotating polariser and the CCD camera.

**POST-EXPERIMENTAL IMAGE PROCESSING**

The post-experimental image processing accounts for the two-dimensional unwrapping of the phase-shifted data and the subtraction of the initial unwrapped phase-shifted data. One of the most important advantages of digital interferometry is the suppression of the optical defects of the apparatus, e.g. possible defects found in the mirrors, prisms, or cell walls. This same advantage is found in the more conventional holographic interferometry as described by Colombani *et al.* [50], where the defects are suppressed by initially recording the interference pattern of the test beam and reference beam in a holographic plate, and then illuminating the same plate only with the test beam. In contrast, in optical digital interferometry an initial phase-shifted data is unwrapped and recorded with the cell filled with a liquid of constant refractive index (i.e. homogeneous liquid without temperature or concentration gradients), which will be subsequently subtracted from the phase difference acquired during the mass diffusion or natural convection experiment.

Figure 2.12 shows the phase-shifted data obtained without placing the cell in the test section. The parallel and equidistant fringes of the phase-shifted data indicate that there are virtually no deformations in our interferometric setup. However, the phase-shifted
Figure 2.20: Post-experimental treatment of phase-shifted data. The phase-shifted data $\phi$ modulo $\pi$ for a homogeneous binary solution inside a Soret cell (see Fig. 2.39) is shown in the left. The unwrapped phase shift $\psi$ is obtained. The unwrapped phase map corresponds to the deformed wavefront.

Data shown in Fig. 2.20 indicates that the wavefront is curved when placing the cell in the test section of the interferometer. Here, the cell is filled with a binary solution maintained at constant temperature and concentration, i.e. giving a constant refractive index. The curved wavefront is, therefore, produced solely by the deformation of the quartz walls. See §3.1, §4.2, and Chapter VI for more details on the diffusion cell, the Soret cell, and the Rayleigh-Bénard cell, respectively. Figure 2.20 also shows the unwrapped phase map $\psi(x,z)$ that is obtained from the wrapped phase-shifted data $\phi(x,z)$. This phase difference is an accurate measurement of the deformed wavefront, as indicated. Furthermore, the initial unwrapped data are subtracted from the unwrapped data acquired during the thermodiffusion experiment in order to suppress the phase difference caused by the optical defects in the apparatus (including those of the quartz walls). This process yields the phase difference due to the refractive index variations caused solely by temperature and concentration gradients within the cell.

In §2, a method for conducting high resolution measurements of the phase shift distri-
bution in transparent liquid systems was explained. A polarising Mach-Zehnder interferometer with a rotating polariser was built in order to observe spatiotemporal variations of refractive index within a cell. A phase-shifting algorithm was written in Processing language in order to carry out the image processing of the phase-shifted data. The program was further modified to conduct real-time measurement of one-dimensional concentration (or temperature) profiles within a cell. Important features of this program include, but is not limited to, the phase-shifting processing, display current one-dimensional and averaged unwrapped profile while the phenomena is occurring, and track the temporal variation of the unwrapped phase shift for a predefined grid.

This optical system is validated by studying two well-known phenomena, i.e. isothermal diffusion and thermodiffusion. After the system is validated, a further application to steady natural convection is performed (see Chapter VI).

3 Validation of the optical system for measurement of Fickian diffusion

In this section, the optical apparatus described in §2 is validated by the visualization and measurement of isothermal diffusion in binary solutions. A convectionless system is chosen for the measurement of isothermal diffusion coefficients. Methods that deal with coupled forced convection and mass diffusion, such as the Taylor Dispersion method [143], are usually less accurate. The diffusion experiment consists in obtaining the transient concentration profile in a given binary solution. The diffusion field is initiated by creating a concentration gradient inside a diffusion cell. The phase-shifted data are then acquired at given time intervals. The experimental concentration profile is obtained by assuming a direct proportionality between the unwrapped phase shift and the concentration. This assumption is valid as long as the refractive index and the concentration are linearly related. In the validation, the two well-known aqueous solutions of NaCl and sucrose are used. The refractive index of these binary solutions is linearly proportional to the concentration.
for the concentration ranges considered, as reported by bin Mat Yunus et al. [24]. Even for binary solutions in which the refractive index and concentration do not exhibit a linear relation, as in the case of an ethanol-water solution [87], linearity can be assumed for experiments where the concentration difference is small enough.

### 3.1 Diffusion Cell

The diffusion cells used in this study are rectangular parallelepiped quartz cells that are commercially available and manufactured by Fine Inc. Some of the most frequently used cells in these experiments are shown in Fig. 2.21. For isothermal experiments, the width of the cell (perpendicular to the optical path, OP) could be equal to 1, 2, 5, and 10 mm. The black cells shown in Fig. 2.21 have a width of 2 and 5 mm; these are used in isothermal diffusion experiments where the concentration difference $\Delta C$ is small. Here $\Delta C = C_{\text{high}} - C_{\text{low}}$, where $C_{\text{high}}$ and $C_{\text{low}}$ are the high and low concentrations, respectively. Commercial cells with OP from 1 to 50 are available; the OP for the cells shown in Fig. 2.21 from left to right is 20, 10, 10, 2, and 1 mm. A longer OP increases the sensitivity of the measurement, as stated in Eq. (2.7). The height of the cells is 45 mm. The chosen diffusion cell is fixed in a cell stand (see Fig. 2.24), which is placed at the test section of the interferometer (see Fig. 2.7).
In order to obtain a good quality experiment, an optimum number of fringes should be obtained. If there are too few fringes, the measurement resolution is drastically reduced. On the other hand, if the number of fringes is too large, the detection of the discontinuities for neighbouring pixels is no longer possible disrupting the unwrapping procedure of the phase-shifted data. When the camera is set horizontally so that a 240 pixel resolution is obtained in the direction of the mass flux, a maximum number of 15 fringes can be unwrapped without difficulty. In some experiments the camera is set vertically, as shown in Fig. 2.5, so that a resolution of 640 pixels in the direction of the mass flux is obtained. The resolution almost triples when the camera is set vertically. Therefore, the optimum number of fringes when the camera is horizontal and vertical is approximately 13 and 30, respectively.

To control the number of fringes in an isothermal environment, only two parameters can be modified. One is the concentration difference between the high concentration solution and the low concentration solution (see §3.2), and the other is the thickness of the cell which increases the OP of the test beam. Figure 2.22 shows the relation between the number of fringes observed in the phase-shifted data and the initial concentration difference. The results indicate a direct proportional relation between initial concentration difference, \( \Delta C \) [mg/ml] and the number of fringes observed.

**Figure 2.22:** Relationship between concentration difference and the number of fringes for NaCl in a diffusion cell with 1 mm optical path (OP). (a) Phase-shifted data obtained for different concentration differences \( \Delta C \). (b) The discrete number of fringes as a function of the initial concentration difference. A direct proportional trend is observed.
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Figure 2.23: Relationship between optical path (OP) and the fringe number for a constant $\Delta C = 20$ mg/ml. (a) 5 fringes are observed when the OP is $L = 1$ mm. (b) 11 fringes are observed when the OP is $L = 2$ mm.

difference and the discrete number of fringes. On the other hand, the phase-shifted data in Figs. 2.23(a,b) show that the number of fringes is doubled for a diffusion cell whose width is doubled. This indicates that the phase shift is proportional to the OP, as suggested by Eq. (2.7). Moreover, as shown in Fig. 2.23(c), there is a match between the concentration profiles obtained from these two phase-shifted data. Here, the resolution for the concentration measurement is doubled in the 2 mm thick diffusion cell since the number of fringes is also doubled.

Even though both, the concentration difference $\Delta C$ and the OP, can be varied to optimize the number of fringes for the unwrapping procedure (see Fig. 2.16), $\Delta C$ is usually fixed to a constant and small value. This allows us to investigate the relation between the mean concentration $C_m = (C_{\text{high}} + C_{\text{low}})/2$ and the Fickian diffusion coefficient $D$, while keeping the same $\Delta C$. For example, the concentration dependence of NaCl and sucrose was measured with $\Delta C = 2$ mg/ml at different $C_m$ (see Table 2.1). In this case, we obtain 12 fringes in the phase-shifted data for an OP of $L = 20$ mm. This is a good number of fringes for the unwrapping procedure.
3.2 CREATION OF DIFFUSION FIELDS

In order to avoid mass transport due to convection, the density gradient must be in the same direction as gravity under isothermal conditions. This is done by conducting a typical free diffusion experiment as those first conducted by Graham [70, 71], which consist in placing a low-density solution over a high-density solution. In the present study, the solution density and concentration are directly proportional and, therefore, the low concentration solution is placed over the high concentration solution inside a diffusion cell to maintain the convectionless state. In this way, convection is suppressed and mass transport is only due to Fickian diffusion. The entire system is also kept at constant temperature to avoid thermodiffusion. The temperature within the diffusion cell, monitored with a thermocouple, was set to $T = (25.0 \pm 0.5)^\circ C$. Hence, the determination of the diffusion coefficient at constant temperature can be straightforward from the measurements of the transient concentration profiles.

Even when the lower density solution is placed over the higher density solution, very small concentration differences might prompt undesired mixing. There have been many experimental methods with different procedures that try to create a one-dimensional diffusion field. Bochner et al. [26] injected the high concentration solution first, and then froze it so the low concentration solution could be injected without the diffusion process starting. Later, the experiment was started by abruptly heating the diffusion cell. Even though this method is excellent to reduce the initial disturbance, the temperature control is quite complicated for short time measurements. Komiya et al. [96] used a shearing cell to create the diffusion field in a short period of time with low initial concentration disturbances. However, the contact surface of the shear cells blocks the view at the interface between the high and lower concentration solutions, increasing the difficulty of the unwrapping procedure of the phase map. Therefore, in this set of experiments a simpler injection process, where a low concentration solution is automatically injected over a high concentration solution, is proposed. The injection setup with the Solution Injection
Device (SID), the cell stand, and the diffusion cell are shown in Fig. 2.24. A photo of the experimental setup just before an isothermal diffusion experiment is shown in Fig. 2.25. The experiment procedure is explained in the following.

**Placement of the Diffusion Cell on the Cell Stand**

The quartz cells have a height of 45 mm, a width of 1 mm or 2 mm, and an optical path (OP) of $L = 10$ or $20$ mm (see §3.1 for more details on the diffusion cells). These are the black cells shown in Fig. 2.21, which are used for the validation of the optical system. The OP in the diffusion cell was chosen based on the concentration difference of each experiment. Small concentration differences require larger OP to compensate the reduction in the number of fringes. For example, six fringes were obtained for the smallest con-
Figure 2.25: Photo of the injection setup sketched in Fig. 2.24. (a) The SID and the injection tubes are levelled up so that there is no obstruction to the reference beam, whose optical axis is 200 mm above the optical table (see Fig. 2.9). (b) Photo of the diffusion cell 2 mm × 20 mm × 45 mm fixed in the stand.

concentration difference of 1 mg/ml with an OP of $L = 20$ mm. This is usually a very small number of fringes for a good analysis in conventional interferometers or digital interferometers based on FFT methods. However, the developed phase shifting interferometer allows a high-resolution measurement from interferograms with few fringes (see §2.2).

Manual injection of higher density solution

In order to avoid strong mixture due to buoyancy, the higher density solution (high concentration in the case of NaCl and sucrose) is first placed inside the diffusion cell. A manual injection of this solution is conducted with the conventional 1 ml syringe shown in Fig. 2.26(a). The diffusion cell is then filled from its bottom to mid-height of the visualization range, as shown in the inset of Fig. 2.24. Here, the origin of the vertical axis $z$ is taken at the mid-height of the initial free surface since a prominent meniscus for small-width cells is observed (see Fig. 2.28). In fact, the strict definition of $z = 0$ is irrelevant because a numerical calculation, instead of an analytical solution, is used to determine the
Figure 2.26: Syringe testing for injection of lower density solution. Manual injection with: (a) a conventional 1 mm syringe, and (c) a 250µl Hamilton micro-syringe. (b) Failed injections frequently occurred with the conventional syringes. (d) Smooth injection with a Hamilton micro-syringe.

diffusion coefficient (see §3.4).

Initially, transient concentration profiles were formed by manually injecting the lower density solution over the higher density solution with the 1 ml syringe shown in Fig. 2.26(a). However, injection failures, such as the one shown in Fig. 2.26(b), frequently occurred. This syringe was then replaced with a high precision micro-syringe (Hamilton Inc. Model 80765 and 80865), which is shown in Fig. 2.26(c), in order to achieve a smooth injection without strong disturbances. A typical image of a successful injection is shown in Fig. 2.26(d).

**Automatic injection of lower density solution with SID**

In spite of obtaining a smooth injection by using the micro-syringe, manual injection procedures have two significant disadvantages. Firstly, the repeatability of the initial conditions of the experiment is not possible because the injection flow into the cell cannot be controlled nor measured. Secondly, the experiment procedure becomes more tedious because at $t = 0$, when both solutions become in contact, the stop-watch of the program Emerald must be started (see Fig. 2.18). However, if the operator is already busy with the manual injection of the solution this is not possible if he is alone. In order to overcome
Figure 2.27: Verification of repeatability for automatic injection procedure. The phase-shifted data (modulo $2\pi$) at $t = 4$ s is shown. The solutions (a) NaCl, (b) sucrose, and (c) Lysozyme at 30 mg/ml are placed in the lower mid-half of the cell. The solvent (distilled water, 0 mg/ml) is injected with the SID.

these problems, the injection procedure of the upper low concentration solution is conducted with the originally designed Solution Injection Device (SID) shown in Fig. 2.24. Mixing is almost entirely eliminated by using this device, even for concentration differences as small as 1 mg/ml. The device consists of three micro-syringes (Hamilton Inc. Model 80765 and 80865) and a linear translation stage with a five phase stepper motor (Suruga Seiki Inc. Model KS102-70).

Initially, the low concentration solution is injected by using only the middle syringe at a flow rate of 3.3 ml/s for the first 12 s. Then, injection through all three syringes starts at a total flow rate of 10 ml/s for an injection time of 44 s. This meticulous injection procedure was chosen in order to reduce the disturbances inside the diffusion cell and form a diffusion field as one-dimensionally homogeneous as possible. In order to evaluate the performance of the SID, three injection processes for different substances with similar viscosity were recorded and then compared to verify the repeatability of the experiment. It is important to bear in mind that the geometry of the cell and the viscosity of the solutions are the determining factors for the initial conditions in the experiment. Figure 2.27 indicates that the experiments had a very similar and smooth initial condition without turbulences. Here, a 1 mm thick diffusion cell was used with three different types of binary solutions at the same concentration.

In the validation experiments, the low concentration solution was smoothly injected
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until \( z = (10.0 \pm 0.1) \text{ mm} \). NaCl is the substance that diffuses the fastest, reaching a concentration gradient \( dC/dz \neq 0 \) at \( z \approx 4 \text{ mm} \) by the end of the experiment. Therefore, the infinite-slab condition used for the boundary conditions in the numerical calculation can be guaranteed (see §3.4).

### 3.3 Isothermal Diffusion Experiment

The diffusion experiments conducted to validate the phase-shifting interferometer previously described in §2 were conducted with two well-reported benchmark solutions.

**Benchmark Solutions**

Several diffusion experiments with NaCl and sucrose aqueous solutions were conducted. NaCl (lot no. 3022) and sucrose (lot no. STP670), supplied by Wako Pure Chemical Industries, were used as solutes. NaCl was chosen based on the well-known fact that the diffusion coefficient of ionic solutions varies greatly with concentration near the infinite dilute region. Distilled water was used as solvent. The concentration difference in the NaCl and sucrose experiments was set to \( \Delta C = 2 \text{ mg/ml} \), except for the mean concentration \( C_m = 0.5 \text{ mg/ml} (\Delta C = 1 \text{ mg/ml}) \) and \( C_m = 1490 \text{ mg/ml} (\Delta C = 20 \text{ mg/ml}) \). The concentration set for each experiment is listed in Table 2.1. All the experiments were conducted at a moderate mean concentration, except for one experiment where \( C_m = 1490 \text{ mg/ml} \). Even though there is no reference value for the diffusion coefficient at \( C_m = 1490 \text{ mg/ml} \), it is important to test the method for highly concentrated solutions. Each experiment run was conducted three times to verify the reproducibility.

In the solution preparing process, the solute and water were weighed with an analytical balance of resolution \( 10^{-4} \text{ g} \) and \( 10^{-2} \text{ g} \), respectively. Then, the required amount of solute was added to \( (1000.00 \pm 0.01) \text{ g} \) of distilled water. The solution was then stirred with a magnetic mixer. All binary solutions were prepared at \( T = (25.0 \pm 0.5)^\circ \text{C} \).
Table 2.1: Experimental runs for NaCl and sucrose. These experiments are labelled as NA and SB for NaCl and sucrose, respectively. $C_{\text{high}}, C_{\text{low}},$ and $C_m$ are the high, low, and mean concentrations, respectively. The concentration difference is $\Delta C = 2 \text{ mg/ml}$, except the runs indicated by $^*$. 

<table>
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<th>NA3</th>
<th>NA4</th>
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<tr>
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<table>
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</table>

**Measurement of transient diffusion fields**

The duration of each experiment was 800 s (except for SB1490$^*$). $t = 0$ s is set as the time when the diffusion process starts, i.e. the instant when the high and low concentration solutions come in contact. Phase-shifted data are obtained every 0.1 s and stored in the computer memory for further analysis. From these data, the transient concentration distribution inside the diffusion cell is obtained. Figures 2.15 and 2.16(a) show typical phase-shifted data obtained by using Eq. (2.6) for a free diffusion experiment. Figure 2.16(b) indicates the distribution of the phase difference (modulo $2\pi$) along the segment $\overline{ab}$. Figure 2.16(c) shows the absolute phase difference obtained by connecting the phase-shifted data at discontinuous points beginning from the first pixel (unwrapping procedure). This absolute phase difference is directly proportional to the concentration since the refractive index is directly proportional to concentration. Therefore, the concentration distribution is obtained from Fig. 2.16(c) by applying the concentration boundary conditions. The process described in Fig. 2.16 is conducted while the phase-shifted data is being acquired. The concentration profile is displayed on a monitor in real-time, as shown in Fig. 2.18 (see more explanation in §2.4).

Figure 2.28 shows the isothermal diffusion experiment for NaCl. Figure 2.28(a) shows the concept of the experiment, which consists in placing a lighter solution over a denser
Figure 2.28: Formation of a one-dimensional diffusion field for NaCl. (a) Concept of the experiment. (b) The phase-shifted data obtained from the phase-shifting equation, i.e. Eq. (2.6), are shown for $\Delta C = 4$ mg/ml and $C_m = 2$ mg/ml. (c) Phase-shifted data are shown during the injection process and during the pure diffusion phase of an isothermal diffusion experiment for $\Delta C = 2$ mg/ml and $C_m = 1$ mg/ml. Notice that the number of fringes is the same for (b) $\Delta C = 4$ mg/ml and (c) $\Delta C = 2$ mg/ml since the OP is 10 and 20 mm, respectively. A one-dimensional diffusion field is clearly observed for $t \geq 100$ s.
Figure 2.29: Transient diffusion field for sucrose. The phase-shifted data is shown from \( t = 100 \) s to \( t = 800 \) s. It is clear that at \( t = 100 \) s a one-dimensional diffusion has not been yet reached. Therefore, the phase-shifted data at \( t = 200 \) s is used as initial condition for the numerical calculation (see §3.4).

solution in order to keep the hydrodynamic stability, forming a quasi-one-dimensional diffusion field. Figure 2.28(b) shows the phase-shifted data obtained during a diffusion experiment of NaCl at a concentration difference of \( \Delta C = 4 \) mg/ml, a mean concentration of \( C_m = 2 \) mg/ml, and OP equal to \( L = 10 \) mm. The temperature within the cell is \( T = 25^\circ \) C. Clear phase-shifted data were obtained. Figure 2.28(c) shows another isothermal diffusion experiment with NaCl for \( \Delta C = 2 \) mg/ml, \( C_m = 1 \) mg/ml, and \( L = 20 \) mm. The same number of fringes was obtained following the relation between refractive index and concentration described in Eq. (2.7). The formation of the diffusion field during the injection process, as described in §3.2, is shown in detail in Fig. 2.28(c) for \( t \leq 30 \) s.

Figures 2.28(c) and 2.29 show the phase-shifted data in the diffusion experiments of NaCl and sucrose at \( C_m = 1 \) and 100 mg/ml, respectively (see experimental runs NA1 and SB100 in Table 2.1). In both experiments the concentration difference was set to 2 mg/ml. Figure 2.30 shows the concentration profiles obtained every 100 s for NaCl and sucrose, respectively. Here, the abscissa axis indicates the position \( z \) [mm], while the ordinate axis indicates the concentration \( C \) [mg/ml]. Mass diffusion occurs from the lower high concentration solution (\(-z\)) to the upper low concentration solution (\(+z\)). From these results, it is evident that NaCl diffuses faster than sucrose. Furthermore, the results show
Figure 2.30: Experimental results for the measurement of the transient concentration profile for both benchmark binary solutions. (a) Transient concentration profile for NaCl; the profiles are obtained from the phase-shifted data of Fig. 2.28(c). (b) Transient concentration profile for sucrose; the profiles are obtained from the phase-shifted data shown in Fig. 2.29.
Figure 2.31: Dimensionless concentration profiles of sucrose at $t = 800$ s for the mean concentrations of $C_m = 1, 100, 400,$ and $1490$ mg/ml. The effects of the concentration on the diffusion process are evident: higher concentration results in a slower diffusion.

that the concentration profile is a symmetric function with respect to the interface location at $z = 0$. This suggests that the diffusion coefficient does not vary significantly within the diffusion field due to the small concentration difference between the upper and lower boundaries. In the case where there is a strong dependence of the diffusion coefficient within the diffusion field, the interface location (defined as the location corresponding to $C_m$) would move away from its initial location as diffusion proceeds in the experiment [158, 174].

Figure 2.31 shows the dimensionless concentration profiles of sucrose for the mean concentrations of $C_m = 1, 100, 400,$ and $1490$ mg/ml at $t = 800$ s. Here, the concentration was normalized by $(C_{\text{high}} - C_{\text{low}})$, where $C_{\text{high}}$ and $C_{\text{low}}$ are the high and low concentrations, respectively. These results indicate that there is a decrease in the diffusion speed as the mean concentration of the solution increases. Once more, the quasi-symmetric concentration profiles suggests that the diffusion coefficient for each experiment is almost constant. A strong dependence of the diffusion coefficient with concentration would result in a non-symmetric concentration profile [158].
Finally, the diffusion coefficient for each mean concentration is determined from the experimental transient concentration profiles by inverse analysis, as described in the next section.

### 3.4 Determination of Diffusion Coefficients

The effects of gravity are neglected in this study. In general, gravity has a macroscopic and/or microscopic effect on the mass transport phenomena. The macroscopic effect refers to the bulk motion of the flow, which is suppressed by having mass diffusion in a convectionless system. The microscopic effect refers to a possible precipitation of the molecules due to gravity forces. This precipitation can be evaluated by the Péclet number, as described by Ramaswamy [172], which is defined as the rate of advection to the rate of mass diffusion. This number quantifies the effect that gravity has on possible molecule sedimentation. For sucrose, as well as for molecules with size of the order of angstroms, the Péclet number is sufficiently small to neglect the effects of gravity in the mass diffusion process, i.e. mass diffusion is dominated by thermal motion and finite-size effects.

Therefore, mass transport in each diffusion experiment is only due to mass diffusion. The diffusion coefficient for each mean concentration is determined by comparing the experimental transient concentration profiles with a numerical calculation of the diffusion field. The mass conservation equation for the diffusing species based on Fick’s law is

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2},
\]

where \( C \) [mg/ml] is the concentration of the diffusing species, \( x \) [m] is the space coordinate along the diffusion axis, and \( D \) [m^2/s] is the mass diffusion coefficient, which is one of the two properties of main interest in this chapter (the other is the Soret coefficient). Equation (2.8) assumes a one-dimensional isotropic diffusion in which the diffusion coefficient is independent of concentration throughout the calculation range. The assumption of a constant diffusion coefficient is only valid in the case where the concentration difference
is sufficiently small. Although the term “sufficiently” is ambiguous at this point, the analysis results support the veracity of this assumption. Furthermore, as pointed out in §3.3, the symmetry of the transient concentration profiles together with the stationary interface location suggest that the diffusion coefficient does not vary significantly within the diffusion field [158, 174].

Komiya et al. [97] used the current phase-shifting technique together with a fitting of the analytical solution of Eq. (2.8) in order to determine pseudo-binary diffusion coefficients in dilute ternary systems. However, the use of the analytical solution increased the error of the measurement since it is impossible to experimentally acquire an initial stepwise concentration distribution for the current visualization range. In this study, a fitting procedure with a numerical solution, which takes into account the characteristic initial conditions, is used in the inverse analysis to determine the diffusion coefficient. The fully implicit discretisation equations were obtained by the finite volume method and were solved for the following boundary conditions:

\[
\begin{align*}
    z \to -\infty, \quad C(z) &= C_{\text{high}}, \\
    z \to \infty, \quad C(z) &= C_{\text{low}},
\end{align*}
\]

where \(C_{\text{high}}\) and \(C_{\text{low}}\) refer to the concentration of the high concentration and low concentration solutions, respectively. \(z = 0\) is set as the position of the free surface of the high concentration solution prior to the injection of the low concentration solution, as shown in the inset of Fig. 2.24. Furthermore, the initial conditions for Eq. (2.8) are set as the experimental concentration distribution measured at \(t = 100\) s for NaCl, and \(t = 200\) s for sucrose. This is because the effects of the initial mixing last longer for sucrose than for NaCl, as observed at \(t = 100\) s in Figs. 2.28–2.31.
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Figure 2.32: Grid points and the control volume for the one-dimensional transient diffusion calculation. The fully implicit discretised equations for the numerical calculation were obtained by the finite volume method, as described by Patankar [153].

NUMERICAL SOLVER FOR ONE-DIMENSIONAL ISOThERMAl DIFFUSION

The numerical calculation to solve Eq. (2.8) is one of the simplest, since there is no convection term and the mass diffusion coefficient is assumed constant. The calculation domain was discretised by an equidistant mesh, as shown in Fig. 2.32. The total grid point number was set to 1000 in this calculation. The fully implicit discretisation equations for the numerical calculation were obtained by the finite volume method, as described by Patankar [153]. The discretisation equations are

\[ aC_{i,t} = b(C_{i+1,t} + C_{i-1,t}) + dC_{i,t-1}, \]  

(2.10)

where

\[ b = \frac{D}{\Delta z}, \]  

(2.11a)

\[ d = \frac{\Delta z}{\Delta t}, \]  

(2.11b)

\[ a = 2b + d, \]  

(2.11c)

and \( \Delta z \) [m] is the grid width and \( \Delta t \) [s] the time step which was set to 0.1 s. These equations are derived by integrating Eq. (2.8) over the control volume of grid point \( i \). In this
3 Validation of the optical system for measurement of Fickian diffusion

Figure 2.33: Validation of the transient one-dimensional diffusion code by comparison with analytical solution. The numerical and analytical solutions are compared. (a) The step function is used as initial condition in the numerical calculation. (b) The analytical solution at $t = 225$ s is used as initial condition (and considered to correspond to $t = 0$ s) in the numerical calculation. A good agreement between both results is obtained.

Integration, a piecewise-linear concentration profile between grid points was assumed in a fully implicit calculation. The solution of the linear algebraic Eq. (2.10) was obtained by the TriDiagonal-Matrix Algorithm (TDMA) [153], also known as the Thomas algorithm.

In order to validate transient one-dimensional diffusion code, a comparison with the analytical solution of Eq. (2.8) was made. The analytical solution of the diffusion equation is in the form

$$C(z) = \frac{C_{\text{high}} + C_{\text{low}}}{2} - \frac{C_{\text{high}} - C_{\text{low}}}{2} \frac{2}{\sqrt{\pi}} \int_0^\zeta \exp\left(-\gamma^2\right) d\gamma, \quad (2.12)$$

where

$$\zeta = \frac{z}{2\sqrt{Dt}}. \quad (2.13)$$

The analytical solution results obtained between $z_{\text{min}} = -4$ mm and $z_{\text{max}} = 4$ mm, for $C_{\text{high}} = 10$ mg/ml, $C_{\text{low}} = 0$ mg/ml, and $D = 1.5 \times 10^{-9}$ m$^2$/s, are shown by the dashed
lines in Fig. 2.33. The solid lines in Fig. 2.33(a) indicate the numerical calculation based on the discretised Eq. (2.10) for a step function as initial conditions. A good agreement between the numerical and analytical results is obtained. Furthermore, in order to verify that the code can manage an initial non-stepwise concentration profile, the analytical solution at \( t = 225 \) s was used as initial condition in the numerical calculation. The results are shown in Fig. 2.33(b). Again, the comparison between the analytical and numerical results shows a good agreement. The perfect match between the analytical and numerical results validates the numerical solver for one-dimensional isothermal diffusion with constant mass diffusion coefficient.

**Objective Function and Inverse Analysis**

After assigning the initial and boundary conditions to Eq. (2.8), the task at hand is to find a numerical diffusion coefficient, termed \( D_{cal} \), that matches that of the experimental concentration profiles at \( t = 200 \) s, 300 s, ..., 800 s. This diffusion coefficient is equal to the diffusion coefficient of the diffusive substance at the mean concentration \( C_m \), and it is numerically termed \( D_{opt}(C_m) \) (the subscript \( opt \) stands for optimized). In order to compare the numerical concentration distribution \( C_{cal}(z,D_{cal},t-t_{ini}) \) with the experimental concentration distribution \( C_{exp}(z,t) \) at a reference time \( t \) [s], we use the objective function defined as the area between the two concentration profiles:

\[
\delta(D_{cal},t) = \int_{z_{min}}^{z_{max}} |C_{cal}(z,D_{cal},t-t_{ini}) - C_{exp}(z,t)| \, dz. \tag{2.14}
\]

Here, \( \delta \) [mm · mg/ml] is the objective function, \( D_{cal} \) [m²/s] is the diffusion coefficient used in the numerical calculation, \( t_{ini} \) [s] is the time when the initial condition for the numerical calculation was taken, \( z_{min} \) and \( z_{max} \) are the minimum and maximum positions visible by the CCD camera for which the concentration is taken as described by the boundary conditions in Eq. (2.9). Moreover, the objective function becomes a function of \( D_{cal} \) for a given time \( t \), and by minimizing \( \delta \) we can obtain the value of \( D_{cal} \) that
matches the diffusion coefficient of the species inside the diffusion cell, i.e. $D_{opt}(C_m)$ at $t$. Since the objective function $\delta$ only depends on the variable $D_{cal}$ at a time $t$, a simple one-dimensional search is executed for its minimization. The one-dimensional search method chosen in this study is the Golden Section Method (GSM) [205], which is a popular technique for estimating the maximum, minimum, or zero of a one-variable function. This technique is popular for several reasons. First, while the function is assumed to be unimodal, it does not need to have continuous derivatives. Second, as opposed to other curve-fitting techniques, the convergence properties of GSM are known. Finally, the method is easy to programme.

The idea of the GSM is explained in Fig. 2.34. Here, a wide range between the lower bound, i.e. value of $D_l$, and the upper bound, i.e. value of $D_u$, is chosen such that the numerical diffusion coefficient $D_{opt}$, for which the objective function $\delta$ is minimum, is contained within this range. The bounds are then reduced as rapidly as possible by determining the values of $D_1, D_2, D_3, \ldots$. In the case of diffusion in liquids, almost all
diffusion coefficients fall in the range $10^{-10}$-$10^{-8}$ m$^2$/s, so the initial range for $D_l$ and $D_u$ were taken as $10^{-11}$ m$^2$/s and $10^{-7}$ m$^2$/s, respectively. First, two intermediate points $D_1$ and $D_2$ such that $D_1 < D_2$ are selected as shown in Fig. 2.34. In GSM, the interior values $D_1$ and $D_2$ are chosen to be

$$D_1 = (1 - \tau_G)D_l + \tau_G D_u,$$  \hspace{1cm} (2.15a)

$$D_2 = \tau_G D_l + (1 - \tau_G)D_u,$$  \hspace{1cm} (2.15b)

where $\tau_G$ is the golden section number (not to be confused with the golden ratio) defined as

$$\tau_G = \frac{3 - \sqrt{5}}{2} \approx 0.38197.$$

The objective function at these points is evaluated to obtain $\delta_1$ and $\delta_2$. Because $\delta$ is assumed to be unimodal, it follows that either $D_1$ or $D_2$ will form a new bound on the minimum. In this case, $\delta_2$ is greater than $\delta_1$, so $D_2$ forms a new upper bound and now a new set of bounds, i.e. $D_l$ and $D_u \leftarrow D_2$, are used in the next iteration. By using the golden section number $\tau_G$ as weight factor in Eqs. (2.15), the ratio of $D_2 - D_1$ to the total interval $D_u - D_l$ will always be the same. Therefore, for the case shown in Fig. 2.34, $D_1$ will become the new $D_2$ and $D_3$ will become the new $D_1$ which is calculated by Eq. (2.15a). If $\delta_1$ had been larger than $\delta_2$, $D_1$ would have formed a new lower bound, i.e. $D_l \leftarrow D_1$, and $D_2$ will become the new $D_1$. The $\tau_G$ chosen in Eqs. (2.15) allows an ideal sequence for dividing the intervals in order to find the minimum value of $\delta$ with as few function evaluations as possible [205]. By repeating this process, the bounds that bracket the minimum are eventually narrowed to whatever tolerance is desired.

Now that we have introduced a validated numerical solver for Eq. (2.8), the objective function (2.14), and the optimization technique (GSM), let us validate the inverse analysis by using an analytical transient concentration profile as a dummy experimental concentration distribution. Figure 2.35(a) shows the analytical solution of the diffusion field of
Validation of the optical system for measurement of Fickian diffusion

(a)

Figure 2.35: Validation of the objective function minimization algorithm. (a) Dummy function using the analytical solution (2.12) of Eq. (2.8). (b) Minimization of the objective function $\delta$ by GSM for $t = 500$ s (see Fig. 2.34).

A substance whose diffusion coefficient is $D_{\text{dummy}} = 8.401 \times 10^{-10}$ m$^2$/s at $t = 100$ s, 200 s, ..., 900 s. This profile is used as the experimental concentration distribution in the objective function (2.14). $\delta$ is then minimized by taking the initial time as $t_{\text{ini}} = 100$ s and reference time as $t = 500$ s. Figure 2.35(b) shows the calculated values of $D_1$ and $D_2$, as well as the corresponding values for $\delta$. As shown in Fig. 2.35(b), the values of the numerical diffusion coefficients $D_1$ and $D_2$, which are determined by GSM, sharply converge near the value of the dummy mass diffusion coefficient $D_{\text{dummy}}$, making $\delta$ almost zero. In this case 29 iterations were necessary for the GSM algorithm to converge. Each iteration determines the pair of values for $D_1$ and $D_2$. The convergence criterion is expressed by

$$|D_1 - D_2| \leq \epsilon$$ (2.16)

where $\epsilon$ is set to $10^{-14}$ m$^2$/s for all the calculations. Finally, the optimized value of the mass diffusion coefficient $D_{\text{opt}}$, i.e. the value at which $\delta$ is minimum, was set as
Table 2.2: Test of the inverse analysis. The dummy diffusion coefficient that is used to create $C_{\text{exp}}$ was set to $D_{\text{dummy}} = 8.401 \times 10^{-10}$ m$^2$/s. $D_{\text{opt}}$, which is defined by Eq. (2.17) after the convergence expressed by Eq. (2.16), is listed at different reference times $t$. All numerical calculations converged at the 29th iteration.

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$$D_{\text{opt}} = \frac{D_1 + D_2}{2}. \quad (2.17)$$

Table 2.2 shows the optimization results for all reference times $t$, i.e. the value of $D_{\text{opt}}$ for which $\delta$ is minimum. In all the calculations, it took only 29 iterations for the algorithm to converge. Furthermore, since a simple one-dimensional numerical calculation has been done, the physical time of the analysis is very short. It took less than 90 s to determine the values shown in Table 2.2 executing the programme on a personal computer with average performance.

Now that the code to determine mass diffusion coefficients in isothermal binary solutions has been validated, the mass diffusion coefficient can now be directly determined from an experimental transient concentration profile $C_{\text{exp}}(z,t)$. This means that, as pointed out by Eq. (2.14), $\delta$ is also a function of $t$. Therefore, the value of $D_{\text{opt}}$ for which $\delta$ becomes minimum is calculated for all $t$ (see Table 2.2) and then averaged to determine the diffusion coefficient of the substance at the corresponding mean concentration. The averaged $D_{\text{opt}}(C_m)$ is labelled according to the substance that is being measured, e.g. $D_{\text{NaCl}}(C_m)$ or $D_{\text{sucrose}}(C_m)$. This determination method is carried out for experiments at different mean concentrations in order to obtain a discretised concentration dependency of the diffusion coefficient of NaCl and sucrose. All the algorithms in this section were written in Fortran 90.
Table 2.3: Discretised concentration dependence of the diffusion coefficient for NaCl-water at $T = 25^\circ C$. $\delta$ is minimized for various $t$. The average diffusion coefficient and standard deviation for each mean concentration ($C_m$) and considering $t \geq 300$ s are indicated in bold. $\Delta C$ in all the experiments is 2.0 mg/ml, except for *, where the concentration difference was set to 1.0 mg/ml.

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<td>1.45</td>
<td>1.45</td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>1.30</td>
<td>1.32</td>
<td>1.33</td>
<td>1.37</td>
<td>1.37</td>
<td>1.38</td>
<td>1.39</td>
<td>1.418 0.075</td>
</tr>
<tr>
<td>7.0</td>
<td>1.34</td>
<td>1.42</td>
<td>1.40</td>
<td>1.41</td>
<td>1.43</td>
<td>1.45</td>
<td>1.38</td>
<td>1.415 0.024</td>
</tr>
<tr>
<td>8.0</td>
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<td>1.36</td>
<td>1.37</td>
<td>1.40</td>
<td>1.41</td>
<td>1.41</td>
<td>1.47</td>
<td>1.427 0.026</td>
</tr>
<tr>
<td>9.0</td>
<td>1.53</td>
<td>1.44</td>
<td>1.40</td>
<td>1.35</td>
<td>1.47</td>
<td>1.38</td>
<td>1.45</td>
<td>1.416 0.047</td>
</tr>
<tr>
<td>10.0</td>
<td>1.73</td>
<td>1.43</td>
<td>1.48</td>
<td>1.41</td>
<td>1.41</td>
<td>1.41</td>
<td>1.39</td>
<td>1.422 0.031</td>
</tr>
</tbody>
</table>

Table 2.4: Discretised concentration dependence of the diffusion coefficient for sucrose. The objective function $\delta$ is minimized for various $t$. The average diffusion coefficient and standard deviation of each diffusion experiment are indicated in bold. The concentration difference in all the experiments is 2.0 mg/ml.

<table>
<thead>
<tr>
<th>$C_m$ [mg/ml]</th>
<th>300 s</th>
<th>400 s</th>
<th>500 s</th>
<th>600 s</th>
<th>700 s</th>
<th>800 s</th>
<th>$D_{sucrose}$ $[m^2/s \times 10^{-10}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>4.93</td>
<td>5.11</td>
<td>5.36</td>
<td>5.08</td>
<td>5.20</td>
<td>5.11</td>
<td>5.131 0.144</td>
</tr>
<tr>
<td>50.0</td>
<td>4.61</td>
<td>4.55</td>
<td>4.64</td>
<td>4.63</td>
<td>4.69</td>
<td>4.93</td>
<td>4.676 0.134</td>
</tr>
<tr>
<td>100.0</td>
<td>5.02</td>
<td>4.66</td>
<td>4.58</td>
<td>4.16</td>
<td>4.00</td>
<td>4.23</td>
<td>4.441 0.378</td>
</tr>
<tr>
<td>200.0</td>
<td>4.54</td>
<td>3.80</td>
<td>3.72</td>
<td>3.71</td>
<td>3.78</td>
<td>3.59</td>
<td>3.857 0.341</td>
</tr>
<tr>
<td>300.0</td>
<td>3.45</td>
<td>2.77</td>
<td>2.98</td>
<td></td>
<td></td>
<td></td>
<td>3.065 0.347</td>
</tr>
<tr>
<td>400.0</td>
<td>2.67</td>
<td>2.97</td>
<td>3.00</td>
<td>3.01</td>
<td>3.08</td>
<td>3.18</td>
<td>2.982 0.172</td>
</tr>
</tbody>
</table>
3.5 RESULTS AND DISCUSSION

The diffusion coefficients are obtained by minimizing Eq. (2.14), where $C_{\text{exp}}(z,t)$ are the measured transient concentration profiles, as those shown in Fig. 2.30. The results of the optimum diffusion coefficient for all experiments in terms of $t$ are shown in tables 2.3 and 2.4. These results show that the diffusion coefficient does not vary significantly with $t$ for a given mean concentration; therefore, the diffusion coefficient is independent of the concentration distribution within the cell. If there were a strong dependence of the diffusion coefficient with concentration, the determined diffusion coefficient would vary significantly. Hence, the results indicate that the assumption of constant diffusion coefficient is valid enough for the concentration ranges considered. The small variations of the diffusion coefficient observed in both tables, for the same mean concentration, are mainly due to a bias error of the measurement device and to small variations of the local diffusion coefficient within the cell. Therefore, the experimental diffusion coefficient for NaCl and sucrose was taken as the average of all $t$ starting from $t = 300$ s. The experimental error is taken as the standard deviation of the averaged values.

The average NaCl diffusion coefficients of Table 2.3 are plotted in Fig. 2.36(a), together with literature values [134]. The vertical bars correspond to the standard deviation. The determined concentration dependence of the diffusion coefficient for NaCl agrees with the literature within a 5.0% margin. Figure 2.36(a) shows how the diffusion coefficient of NaCl decreases steeply until 4 mg/ml, and then remains almost constant until 10 mg/ml. The measurement error was large for the concentration difference of 1 mg/ml at mean concentration 0.5 mg/ml. This is due to two reasons: firstly, the diffusion coefficient of NaCl varies significantly near the infinite dilute region [134] resulting in an increase of measurement error for the method in which the diffusion coefficient is taken as constant; secondly, smaller concentration differences result in fewer fringes that in turn decrease the resolution of the concentration profiles. Therefore, the standard deviation of the measurement is systematically smaller for the other mean concentrations which corre-
Figure 2.36: Validation results for benchmark binary solutions of NaCl and sucrose. (a) Concentration dependence of the diffusion coefficient for NaCl; see Table 2.3 for precise values. (b) Concentration dependence of the diffusion coefficient for sucrose; see Table 2.4 for precise values. The vertical bars indicate the standard deviation for each measurement. The literature values [134] are also shown.
where \( u_i \) is the ion mobility, \( z_i \) is the ionic charge (equal to +1 for Na\(^+\)), \( F \) is Faraday’s constant, and \( w \) is the electrostatic potential. Each of these terms deserves discussion. First, the mobility \( u_i \) is a physical property of the ion, a phenomenological coefficient that must be measured by experiment. This mobility is often taken to be \( \frac{1}{6} \pi l_0 R_0 \), which, we recall, is a feature of the Stokes–Einstein equation. In fact, the use of this value simply restates our ignorance of mobility in terms of an effective ion radius, \( R_0 \).

Because the mobility is almost equivalent to the diffusion coefficient, it is something of a cultural artifact. It is included here because many papers dealing with electrolyte transport report their results in terms of mobilities, not in terms of diffusion coefficients. Faraday’s constant is even more of a cultural artifact: it is a unit conversion factor explicitly included whenever this equation is written. The apparent supposition is that no one can properly use electrostatic units without a warning.

The charge and potential in Eq. 6.1-2 make explicit the electrical effects connecting the ions. Including the charge seems sensible; note that if the ion has a negative charge, the direction of the electrical effect is reversed. The potential also looks sensible. It has two distinct parts. One part includes the effect of any potential applied to the system, for example, by electrodes attached to a battery. A second part is the potential generated by the different diffusion rates of diffusion ions. For example, for sodium chloride, the potential includes the electrostatic interaction of the quicker chloride ions and the more sluggish sodium ions. It is thus the route by which we average ion diffusion coefficients.

To rewrite Eq. 6.1-2 as a flux relation, we take advantage of the fact that we are working in dilute solution and so assume that the solution is ideal:

\[
l_i = \frac{RT}{c_i}
\]

When this result is combined with Eq. 6.1-2, we get

\[
\frac{v_i}{C_0} = \frac{u_i RT}{\frac{1}{3}C_1 + C_3} = \frac{z_i F}{w RT/C_1 C_3} \frac{1}{3}C_1 + C_3
\]

Thus far in this section, the diffusion process of ionic substances has been assumed to be binary. However, when the crystal of NaCl is dissolved in an aqueous solution, the Na atoms are separated from the Cl atoms by the H\(^+\) and OH\(^-\) atoms present in water to form Na\(^+\) cations and Cl\(^-\) anions. Therefore, strictly speaking, this solution is not binary but ternary. Nevertheless, the experimental results shown in Fig. 2.30 indicate that the behaviour of the diffusion of NaCl is binary in nature, and due to its similarities with the transient concentration profiles of the non-ionized sucrose, it can be treated as a binary diffusion. The physical explanation for this phenomenon lies in the electrostatic interactions between both ions. As shown in Fig. 2.37 [55], the two ions have the same charge and are present at the same local concentration. The larger cations inherently move more slowly than the smaller anions. However, because of electroneutrality, both
ions have the same net motion. The mass diffusion coefficient at \( T = 25^\circ C \) for \( \text{Na}^+ \) and \( \text{Cl}^- \) have been reported to be approximately \( 1.334 \times 10^{-9} \text{ m}^2/\text{s} \) and \( 2.032 \times 10^{-9} \text{ m}^2/\text{s} \), respectively [137]. This indicates that the results obtained in Fig. 2.36 are indeed between these two values. Therefore, the hypothesis of the interaction between ions due to the electrostatic forces, which makes the diffusion process in the ionic solution behave as binary diffusion, is valid.

The derived concentration dependence of the diffusion coefficient for sucrose, listed in Table 2.4, is plotted in Fig. 2.36(b) together with its literature values. A good agreement with the literature [134] is also obtained. Figure 2.36(b) indicates an inversely proportional relation between the diffusion coefficient and concentration, in contrast with the NaCl results, for the concentration values studied. In the sucrose experiments a larger standard deviation is observed, which is over 10% of the determined value for the experiments at high concentrations. This high error is attributed to the initial mixing that affects the overall result, as opposed to the case of NaCl where diffusion is fast and the initial non-one-dimensional concentration distribution disappears within the initial 100 s. Furthermore, the viscosity of NaCl is much smaller than that of sucrose, as reported by Chenlo et al. [45]; therefore, initial high concentration regions found near the walls at the beginning of the experiment disappear faster for the NaCl solution than for the sucrose solution, as indicated by the phase-shifted data at \( t = 100 \text{ s} \) in Figs. 2.28 and 2.29. Based on the one-dimensional isoconcentration lines condition which could be estimated from these phase-shifted data, the initial conditions of the numerical calculation were taken at \( t = 100 \text{ s} \) for NaCl and \( t = 200 \text{ s} \) for sucrose.

The concentration dependence of the diffusion coefficient provides a scope into the molecular behaviour inside the binary solution. In the case of sucrose, for example, the drop in the diffusion coefficient with concentration indicates that the solute molecules, expected to have a Brownian motion, are colliding with each other, and consequently, have a decreasing mean free path. On the other hand, the ions in the NaCl solution, i.e. \( \text{Na}^+ \) and \( \text{Cl}^- \), interact strongly even in the highly dilute region due to the electrostatic
forces. Furthermore, the diffusive behaviour in binary solutions can also be investigated near the saturated region, using small concentration differences for which the relation between refractive index and concentration is linear. In the saturated region, however, a significantly high viscosity could be found, e.g. for sucrose. This is a problem when trying to create the diffusion field as explained in §3.2. Thermodiffusion, on the other hand, can be used to create an initial concentration difference, allowing us to get rid of any perturbing initial manipulation to create this initial state. This process is carried out in the isothermal diffusion phase of the thermodiffusion experiment which is explained in the following section.

4 VALIDATION OF THE OPTICAL SYSTEM FOR MEASUREMENT OF THERMODIFFUSION

In this section, the measurement method of thermodiffusion by orthogonal phase-shifting interferometry (see §2.3) is validated. This high-resolution interferometer is used to measure transient concentration profiles in binary solutions subject to a linear temperature gradient. A convectionless thermodiffusion field is created in a binary solution sample that is placed inside a Soret cell. The experimental procedure is explained in §4.4. The Soret cell consists of a parallelepiped cavity with a horizontal cross-section area of 10 × 20 mm², a variable height of 1-2 mm, and transparent lateral walls, as explained in §4.2. The small height of the cell reduces the volume of the sample, shortens the measurement time, and increases the hydrodynamic stability of the system. The so-called contrast factors are measured with an additional free diffusion experiment, as explained in §4.3. The contrast factors relate the unwrapped phase and concentration gradients. This measurement technique is then independent and robust. The Soret coefficient is determined from the concentration and temperature differences between the upper and lower boundaries measured by the interferometer and thermocouples, respectively, as explained in §4.1. The Fickian diffusion coefficient can also be obtained in a second experiment stage,
where the temperature difference is decreased to zero, by fitting a numerical solution to
the experimental concentration profile, as explained for the isothermal diffusion experi-
ments in §3.4. The method is validated through the measurement of thermodiffusion in
the well-known liquid pairs of ethanol-water (ethanol 39.12 wt%) and isobutylbenzene-
dodecane (50.0 wt%), the second solution being one of the three binary solutions used in
the Fontainebleau benchmark [162].

The binary solutions were prepared at a room temperature $T_{room} = 25^\circ$C. The con-
centration in the first two binary solutions is expressed in units of weigh percent [wt%] because each component is liquid in its pure form at $T_{room}$. On the other hand, the units of concentration [mg/ml] are preferred in the case of the protein solutions due to the solid state of the pure proteins at $T_{room}$. Hence, in §3 the units of concentration for NaCl and sucrose were also [mg/ml] instead of [wt%]. Table 2.5 shows the name of the components used and their corresponding molecular mass, density (for those components in pure li-
quid form), and supplier with its lot number. The solutions were prepared in a sealed environment to avoid variation of the concentration due to vaporization.

4.1 Evaluation method

Some of the theory that is presented in this subsection has been discussed in Chapter I §1.1. The important points relevant to the evaluation method of Soret coefficients are explained once more for the sake of clarity.
The Soret coefficient $S_T$ in binary systems is defined as

$$S_T = \frac{D_T}{D}, \quad (2.18)$$

where $D_T$ and $D$ are the thermodiffusion coefficient and isothermal diffusion coefficient, respectively, which both enter the mass flux equation defined as

$$j = -\rho D \nabla C - \rho C_0 (1 - C_0) D_T \nabla T, \quad (2.19)$$

where $j$ is the mass flux, $\rho$ is the total density, $T$ is the temperature, $C$ is the concentration of the considered component expressed as the mass fraction (non-dimensional), and $C_0$ is the mean concentration of one species. The weight factor $C_0 (1 - C_0)$ is associated with $D_T$ to define the constant of proportionality between mass flux and temperature gradient. The weight factor indicates that thermodiffusion does not exist in pure fluids, i.e. $C_0 (1 - C_0) = 0$, but as a matter of fact the thermodiffusion coefficient $D_T$ usually has a finite value in the infinite dilute region. In contrast, $D$ is simply defined as the phenomenological constant of proportionality between mass flux and concentration gradient. Each coefficient $D_T$ and $D$ is defined in accordance with the laws of mass diffusion that were discovered in the experimental works reported by Soret [188] and Graham [70, 71], respectively.

If a binary solution is placed inside a Soret cell that has adiabatic sidewalls and a constant temperature difference $\Delta T$ between its upper and lower walls, a constant concentration difference $\Delta C$ between the upper and lower boundaries is reached after an infinite time when $S_T \neq 0$. In this steady state, the mass flux becomes zero ($j = 0$) and from Eqs. (2.18) and (2.19), the Soret coefficient in a binary system is obtained by

$$S_T = -\frac{1}{C_0(1 - C_0)} \frac{\Delta C}{\Delta T}. \quad (2.20)$$

Here, $S_T$ is usually a concentration and temperature dependent thermophysical property with a positive or negative value. Therefore, Eq. (2.20) is only valid for small differences
of concentration and temperature. Equation (2.20) also indicates that $S_T$ is positive when the considered molecules migrate to the cold region, i.e. this species is thermophobic, and $S_T$ is negative when the considered molecules migrate to the hot region, i.e. this species is thermophilic. In a binary mixture, the two components have related concentrations and opposite Soret coefficients. It is then enough to express the results with regard to one of the components, considered as the reference component. Note that the denser component is often chosen as reference component. Figure 2.38 shows a typical stability diagram of a steady-state binary system [84, 217] enclosed in a Soret cell in terms of the critical Rayleigh number, $Ra_c$ and the Soret coefficient, $S_T$ corresponding to the denser component. The Rayleigh number is defined as

$$Ra = \frac{g \beta h^3 (T_{lower} - T_{upper})}{\nu \kappa}, \quad (2.21)$$

where $g$ is the acceleration of gravity, $\beta$ is thermal expansion coefficient, $h$ is the height
of the cell, υ is the kinematic viscosity, κ is the thermal diffusivity, \( T_{\text{lower}} \) and \( T_{\text{upper}} \) are the lower and upper boundary temperatures, respectively. With this choice, \( Ra \) is positive when the net heat flux is upward, i.e. the sample is heated from below. The critical Rayleigh number \( Ra_c \) indicates the threshold for convection to set in. As shown in Fig. 2.38, a stable convectionless state is always achieved by heating a thermophobic \( (S_T > 0) \) denser component from above \( (Ra < 0) \). This situation corresponds to that used in most convectionless methods recently developed [99,125]. However, as indicated in Fig. 2.38, heating from below \( (Ra > 0) \) creates a more stable state than heating from above for a binary solution with a thermophilic denser component when \( |S_T| \) is sufficiently high. This is the choice made by Colombani et al. [51] to measure the pure Soret effect free from any convective disturbance. Regarding cavities heated from above \( (Ra < 0) \) with negative \( S_T \), Melnikov et al. [119] conducted three-dimensional calculations on Soret driven instability of convective flows in such cavities.

In this study, the aim is to conduct an active control of the temperature between the upper and lower boundaries of a Soret cell, i.e. controlling \( \Delta T \), and perform a phase-shifting interferometric measurement of the concentration difference in a solution between the upper and lower liquid/wall boundaries, i.e. measuring \( \Delta C \). The binary solution used in each experiment is prepared at the desired concentration \( C_0 \). The Soret coefficient \( S_T \) is then determined by substituting \( \Delta T, \Delta C, \) and \( C_0 \) in Eq. (2.20).

Furthermore, the mass diffusion coefficient is determined from the isothermal diffusion experimental phase, following the same procedure as in §3.4.

### 4.2 Soret Cell

The Soret cell designed for this study is shown in Fig. 2.39. A photo of the Soret cell built from this design is shown in Fig. 2.40, prior to its use in a thermodiffusion experiment. The binary solution is placed inside a rectangular parallelepiped cavity with a horizontal cross-section area of \( 10 \times 20 \) mm\(^2\) and a variable height of 1–2 mm, as shown in the lateral and horizontal cross-section views in Figs. 2.39(b,c). The upper and lower boundaries are
Figure 2.39: The Soret cell where the binary solution is injected. (a) Three-dimensional model of the cell, (b) its lateral cross-section, and (c) a horizontal cross-section view of the cavity where the sample is placed. The lateral walls of the cell are transparent to allow the passage of the two orthogonal test beams of the interferometer shown in Fig. 2.7. The temperature control of the upper and lower copper boundaries is conducted by Peltier modules integrated to a PID system. Two holes are drilled in the quartz wall to fill the cavity with the solution and to introduce the thermocouples to measure the temperature just at the copper/liquid boundary.
made of copper, which has a high thermal conductivity so that a rapid temperature control is achieved. The lateral walls are made of quartz to allow the passage through the sample of two orthogonal laser beams, i.e. test beams $L_1$ and $L_2$. See §2.3 for details on the optical method.

A standard quartz cell with high optical quality (Fine Inc., $W \times L \times H = 10 \times 20 \times 45$ mm$^3$) was cut into a bottomless four-sided quartz glass that was subsequently clamped between two thermostabilized copper blocks, as shown in Fig. 2.39(a). The quartz glass is attached to the copper blocks by a thermoplastic adhesive or vinyl tape that can be removed after finishing the experiment. This avoids leaks and allows the detachment of the quartz part for cleaning and further use. Moreover, two holes of 1 mm in diameter were drilled near the edges of the cell with a double purpose: to inject the binary solution, and to introduce the thermocouples that are used to measure the temperatures of the upper and lower boundaries inside the cell. In order to avoid bubbles, the binary solution is injected through one hole using a micro-syringe (Hamilton Company, 500 µm) while removing the air from the other hole; this procedure is conducted with the cell turned 90° with its holes facing upwards to facilitate the exit of air. It is imperative that the binary solution
entirely fills the cell without leaving any bubbles; a small bubble could grow within the cell due to evaporation of the solvent into the surrounding air through the glass holes, blocking the optical beam used in the measurement. In any case, the cell is sealed with a thermoplastic adhesive to avoid contact with the surrounding air in experiments using highly volatile liquids, such as ethanol, because an open cell might also result in undesired concentration gradients near the free boundaries due to evaporation. On the other hand, it is not necessary to seal the cell when the binary solution has low volatility, as in the case of diluted protein aqueous solutions (see Chapter III). Not sealing the cell guarantees that the pressure inside the cavity is kept at atmospheric pressure regardless of the thermal expansion of the liquid and its cell boundaries. Nevertheless, the effects of the thermal expansion are negligible in these experiments because the temperature difference is small. A large temperature difference would not only affect the hydrostatic pressure, but might also result in a rupture of the quartz walls due to the thermally induced stress.

Mialdun et al. [125] took extra precautions to avoid bubbles by degassing the sample. They used a degasser designed for solvents in high performance liquid chromatography (HPLC) applications. In this study, the use of a degasser is less relevant because the measurement time is about $1/10$ of that reported in the experiments of Mialdun et al. [125].

**Rapid heat transfer control**

The temperature control of the upper and lower boundaries is conducted by a single computer-driven PID system, enabling temperature stability of $\pm 0.01$ K. Takeda et al. [193] used a similar PID setup in a cryoprobe that is used in safe and reliable cryosurgery. A schematic of the feedback loop is shown in Fig. 2.41(a) for the temperature control of the upper copper block. The CPU independently controls the current that passes through the Peltier modules (Kelk Ltd., KSM09007C, $P_{\text{max}} = 7.2$ W, $I_{\text{max}} = 9.0$ A). The PID algorithm and the drivers employed were partially developed by LabView (National Instruments Corp.) The temperature at the copper/liquid boundary is measured by T-type
Development of phase-shifting interferometry for measurement of mass diffusion

Figure 2.41: PID temperature control at the copper/liquid boundaries. (a) The feedback loop of the control system. The temperature is measured just at the liquid interface by extra thin T-type thermocouples. The measured temperature is processed by the CPU, which in turn sets the output current based on the PID gains. (b) The temperature control for the upper and lower boundaries is simultaneously performed to set a constant temperature difference $\Delta T$ and a mean temperature $T_m$. The overshoot $\delta T'$ and settling time $t_s$ depend on the proportional, integral, and derivative gains ($K_p$, $K_i$, and $K_d$, respectively).

The type of heat sink used determines the controllable temperature range of the Peltier modules. Coolant exchangers are preferable as a heat sink for large temperature differences or a long experimental time [125]. The use of liquid nitrogen as a heat sink is the best choice for temperatures lower than 0°C [193]. In this set of experiments, standard fins were employed since the temperature ranges inside the cell are within $\pm 5°C$ of the room temperature $T_{room}$ and the experimental time is within a couple of hours. The use of fins as heat sink provides a simple setup without moving components that might affect the optical measurement, which is very sensitive to vibrations.

The program controls the mean temperature $T_m$ within the cell and the temperature difference $\Delta T$ between the upper and lower copper/liquid boundaries. Here, $T_m$ is set equal to the temperature of the cell surroundings in order to minimize the convection near the lateral walls. Figure 2.41(b) shows the temperature control of the boundaries for a typical thermodiffusion experiment. Here, $T_m = 25°C$ and $\Delta T = 5 K$ when the distance

thermocouples. These were calibrated inside iced water at 0°C.

The program controls the mean temperature $T_m$ within the cell and the temperature difference $\Delta T$ between the upper and lower copper/liquid boundaries. Here, $T_m$ is set equal to the temperature of the cell surroundings in order to minimize the convection near the lateral walls. Figure 2.41(b) shows the temperature control of the boundaries for a typical thermodiffusion experiment. Here, $T_m = 25°C$ and $\Delta T = 5 K$ when the distance
between the copper walls is set to $h = 2$ mm; the resulting overshoot $\delta T'$ and settling time $t_s$ are $0.71^\circ C$ and 44 s, respectively. These depend on the proportional gain $K_p$, integral gain $K_i$, and derivative gain $K_d$, which are used in the PID algorithm shown in the block diagram of Fig. 2.41(a). In the experiments reported in this study, the PID gains were set to $K_p = 0.5$, $K_i = 0.1$, and $K_d = 0.015$. Several experiments were performed to choose a suitable value for each gain.

**Design Parameters**

Similar Soret cells to that shown in Figs. 2.39 and 2.40 have been used in interferometric measurements. Colombani et al. [51] used a cell with cavity dimensions of $W \times L \times H = 10 \times 10 \times 30$ mm$^3$; Mialdun and Shevtsova [125] used a cell with dimensions $W \times L \times H = 22 \times 22 \times 6.3$ mm$^3$. However, the measurement time reported by these research groups was around 200 h and 15 h, respectively. The characteristic measurement time $\tau$ of the thermodiffusion experiment is bound to the strength of the Fickian diffusion (isothermal diffusion coefficient) $D$ and to the diffusion length $h$ as follows

$$\tau = \frac{h^2}{\pi^2 D}. \quad (2.22)$$

Therefore, decreasing the height of the cell $h$ would drastically reduce the measurement time for a given Fickian diffusion coefficient. Equation (2.22) also indicates that for macromolecules, which have a smaller $D$ as predicted by the Stokes-Einstein equation, the measurement time increases. This makes the measurement of thermodiffusion in biological systems a more difficult task since most biomolecules, such as proteins, are macromolecules with a diffusion coefficient in the order of $10^{-10} - 10^{-11}$ m$^2$/s. Furthermore, as indicated by Eq. (6.1), decreasing $h$ would drastically increase the stability of the system while preserving the heating-from-above configuration ($Ra < 0$). This is of particular importance in measurements where the sign of the Soret coefficient is unknown. Therefore, for our measurements in protein solutions, it is important to choose a cell with a small
height. Such cell bears more resemblance to those cells used in OBD studies, as in the experiment described by Königer et al. [99].

In this section, we focused on designing a Soret cell with a short height within the optical constrains. The small height $h$ reduces the sample volume ($Volume \propto h$), shortens the measurement time ($\tau \propto h^2$, see Eq. (2.22)), and increases the hydrodynamic stability of the system ($Ra \propto h^3$, see Eq. (6.1)). The optical problems related to a short $h$ will be further discussed.

4.3 CONTRAST FACTOR EXPERIMENT

Although a phase map resulting from refractive index variations due to concentration gradients is obtained with the optical system described above, we still need the corresponding $\Delta \psi / \Delta C$ ratio to obtain the concentration profile within the cell. Hence, preliminary measurements of the $\partial \psi / \partial C$ ratio are required. In the OBD studies, the ratio $\partial n / \partial C$ is used to couple the optical measurements with the concentration; here, $n$ is the refractive index. This ratio is usually termed contrast factor. Likewise, the ratio $\partial n / \partial T$ also becomes relevant in non-isothermal experiments, such as in thermodiffusion experiments, because the refractive index is a temperature-dependent property. Nonetheless, the effects of $\partial n / \partial T$ on the wavefront can be optically suppressed in a thermodiffusion field where the temperature profile is linear within a small temperature difference. Therefore, in this set of experiments only the $\partial \psi / \partial C$ ratio is required to measure the two-dimensional concentration field. The phase difference variation $\Delta \psi$ is linearly related to the refractive index variation $\Delta n$ through the optical path $L$ and the wavelength of the laser $\lambda_{\text{beam}}$, as indicated in Eq. (2.7), i.e.

$$\Delta n(x, z) = \frac{\lambda_{\text{beam}}}{2\pi L} \Delta \psi(x, z).$$

The variation of the refractive index $\Delta n$ in this equation includes the contributions from both temperature and concentration [125] when neither contribution is optically sup-
pressed. The contribution of pressure is neglected since the pressure inside the cell is constant.

In spite of the importance of the contrast factors $\partial n/\partial C$, most measurements of thermodiffusion rely on contrast factors that are reported in the literature while other studies develop independent measurement methods, e.g. for the Fontainebleau benchmark mixtures. In this section, the aim is to conduct the Soret coefficient measurement with the same optical instrument through two experiments, providing a robust and independent measurement apparatus. Here, instead of the conventional ratio $\partial n/\partial C$, we measure the contrast factors $\partial \psi/\partial C$ with the phase-shifting interferometer in order to have a direct relation to the concentration profile within the cell. We then find $\partial n/\partial C$ by using (2.7) to assess the accuracy of the measurement.

**DETERMINATION OF CONTRAST FACTORS**

The measurement of the contrast factors is done through isothermal diffusion experiments initially developed to determine isothermal mass diffusion coefficients. A detailed explanation of the isothermal diffusion experiment is found in §3. The same kind of experiment is performed to measure the contrast factors. In this section, the measurement of Fickian diffusion coefficients during the isothermal diffusion phase of the experiment is relegated to a secondary objective. Moreover, important information concerning the data analysis is provided in addition to §3.3.

Figure 2.42(a) shows the unwrapped phase shift between the lower and upper boundaries in an isothermal diffusion experiment using the binary system NaCl-water ($\Delta C = 4 \text{ mg/ml, } C_m = 2 \text{ mg/ml}$). The insets show the phase-shifted data acquired at each corresponding time. The lower and upper visible boundaries at $z = -4.59 \text{ mm}$ and $z = 4.78 \text{ mm}$, respectively, are immersed, i.e. Fickian diffusion through these boundaries can occur. The lateral vertical boundaries are impermeable. The data were averaged in the horizontal direction (isoconcentration direction perpendicular to $z$) after unwrapping. The intensity gradients between fringes in the phase-shifted data indicate that the phase dif-
Figure 2.42: Determination of $\partial \psi / \partial C$ for a dilute NaCl solution. (a) The unwrapped phase diagram obtained from the phase-shifted data shown in the insets. The phase diagram profile $\psi$ is the unwrapped data averaged in the horizontal direction perpendicular to $z$. (b) The phase difference $\Delta \psi$ between the upper and lower boundaries. The phase difference $\Delta \psi$ averaged in time is then divided by the concentration difference to obtain the ratio $\Delta \psi / \Delta C$. This value is used in the thermodiffusion experiments to determine the concentration profile within the Soret cell.

ference is increasing with the vertical position $z$. Furthermore, the unwrapped phase shift profiles do not perfectly intersect at the center because the intensity of the phase-shifted data in the homogeneous lower part of the solution varies at different times. This is due to temporal accumulative errors of the phase-shifting image processing. The proper boundary conditions are thus required in order to obtain the concentration profiles from each phase-shifted data. The phase difference between the lower and upper immersed boundaries of the unwrapped phase-shifted data is shown in Fig. 2.42(b) as a function of time. The phase difference remains almost constant with a positive value $\Delta \psi_{ave} = (21.58 \pm 0.12) \pi$ since there is no mass transport through the upper and lower observation limits, which correspond to immersed boundaries. If the fringes reach the upper or lower extremes, then there is diffusion through the corresponding immersed boundaries and, as a consequence, the phase difference $\Delta \psi$ is reduced. A homogeneous solution is obtained when the experimental time tends to infinite, i.e. $\Delta \psi$ becomes zero. The transient concentration profile within the cell is obtained by introducing the corresponding
concentration difference to each profile shown in Fig. 2.42(a).

In the trial experiment shown in Fig. 2.42(a), the average phase difference per units of concentration deduced from Fig. 2.42(b) is $\Delta \psi_{\text{ave}} / \Delta C = -(5.394 \pm 0.03) \pi$ [rad ml mg$^{-1}$]. Moreover, the phase shift between the reference and test beams is directly proportional to the OP within the cell for a constant refractive index. As a consequence, the phase difference between the upper and lower boundaries is also directly proportional to the OP. In this study, we characterize the influence of the concentration difference ($\Delta C$) and the OP ($L$) on the refractive index by using the following contrast factor $\eta$ defined as

$$\eta = \frac{\Delta \psi}{\Delta C \cdot L}. \quad (2.23)$$

In the case of the trial experiment shown in Fig. 2.42(a), $\eta = -(0.539 \pm 0.003) \pi$ [rad ml mg$^{-1}$ mm$^{-1}$]. The units for the concentration could be either [mg/ml] or [wt%] depending on the type of the components involved. Substituting $\Delta \psi$ obtained from Eq. (2.23) in Eq. (2.7) yields

$$\left( \frac{\partial n}{\partial C} \right)_{p,T} = \frac{\lambda_{\text{beam}} \eta}{2\pi}. \quad (2.24)$$

In our measurement system, the temperature contribution to the refractive index is optically suppressed by a simple adjustment of the reference mirror (see §4.4) and, therefore, only the contribution due to the concentration difference is considered in Eq. (2.24).

**DETERMINATION OF ISOThermal DIFFUSION COEFFICIENTS**

The primary objective of the contrast factor experiment is to determine the contrast factors. In addition, the isothermal diffusion coefficients can also be determined since the experiment is the same as that described in §3.3, i.e. the isothermal diffusion experiment. The values thus obtained are given in Table 2.6. These coefficients could be used as reference to compare with the isothermal diffusion coefficients determined during the isothermal diffusion phase in a thermodiffusion experiment.
4.4 ThermoDiffusion Experiment

The experimental procedure is divided into five steps. First, (A) the Soret cell is placed in the test section of the optical system and the mirrors of both reference beams are adjusted to obtain the infinite fringe condition in each interferogram. Then, the thermodiffusion field is initiated by (B) setting a temperature difference between the upper and lower copper/liquid boundaries, which leads to a linear temperature profile within the cell in less than one minute. Next, (C) the fringes obtained due to the linear temperature profile are suppressed in one of the interferometers by adjusting its reference mirror. The most important measurement of the experiment is done by (D) recording the phase-shifted data until a linear concentration profile is reached within the cell, i.e. the interferogram fringes become equidistant. Finally, (E) the temperature difference within the cell is set to zero to visualize the isothermal diffusion. An explanation of each step is given.

(A) Placement of the Soret Cell Filled with the Binary Solution

The Soret cell (see Fig. 2.39) is completely filled with a binary solution and then placed in the test section of the orthogonal phase-shifting interferometer shown in Fig. 2.7. The cell is aligned so that the incidence of the test beams is normal to the quartz walls. After placing the cell, the real-time phase-shifting image processing is started in both interferometers. The phase-shifted data is brought to an infinite fringe condition by adjusting the mirrors of the reference beams $M1$ and $M4$ (see last step in Fig. 2.12); it is recommended to fix the test beam mirrors $M2$ and $M3$ in order to guarantee the perpendicularity of the incident beams.

(B) Inducing the ThermoDiffusion Field within the Soret Cell

The experiment is initiated by creating a temperature difference between the upper and lower copper/liquid boundaries. Since the Lewis number for binary liquid systems is usually in the order of $10^2$, the temperature field within the cell reaches a steady state much
faster than the concentration field. Therefore, when applying a temperature difference of $\Delta T$ within a two-millimeter spacing, it takes only about 15 s for the temperature to reach a linear profile in water (within 1% of the initial temperature difference), whereas more than one hour is required for the molecules to reach a quasi-steady state within the cell.

(C) Elimination of the Fringes Due to the Linear Temperature Profile

In the first couple of minutes of the experiment, the linear temperature profile formed within a 1–2 mm height cell creates a linear refractive index profile. Thermodiffusion is much slower than heat conduction and, therefore, the refractive index is almost linear in the vertical direction. Immediately after the linear temperature profile is achieved, the tilt of the mirror $M1$ is adjusted to optically suppress the influence of the temperature on the interferograms. The inclination adjustment is done manually within 25 s. The reference beam mirror ($M1$) is adjusted instead of the test beam mirror ($M3$) to keep the incident test beam perpendicular to the quartz glass. The thermodiffusion effect is only observed with the first interferometer (with $L1$ as light source), i.e. the mirror $M4$ remains fixed and unadjusted. The process of suppressing the fringes due to $\partial n/\partial T$ is the same as that shown in Fig. 2.12(a), in which the mirrors $M1$ and $M4$ are adjusted so that the wavefronts of the test beam and reference beam become parallel to each other, i.e. the necessary condition to obtain an infinite fringe interferogram.

(D) Visualization of the Soret Effect – Thermodiffusion Phase

The phase-shifted data from the first interferometer is visualized in an external monitor and is stored every 1 s for post-experimental image processing. The high-resolution visualization of the Soret effect is the main contribution of this study. A high-resolution visualization of thermodiffusion has only been conducted by Mialdun and Shevtsova [125] with an FFT method. This measurement continues until the fringes of the phase-shifted data reach an equidistant state.
(E) VISUALIZATION OF FICKIAN DIFFUSION – ISOTHERMAL DIFFUSION PHASE

After linear concentration and temperature profiles within the cell are reached, the temperature difference between the copper/liquid boundaries is brought to zero and the temperature of the cell then returns to the room temperature. Here, the second interferometer (with \( L_2 \) as light source) is used to visualize isothermal diffusion. The recording process continues until the fringes in the phase-shifted data disappear.

After culminating the five steps (A)–(E) mentioned above, the thermodiffusion and isothermal diffusion phases can be indefinitely repeated with the first and second interferometric setups of OPSI, respectively, without the need of readjusting the reference mirrors while applying the same temperature difference \( \Delta T \) between the upper and lower copper/liquid boundaries.

4.5 RESULTS AND DISCUSSION

CONTRAST FACTORS

Figure 2.43 shows an isothermal diffusion experiment conducted with the ethanol-water binary solution. The lighter ethanol-water solution (ethanol 39.49 wt%) is placed over a denser solution (ethanol 37.55 wt%) inside a four-side transparent diffusion cell (Fine Inc. \( W \times L \times H = 2 \times 10 \times 45 \text{ mm}^3 \)). The diffusion process is observed with OPSI, instead of the single phase-shifting interferometer described in §3.3. The direction of each test beam in relation with the position of the cell is shown in Fig. 2.43(a); the corresponding cell dimensions and system of coordinates are also indicated. In this setup, the optical path within the diffusion cell for the test beam \( L_2 \) is five times larger than for \( L_1 \) and, therefore, the resolution for the measurement conducted with the former is five times better than that conducted with the latter. Figures 2.43(b) and (c) show the phase-shifted data obtained by using the interferometers with light source \( L_1 \) and \( L_2 \), respectively. For \( L_1 \), the spatial visualization range is \( W \times H = 1.05 \times 2.92 \text{ mm}^2 \) and
Figure 2.43: Isothermal diffusion of an ethanol-water solution at ethanol mean concentration $C_m = 38.52$ wt% and $\Delta C = 1.94$ wt% measured with OPSI (see Fig. 2.7). (a) The upper view of the diffusion cell with its dimensions and the direction of each test beam. (b) The diffusion process observed with the test beam $L1$ (OP 2 mm). (c) The diffusion process observed with the test beam $L2$ (OP 10 mm). The phase difference between the upper and lower boundaries is taken after $t = 45$ s. The vertical positioning of the diffusion cell is adjusted until $t = 85$ s.

the surrounding visualization boundaries are immersed surfaces. For $L2$, the visualization range is $W \times H = 2 \times 2.84$ mm$^2$ with its width corresponding to the length of the cell ($L = 2$ mm), i.e. the lateral boundaries are impermeable walls while the upper and lower boundaries are immersed.

At $t = 0$ s, the lighter solution is put in contact with the denser solution. The part of the cell that still has air is only visible with the beam $L1$ because the meniscus at the corners of the cell blocks the beam $L2$. At $t = 10$ s, the diffusive region is thin and clearly visible with $L1$ but not with $L2$, where it appears thicker; this is due to the influence of the initial meniscus and the non-one-dimensionality of the diffusive field within the cell. At $t = 20$ s, the vertical positioning of the cell is adjusted so that the diffusion process view is centered. The diffusion area is delimited by the lower and upper fringes, as indicated by the rectangles at $t = 10$ s and 20 s in Fig. 2.43(b). This means that the areas with the same phase shift (below the lower fringe and above the upper fringe)
II DEVELOPMENT OF PHASE-SHIFTING INTERFEROMETRY FOR MEASUREMENT OF MASS DIFFUSION

Figure 2.44: Optical measurements from an isothermal diffusion experiment in an ethanol-water binary solution at ethanol mean concentration $C_m = 38.52$ wt% and $\Delta C = 1.94$ wt%. (a) The portion surrounded by the vertical rectangle of the phase-shifted data shown in Fig. 2.43(c) is unwrapped and then averaged in the $x$ direction; the resulting profiles are adjusted in the phase difference domain assuming that the mass flux through both boundaries is equal. (b) The temporal variation of $\Delta \psi$; it remains constant as long as there is no mass flux through the immersed boundaries, as indicated by the phase-shifted data at $t = 80$ s.

indicate a homogeneous concentration area and, as a consequence, there is no Fickian diffusion because $\partial C / \partial x = 0$. At $t = 45$ s, the diffusion field at the center is quasi-one-dimensional and, therefore, it can be used to determine the phase difference between the boundaries ($\Delta \psi$); here $\Delta \psi_{\text{ethanol-water}} = 18.74 \pi$. However, at $t = 50$ s we can see with $L2$ a bulk of heavy solution falling near the right wall. This is due to a mistake in the injection procedure and is a cause of error in the measurement of the Fickian diffusion coefficient. In the isothermal diffusion experiments, only the data obtained with $L2$ is used because a higher resolution is obtained with this interferometer (the resolution in the concentration domain is proportional to the number of fringes). At $t = 85$ s, the vertical position of the cell is fixed, so that the phase-shifted data after $t = 85$ s can be used to determine the diffusion coefficient from the transient concentration profiles.

Figure 2.44 shows the optical measurements obtained from the phase-shifted data shown in Fig. 2.43(c). Figure 2.44(a) shows the phase difference profile between the
Table 2.6: Measurement of the contrast factor $\eta$ and diffusion coefficient for the two benchmark binary solutions at mean concentration $C_m$. The concentration in the contrast factors is given for the denser components, which are underlined for each solution. The reference values for ethanol-water (water 60.13 wt%) and isobutylbenzene-dodecane (IBB-C12 50 wt%) are included.

<table>
<thead>
<tr>
<th>Binary solution</th>
<th>ethanol-water</th>
<th>IBB-C12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean concentration, $C_m$ [wt%]</td>
<td>61.48</td>
<td>50.0</td>
</tr>
<tr>
<td>Contrast factor, $\eta$ [(wt% mm)$^{-1}$]</td>
<td>$-0.97\pi$</td>
<td>$1.93\pi$</td>
</tr>
<tr>
<td>$\left( \frac{dn}{dC} \right)_{(p,T)} \times 10^{-2}$ This study</td>
<td>$-3.07$</td>
<td>$6.01$</td>
</tr>
<tr>
<td>Reference</td>
<td>$-3.55$ [98]</td>
<td>$6.28 \pm 0.04$ [98]</td>
</tr>
<tr>
<td>$D$ [m$^2$/s $\times 10^{-10}$] This study</td>
<td>$4.31 \pm 0.92$</td>
<td>$9.57 \pm 0.24$</td>
</tr>
<tr>
<td>Reference</td>
<td>$4.32$ [162]</td>
<td>$9.50 \pm 0.4$ [163]</td>
</tr>
</tbody>
</table>

test and reference beams obtained by unwrapping the phase-shifted data inside the region indicated by the rectangles after $t = 45$ s, averaging at each height $z$, and shifting the curves in the phase difference domain assuming that there is an equal mass flux through both boundaries. The adjustment in the phase difference domain is necessary since the unwrapping alone produces time-unrelated phase difference profiles for each phase-shifted data, such as the one shown in Fig. 2.42(a). The data near the wall boundaries should be avoided until the diffusion field within the cell has reached a completely one-dimensional state. Figure 2.44(b) shows the phase difference between the boundaries $\Delta \psi$ as a function of time. This figure suggests that after $t = 100$ s there is a mass flux through the immersed boundaries. $\Delta \psi$ is then averaged between $t = 45$ s and $t = 90$ s. In this case, $\psi_{ave} = 18.74\pi$ rad, $\Delta C_{\text{ethanol}} = 1.94$ wt%, and $L = 10$ mm and, therefore, the contrast factor defined by Eq. (2.23) at a mean ethanol concentration of 38.52 wt% is $\eta_{\text{ethanol-water}}(38.52\text{wt%}) = 0.97\pi$ [rad wt%$^{-1}$ mm$^{-1}$]. The contrast factor has the opposite sign if the reference component in the binary system is changed. The measured contrast factors for the two benchmark binary solutions are listed in Table 2.6.

Figure 2.45 shows the isothermal diffusion field for the isobutylbenzene-dodecane binary solution. The experimental concentration profiles (gray circles) and their corre-
Figure 2.45: Transient concentration profiles within the diffusion cell for the isobutylbenzene-dodecane binary solution. The experimental and numerical profiles are indicated by gray circles and solid lines, respectively. The visualization range is from $z = 0$ to $z = 2.83$ mm. The fitted experimental results are also shown. In the numerical calculations, the first experimental profile is used as initial condition and considered to correspond to $t = 0$ s. The phase-shifted data for $t = 0$, 100, and 500 s is shown in the insets. The diffusion coefficient at $t = 500$ s is $D_{opt} = 9.56 \times 10^{-10}$ m$^2$/s. The average diffusion coefficient for all fits and its corresponding standard deviation is shown in Table 2.6.
sponding fittings (solid lines) are shown at intervals of 100 s. The fitting of the numerical solution to the experimental results was conducted by inverse analysis (see §3.4). The visualization range is from $z = 0$ to $z = 2.83$ mm, i.e. the upper and lower boundaries are immersed as indicated by the concentration gradients at the boundaries. The phase-shifted data at $t = 0$ s, 100 s, and 500 s are shown in the insets. The diffusion coefficient obtained at $t = 500$ s is $D = 9.56 \times 10^{-10}$ m$^2$/s.

The isothermal diffusion coefficient $D$ obtained by averaging the determined $D_{\text{opt}}$ for each reference time $t$ is listed in Table 2.6 with its corresponding standard deviation for the two benchmark liquid pairs: ethanol-water (water 61.48 wt%) and isobutylbenzene-dodecane (50.0 wt%). The reference value of the diffusion coefficient for these liquid pairs is included. A good agreement with the literature was found for these solutions. However, the standard deviation for the diffusion coefficient of the ethanol-water mixture is quite high, about 20% of its value; the disturbance observed at $t = 50$ s, which is shown in Fig. 2.43(c), must have influenced the accuracy of the measurement of the diffusion coefficient. The main goal of this experiment is to measure the contrast factor, so re-conducting the experiment only for diffusion measurements is unnecessary.

**Benchmark mixtures**

Thermodiffusion experiments were conducted with two well-studied binary mixtures, i.e. ethanol-water and isobutylbenzene-dodecane, in order to validate the proposed method. Figure 2.46 shows the phase-shifted data obtained in a thermodiffusion experiment for an ethanol-water solution at an initial homogeneous concentration of 39.12 wt% for the ethanol component (water 60.88 wt%). Two phase-shifted data are simultaneously obtained by OPSI (see Fig. 2.7). Here, the OP within the cell for $L1$ and $L2$ is 20 mm and 10 mm, respectively, just as in Fig. 2.39(c). Therefore, the resolution of the concentration measurement with $L1$ is double of that obtained with $L2$.

The ethanol-water binary solution is injected inside the Soret cell, which is then placed in the test section of the OPSI system. As shown in Fig. 2.46, the thermodiffusion field is
Induction of the thermodiffusion field and adjustment of mirror \( M_1 \) (steps B. and C.)

Thermodiffusion phase (step D.), \( \Delta T = 5 \) K, \( T_m = 25 \) °C

Isothermal diffusion phase (step E.), \( \Delta T = 0 \) K, \( T_m = 25 \) °C

Figure 2.46: Visualization of the thermodiffusion and isothermal diffusion fields of the ethanol-water binary solution (ethanol 39.12 wt%) inside the Soret cell by OPSI (see Fig. 2.7). The views from the orthogonally aligned interferometers with light sources \( L_1 \) (OP 20 mm) and \( L_2 \) (OP 10 mm) are shown at different experimental times. The entire height of the cell, i.e. 2 mm, is recorded by the phase-shifted data. The induction of the thermodiffusion field is conducted by applying a temperature difference of \( \Delta T = 5 \) K (\( T_m = 25 \) °C) and adjusting the tilt of the mirror \( M_1 \). The temperature reaches a linear profile between the copper blocks within 75 s. The mirror adjustment is finalized at 80 s, which is the time at which the measurement of the thermodiffusion phase is initialized. At \( t = 7000 \) s, the ethanol concentration profile has reached a quasi-steady state. At \( t = 7001 \) s, the binary solution is set to an isothermal state (\( T = 25 \) °C) and the Fickian diffusion process is then visualized with the test beam \( L_2 \) until the binary solution becomes homogeneous.
induced by applying a temperature difference of $\Delta T = 5$ K (mean temperature $T_m = 25^\circ$C) with the temperature control system previously described; $T_{room}$ is $25^\circ$C throughout the course of the experiment. Figure 2.47(a) shows the temporal variation of the temperature during the transition from isothermal condition to a linear temperature profile. We can see that at $t = 50$ s the temperature at the upper and lower boundaries has reached a quasi-constant value of $T_H = 27.5^\circ$C and $T_C = 22.5^\circ$C, respectively. After reaching a linear temperature profile between these boundaries, as indicated by the isophase (infinite fringe) condition for $L1$ at $t = 75$ s (see Fig. 2.47(a)) and $t = 80$ s (see Fig. 2.46), there is a constant thermodiffusive mass flux throughout the binary solution. This infinite fringe condition at the beginning of the thermodiffusion phase is achieved by manually adjusting the tilt of the reference mirror $M1$. In contrast, the fringe pattern obtained with $L2$ is too dense to subtract an unwrappable phase-shifted data with the CCD camera of pixel resolution $640 \times 480$. Hence, the thermodiffusion measurement is conducted only with $L1$, as shown in Fig. 2.46. Then, fringes start appearing near the upper and lower boundaries due to thermophoretic induced concentration gradients, as shown in the phase-shifted data at $t = 300$ s and $t = 400$ s. It is only in the region where fringes appear that mass transport due to Fickian diffusion occurs and opposes thermodiffusion, as described by Eq. (2.19). At this point, we can know if the species are thermophobic ($S_T > 0$) or thermophilic ($S_T < 0$) by comparing the phase-shifted data obtained with $L1$ (thermodiffusion phase in Fig. 2.46) and the phase-shifted data obtained in the preliminary experiments (snapshots in Fig. 2.43). We can see from the preliminary experimental results that the intensity gradient between two fringes in the phase-shifted data is positive (black to white isovalues) when moving upwards (increasing $z$ values); in these experiments the denser solution (which is richer in water) is placed below. Since we also have a positive gradient between two fringes in the thermodiffusion phase shown in Fig. 2.46, we can conclude that in this thermodiffusion experiment the water molecules migrate to the lower cold section of the cell. Therefore, the water molecules in this ethanol-water solution are thermophobic ($S_T > 0$). After $t = 400$ s in the thermodiffusion phase, fringes progressively occupy
the whole height of the cavity until the concentration field reaches a quasi-steady linear state, as indicated by the seemingly equidistant fringes in the phase-shifted data of \( L1 \) at \( t = 7000 \) s. These equidistant fringes are then connected to determine the phase difference \( \Delta \psi \) between the upper and lower boundaries. At \( t = 7000 \) s, \( \Delta \psi \) becomes \( 7.08 \pi \), and by substituting \( \Delta \psi \), \( \eta_{\text{ethanol-water}} \) (obtained in the preliminary experiments), and \( L = 20 \) mm in Eq. (2.23), the concentration difference between the upper and lower boundaries is found to be \( \Delta C = 0.37 \) wt%.

At \( t = 7001 \) s, the temperature control system is used to induce the isothermal phase \((T = 25^\circ \text{C})\) and Fickian diffusion is then visualized with the beam \( L2 \). Figure 2.47(b) shows the temperature control at this stage; its insets show snapshots of the phase-shifted data obtained with \( L2 \) at different times. During this temperature control process, which takes about 70 s, there is a range \((7008 s < t < 7028 s)\) where the temperature at the lower boundary is larger than that at the upper boundary. This might result in hydrodynamic instabilities due to \( Ra > 0 \). In this situation, the Rayleigh number \( Ra = 726 \) is estimated by substituting in Eq. (6.1) the following: \( \Delta T = 2 \) K (more than the maximum \( \Delta T \) in this range), \( l = 0.002 \) m, \( g = 9.8 \) m/s\(^2\), and the corresponding thermophysical properties of the ethanol-water solution \( \beta = 5.94 \times 10^{-4} \) 1/K, \( \nu = 1.08 \times 10^{-6} \) m\(^2\)/s, \( \kappa = 1.18 \times 10^{-7} \) m\(^2\)/s. The resulting \( Ra \) is less than half of the critical Rayleigh number \( Ra_c = 1732.5 \), which was calculated for this geometry by a continuation method previously described [79] (assuming \( \Delta C = 0 \)). Therefore, we can guarantee that there are no disturbances due to natural convection. In fact, the actual critical Rayleigh number should be larger than the calculated \( Ra_c \), because the concentration gradients present in the cell, which were induced by the original temperature gradient of the thermodiffusion phase, are stabilizing. After the temperature has reached a constant value within the cell, quasi-equidistant fringes are observed with \( L2 \) at \( t = 7060 \) s. This indicates that there is a linear concentration profile at the beginning of the isothermal diffusion phase. Moreover, when comparing the number of fringes obtained in the phase-shifted data of \( L1 \) and \( L2 \) at \( t = 7000 \) s and \( t = 7060 \) s, respectively, (i.e. 6 fringes in the former case and 3 fringes in the latter case) it is evident
Figure 2.47: PID temperature control of the upper and lower boundaries in a thermodiffusion experiment for the ethanol-water binary solution at the beginning of (a) the thermodiffusion phase, and (b) the isothermal diffusion phase. The mean temperature is kept at $T_m = 25^\circ C$. At $t = 0$ s, the target temperature difference is set to $\Delta T = 5$ K; it reaches a quasi-steady value at $t \approx 50$ s. A constant linear temperature profile is confirmed at $t = 75$ s by adjusting the tilt of the mirror $M1$ of the phase-shifting interferometer ($L1$). At $t = 7001$ s, the target is $\Delta T = 0$ K. The phase-shifted data for the unadjusted interferometer ($L2$) is shown in the insets at $t = 7001$ s, 7008 s, 7020 s, 7030 s, 7040 s, 7050 s, and 7080 s.
that the resolution of the measurement with $L1$ is double of that with $L2$ due to the longer OP (see Eq. (2.24)). The isothermal diffusion phase is then visualized until the binary solution becomes homogeneous, as indicated by the homogeneous intensity (infinite fringe condition) of the phase-shifted data at $t = 9000$ s in Fig. 2.46.

Figure 2.48 shows the temporal variation of the concentration difference $\Delta C$ between the upper and lower walls for the ethanol-water (Fig. 2.48(a)) and isobutylbenzene-dodecane (Fig. 2.48(b)) binary solutions. $\Delta C$ in Fig. 2.48(a) corresponds to that of ethanol, while $\Delta C$ in Fig. 2.48(b) corresponds to that of dodecane. Since $\Delta C$ is positive for ethanol and dodecane, which are the lightest components in each liquid pair, the hydrodynamic stability of the solution increases with time during the thermodiffusion phase. Here, the contrast factor $\eta$ for ethanol-water at $C_m = 38.5$ wt% and isobutylbenzene-dodecane at $C_m = 50$ wt% (see Table 2.6) was used to determine $\Delta C$. The variation of the contrast factor for the ethanol-water mixture between $C_m = 38.5$ wt% and $C_m = 39.12$ wt% is negligible [87]. Moreover, in the ethanol-water experiment, the OP for the thermodiffusion and isothermal diffusion phases was 20 mm and 10 mm, respectively, i.e. the concentration resolution in the thermodiffusion measurement is two times larger than in the isothermal diffusion measurement. This explains a larger scattering of the concentration difference $\Delta C$ points in the isothermal diffusion phase. In contrast, in the isobutylbenzene-dodecane experiment, the OP for the thermodiffusion and isothermal diffusion phases was 10 mm and 20 mm, respectively, values opposite to the ones chosen in the ethanol-water experiment, and the scattering of $\Delta C$ is now larger in the thermodiffusion phase. These results show that the measurements with a shorter OP result in a larger scattering of $\Delta C$.

The measurements shown in Fig. 2.48 are similar to those conducted with OBD technique where the measurement is based on the temporal variation of a local refractive index within the cell. Nevertheless, the advantages of phase-shifting interferometry become evident when analysing the phase-shifted data in more depth. Figure 2.49 shows the transient concentration profiles for the ethanol-water solution (ethanol 39.12 wt%) obtained from the phase-shifted data of the thermodiffusion phase; the phase-shifted data at $t = 100$ s,
Figure 2.48: Temporal variation of the concentration difference $\Delta C$ between the upper and lower walls for (a) ethanol in the ethanol-water solution, and (b) dodecane in the isobutylbenzene-dodecane (IBB-C12) solution. The lightest component in each liquid pair, i.e. (a) ethanol and (b) dodecane, is taken as reference for the concentration difference. The total experimental time is 12000 s for the former case and 7000 s for the latter case. Some snapshots of the phase-shifted data for the ethanol-water experiment are shown in Fig. 2.46. The temperature difference between the upper and lower boundaries in the thermodiffusion phase of ethanol-water and isobutylbenzene-dodecane is $\Delta T = 5$ K and $\Delta T = 6$ K, respectively. The OP in the measurement shown in (a) is 20 mm for the thermodiffusion phase and 10 mm for the isothermal diffusion phase. The OP in the measurement shown in (b) is 10 mm for the thermodiffusion phase and 20 mm for the isothermal diffusion phase. The scattering for the $\Delta C$ points is larger for the short OP measurements.
Figure 2.49: The concentration profiles for the ethanol component in the ethanol-water binary solution are plotted during its thermodiffusion phase. The Soret effect drives the ethanol molecules to the upper region, i.e. the high temperature region, and the water molecules to the lower region, i.e. the low temperature region. Therefore, the ethanol and water molecules have thermophilic and thermophobic behavior, respectively.

600 s and 7000 s are also shown as insets (see more snapshots in Fig. 2.46). The thermophilic nature of the ethanol molecules in this liquid pair is evident. Moreover, we can confirm that the concentration profile within the cell in its steady state is quasi-linear. This final state corresponds to the state where the Fickian diffusion and thermodiffusion, whose rates are written in Eq. (2.19), balance each other. We can also see in Fig. 2.49 that there is some waving of the concentration profiles, particularly near $z = 0$, i.e. close to the lower cold boundary. This is due to the beam deflection problem shown in Fig. 2.50.

In addition to the beam deflection of the test beam, as described by Mialdun and Shevtsova [125], the beam deflection problem depicted in Fig. 2.50 also considers that some of the beams which are curved toward the bottom colder side of the cell are reflected upwards by this boundary. This worsens the problem caused only by the deflection. Fur-
Figure 2.50: Beam deflection problem in the Soret cell with focus on the lower cold boundary (for \( Ra < 0 \)). The cold region inside the solution has a higher refractive index \( n \) than the upper hot region and, therefore, the beam is curved towards the bottom colder side of the cell. This problem is worsen with the reflection of the beam on the lower copper block.

thermore, this problem is still worsen when the OP within the cell or the temperature difference between the walls \( \Delta T \) is larger, making measurements with very long OP or large \( \Delta T \) quite problematic. In order to reduce the beam deflection problem for the beams which are not reflected by the lower copper wall, the focus point of the test beam was set to match the inner plane of the glass wall that is nearest to the CCD camera, as suggested by Mialdun and Shevtsova [125], for each test beam \( L1 \) and \( L2 \). The problem for the beams which are reflected can be reduced by applying a smaller \( \Delta T \) (see Fig. 3.24). These measures improved the quality of the measurement during the thermodiffusion phase.

Figure 2.51 shows the transient concentration profiles during the isothermal diffusion phase of the isobutylbenzene-dodecane binary solution (50 wt%); the insets show the phase-shifted data at \( t = 3700 \) s and \( 6100 \) s. This measurement indicates that, after the thermodiffusion phase, the isobutylbenzene molecules have accumulated in the lower cold part of the cell, revealing the thermophobic nature of the isobutylbenzene molecules. We can also observe that the concentration gradient at the copper/liquid boundaries is zero, in accordance to the impermeable condition \( (j = 0) \) at the wall with \( \Delta T = 0 \) K. In contrast, in
a thermodiffusion phase, a concentration gradient is found in the vicinity of the wall (see Fig. 2.49) accounting for the equilibrium between Fickian diffusion and thermodiffusion in an unchanged $j = 0$ condition. Furthermore, the transient concentration profiles in the isothermal phase can be taken as $C_{\text{exp}}$ in Eq. (2.14) in order to minimize the objective function $\delta$ and yield the isothermal diffusion coefficient of the liquid pair at $T_m$. Hence, thermodiffusion can be used as a mean to create an initial concentration condition for an isothermal diffusion experiment. This is a particular advantage for solutions that are too viscous to handle by using more conventional methods [39, 96]. Moreover, the beam deflection problem described in Fig. 2.50 is much less evident during the isothermal diffusion phase ($\partial n/\partial T = 0$) than during the thermodiffusion phase. This occurs because, for the concentration and temperature differences managed in these experiments, the influence of the temperature gradient on the refractive index ($\partial n/\partial T$), which is indicated by

![Graph showing transient concentration profiles during isothermal diffusion phase.](image)

**Figure 2.51:** Transient concentration profiles during the isothermal diffusion phase of the isobutylbenzene-dodecane binary solution (50 wt%). The profiles are shown at times separated by $\Delta t = 100$ s starting at $t = 3700$ s. After the thermodiffusion phase, the isobutylbenzene molecules have accumulated in the lower cold part of the cell, i.e. the isobutylbenzene molecules are thermophobic. The phase-shifted data at two different times is shown in the insets.
Table 2.7: The Soret coefficient $S_T$, the isothermal diffusion coefficient $D$, and the thermodiffusion coefficient $D_T$ for the two benchmark binary solutions measured in the present study at a mean concentration $C_m$. The reference component is underlined. Literature values are listed for comparison.

<table>
<thead>
<tr>
<th>Liquid pair</th>
<th>Ethanol-water</th>
<th>IBB-C12</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_m$ [wt%]</td>
<td>60.88</td>
<td>50.0</td>
</tr>
<tr>
<td>$D$ [m$^2$/s $\times 10^{-10}$]</td>
<td>This study: 4.31 ± 0.92, 9.57 ± 0.24</td>
<td>Reference: 4.32 [162], 9.50 ± 0.4 [163]</td>
</tr>
<tr>
<td>$S_T$ [K$^{-1} \times 10^{-3}$]</td>
<td>This study: 3.09, 3.86</td>
<td>Reference: 3.23 [162], 3.9 ± 0.1 [163]</td>
</tr>
<tr>
<td>$D_T$ (m$^2$ K$^{-1}$/s $\times 10^{-12}$)</td>
<td>This study: 1.33, 3.69</td>
<td>Reference: 1.37 [162], 3.7 ± 0.2 [163]</td>
</tr>
</tbody>
</table>

the dense fringes pattern of $L_2$ at $t = 60$ s in Fig. 2.46, is much larger than the influence of the concentration gradient on the refractive index ($\partial n/\partial C$), which is indicated by the few fringes observed in the isothermal diffusion phase with $L_2$ at $t = 7060$ s in Fig. 2.46.

Table 2.7 shows the Soret coefficients (from Eq. (2.20)), isothermal diffusion coefficients (by optimizing Eq. (2.14)), and thermodiffusion coefficients (from Eq. (2.18)) obtained in this study by using OPSI for the two benchmark solutions. The reference values are also listed. A good agreement with the literature was obtained, validating the experimental technique and the analysis method proposed in this section.
5 Concluding remarks

In this chapter, a novel yet precise technique to visualize isothermal diffusion and thermodiffusion was developed. The construction of a real-time phase-shifting interferometer is described. The principle of the optical technique and the design of the interferometer are explained. The experimental apparatus is validated for the measurement of Soret and Fickian diffusion coefficients by measuring benchmark values. The important points are summarized as follows:

In §2, the real-time phase-shifting interferometer is described in detail. The interferometer comprises a polarising Mach–Zehnder interferometer, a rotating polariser, a CCD camera, and an image-processing unit. A three-phase algorithm is implemented to obtain the phase difference between the test beam and the reference beam from three interferograms consecutively taken at $\theta_r = 0, \frac{2\pi}{3}, \frac{4\pi}{3}$ at time intervals of $\Delta t = 1/30$ s, where $\theta_r$ is the angle of the rotating polariser and $\Delta t$ is the time interval between the interferograms. The isothermal diffusion field was formed inside a diffusion cell with an automated process using a self-designed solution injection device (SID). A program with an original graphical user interface (GUI) and a processing algorithm was written in order to obtain in real-time the phase-shifted data and one-dimensional unwrapped phase maps. It is shown that the error for the measurement of the phase difference is largely reduced in comparison to optical techniques previously reported [116].

In §3, a novel technique to determine the isothermal diffusion coefficient as a function of concentration in aqueous solutions is developed. This method requires several experiments at different mean concentrations for a given binary solution, as in conventional methods. However, by using the phase-shifting interferometer and an inverse analysis coupled with a numerical calculation, each experiment is shortened to only 800 s. This is a very short time compared to conventional methods. In each experiment, a transient diffusion field is created with a narrow concentration difference. Conducting an inverse analysis of the measured transient concentration profile yields the diffusion coefficient.
corresponding to each mean concentration. Here, the use of a numerical calculation for the inverse analysis allows the consideration of more realistic initial conditions taken from initial experimental profiles. The method is validated by comparing the measured concentration dependence of the diffusion coefficient for sucrose and NaCl and the corresponding literature values [134]. A good agreement is obtained.

In §4, two phase-shifting interferometers are simultaneously used to visualize and measure thermodiffusion. The modified optical technique is termed orthogonal phase-shifting interferometry. A Soret cell \((W \times L \times H) = (10 \times 20 \times 1–2) \text{ mm}^3\) was built with lateral transparent walls made of quartz glass and upper and lower boundaries made of copper. The transparent walls permit the measurement of diffusion from two orthogonal views, while the metallic walls allow a rapid temperature control at the copper/liquid boundaries. The temperature control is conducted with Peltier modules regulated with a PID system. Thermodiffusion experiments were conducted with the height of the cell set to 2 mm. This is much less than the height of the cell used by previous research groups that use interferometric methods [51, 122]. A shorter cell height has three main advantages:

1. Reducing the volume sample (directly proportional to the height). This is useful when measuring the thermophysical properties of expensive biomolecules.

2. Shortening the measurement time (directly proportional to the second power of the height). This is necessary to measure thermodiffusion of biomolecules that have the risk of conformational changes. A shorter measurement time is also desirable to procure a more time-efficient measurement suitable for industrial applications.

3. Increasing the hydrodynamic stability of the system by decreasing the Rayleigh number \(Ra\) \((Ra\) is directly proportional to the third power of the height). This is particularly important when measuring negative Soret coefficient, which are known to cause Soret driven instabilities [119].
The main disadvantage of having a shorter cell height is the increase of the error due to the beam deflection problem. A careful alignment of the cell with the test beam of the interferometer can reduce this problem.

The measurement technique is validated by measuring the Soret coefficient of two well-known liquid pairs: ethanol-water (ethanol 39.12 wt%) and isobutylbenzene-dodecane (50.0 wt%), the latter being one of the binary mixtures in the Fontainebleau benchmark [163]. Preliminary experiments were conducted to measure the contrast factor of each liquid pair. These contrast factors serve as a link between the unwrapped phase-shifted data and the concentration, i.e. the measurement technique is independent of reference contrast factors found in the literature. The measured Soret coefficients, isothermal diffusion coefficients, and thermodiffusion coefficients for the two benchmark mixtures are in good agreement with the literature.

The optical techniques used in this chapter can be used to study isothermal diffusion and thermodiffusion of biomolecules (see Chapter III), as well as natural convection in parallelepiped enclosures (see Chapter VI).

Some of the methods and results presented in this chapter were published in [198,200].
III

Visualization and Measurement of Mass Diffusion in Biological Systems
Overview

In Chapter I, the importance of mass transport phenomena was discussed. It was also explained that the most accurate methods to measure mass diffusion coefficients are the optical ones [55]. These make use of transient refractive index profiles to measure the diffusion field inside a diffusion cell. In Chapter II, the design and construction of an optical system that is capable of conducting measurements of diffusion fields much more accurately than conventional optical systems were presented. A highly-accurate measurement method for mass diffusion in liquid mixtures was proposed and validated, for both isothermal diffusion and thermodiffusion.

The improved technique, which is called phase-shifting interferometry, could be one of the most accurate techniques currently available for studying mass diffusion in transparent binary liquids. In addition to the highly-accurate optical setup, the experiment makes use of a small diffusion cell with a solution injection device (SID), or a Soret cell coupled with a temperature control system. This allows a successful measurement with a small amount of sample in a short time. Therefore, phase-shifting interferometry is also suitable for applications in biological systems.

In §1, a brief introduction to mass diffusion in biological systems is given. The importance of such systems, the motivation of this study and its objectives are presented. In §2, free diffusion of protein solutions is investigated. The molecular mass dependence and concentration dependence of the mass diffusion coefficient are discussed. In §3, dilute ternary systems are investigated. These are of great relevance since the diffusive process usually occurs in a multicomponent environment. The possibility to apply this technique for mixture analysis, as an alternative to chromatography, is discussed. In §4, thermodiffusion of biomolecules (thermophoresis) is visualized in a convectionless environment for the first time.
1 INTRODUCTION

BIOMOLECULAR DIFFUSION

Reliable data on the diffusion coefficient in liquids is essential in the pharmaceutical and bioengineering fields. The isothermal diffusion coefficient is used to investigate the mechanisms involving in-situ diffusion in biological systems, e.g., mucosal systems [138], and crystal growth for drug formulations. Even though it is not in the scope of this dissertation, hindered diffusion also has an essential role in developing new drug delivery systems [74]. It has been demonstrated, nevertheless, that an interferometric technique, such as the one developed in Chapter II, can also be used to investigate hindered diffusion [118]. Free and hindered isothermal diffusions promote the mixing of species opposite to the concentration gradient and, therefore, their role can be characterized as passive for the mass transport in biological systems. In contrast, thermodiffusion (also called thermophoresis [132]) has been proposed as a tool to promote mass transport in such systems. Thermodiffusion is a potential alternative to electrophoresis for separation of biomacromolecules, such as proteins and DNA [32]. Therefore, it has a strong potential for drug screening applications as well as basic research [86].

Since the discovery of the law of diffusion by Fick in the 19th century, many methods to determine isothermal diffusion coefficients have been proposed. Early methods, such as Particle Uptake and Diaphragm Cell [190], still prove to be useful in the determination of the diffusion coefficient of certain solutes. However, these methods require a long measurement time and large amount of sample, which are impractical conditions when measuring the everyday growing number of rare proteins and polymers in the industry. In an attempt to overcome these obstacles, correlations that successfully predict the concentration and temperature dependence of globular proteins have been proposed in the literature [196]. However, these models are still limited, because they do not take into account various important factors such as ionic strength, molecular structure, and the
complex interactions between the solute and solvent molecules. Therefore, experimental measurement of the diffusion coefficient is the most reliable way of obtaining accurate values of this important property. Caldwell et al. [37] were among the first to use a Mach-Zehnder interferometer to determine the diffusion coefficient in binary solutions. Even though the method was fairly accurate, a large amount of sample was required. In the case of most proteins, the production in large scale is not possible due to its expensive manufacturing process. Therefore, there is a need of an experimental setup that is capable of obtaining the diffusion coefficient using a small amount of sample, such as the one proposed by Komiya et al. [96].

In contrast, more modern methods such as Pulsed-Gradient Spin-Echo Nuclear Magnetic Resonance (NMR) use an extremely small amount of sample to measure the self-diffusion coefficient. Nesmelova et al. [136] used this technique to obtain the generalized form of the concentration dependence of the self-diffusion coefficient of globular proteins. This method, however, is not effective when dealing with small solute molecules comparable in size to the solvent molecules. Moreover, only information about the self-diffusion coefficient and not the binary diffusion coefficient is obtained. Therefore, there is a need to utilize an experimental setup that is capable of obtaining the binary diffusion coefficient at various chemical potentials for different kinds of solutions, i.e. different solvent and solute molecular size ratios at various concentration and temperature conditions.

Moreover, concerning the thermodiffusion of biomolecules, Iacopini and Piazza [85] have conducted some of the few systematic measurements of thermodiffusion in protein solutions. Piazza et al. [160] discussed the physical mechanisms underlying thermophoresis in colloidal suspensions and macromolecular solutions, and presented a general model suggesting thermophoretic measurements as a sensitive probe of particle–solvent interfacial properties. They reported the Soret coefficient of hen egg-white lysozyme solutions at different temperature, pH, and ionic strengths.
OBJECTIVES

In this chapter, phase-shifting interferometry is proposed as a tool to study diffusion in biological binary systems. The focus is on the diffusion of protein molecules diluted in an aqueous solvent (buffered or unbuffered). The main objectives in this chapter are:

1. Determine the binary diffusion coefficient in protein aqueous solutions for a wide range of molecular size, using less than 500 µg of solute. The diffusion coefficient of seven proteins with molecular size from 6.5 kDa (aprotinin) to 97.2 kDa (phosphorylase b) is measured. The results are compared with the Stokes-Einstein equation and the relationship between the diffusion coefficient and the molecular structure is discussed.

2. Determine the concentration dependence of the mass diffusion coefficient for two protein-aqueous solutions. The results are qualitatively compared with the results of molecular dynamic simulations for hard-sphere and soft-sphere assumptions. Here, lysozyme (14.3 kDa) and bovine serum albumin (66.7 kDa) are the proteins which are discussed.

3. Study isothermal diffusion in dilute ternary systems. The inverse analysis is developed to determine pseudo-binary diffusion coefficients in multicomponent mixtures. Here, the ternary mixture of NaCl-lysozyme-water is studied.

4. Visualize thermodiffusion in dilute protein aqueous solutions. The Soret and Fickian diffusion coefficients are determined from a thermodiffusion experiment. Here, aprotinin (6.5 kDa) and lysozyme (14.3 kDa) are the proteins which are discussed.

The experimental methods described in this chapter encompass the new optical technique described in Chapter II, which can be used as a tool to deepen our understanding of biomolecular thermodiffusion.
2 ISOTHERMAL DIFFUSION IN BIOLOGICAL SYSTEMS

In Chapter II §2, an experimental method to measure isothermal diffusion coefficients was developed. In this section, the proposed optical method is applied to determine mass diffusion coefficients in dilute protein aqueous solutions.

2.1 DIFFUSION IN DILUTE PROTEIN AQUEOUS SOLUTIONS

DIFFUSION CELL

The dimensions of the diffusion cell used in these isothermal diffusion experiments is $W \times L \times H = 2 \text{ mm} \times 20 \text{ mm} \times 45 \text{ mm}$. The small width reduced the sample volume; the large optical path increases the resolution of the measurement; the height of the cell is sufficient to guarantee the infinite slab condition. A photo of the cell is shown in Fig. 2.21 (the black cell to the left).

MATERIALS

In this section, the diffusion coefficients of aprotinin, $\alpha$-lactalbumin, lysozyme, trypsin inhibitor, ovalbumin, BSA, and phosphorylase b were determined. The measurements for NaCl and sucrose (Wako Pure Chemical Industries Inc.) are also included for comparison. Aprotinin, $\alpha$-lactalbumin, trypsin inhibitor, ovalbumin, BSA, and phosphorylase b were produced by Sigma-Aldrich Inc.; lysozyme was produced by Merck Inc. The corresponding molecular mass, protein source, and lot no. are listed in Table 3.1. The proteins were used in their delivered form without further purification. Distilled water at pH 7.0 was used as solvent. The solutions were prepared by measuring the weight of the solute and solvent in a chemical balance at $T_{\text{room}} = 25^\circ\text{C}$, where the density of water was taken as 1000 kg/m$^3$. Aqueous solutions with concentration of 3 mg/ml were prepared for all the solutes listed in Table 3.1, except for aprotinin and phosphorylase b, where a concentration of 2 mg/ml was used. The diffusion experiments were conducted within 24 h of
Table 3.1: Protein solutions used to prepare the binary solutions in the isothermal diffusion experiments. The name of the solute, the source of the proteins, their corresponding molecular masses, and their lot no. are listed. The concentration of the protein-water binary solutions is shown. The species labelled with * are those which can be found in the literature.

<table>
<thead>
<tr>
<th>Name</th>
<th>Source</th>
<th>Molecular mass [Da]</th>
<th>Lot no.</th>
<th>C [mg/ml]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl*</td>
<td>–</td>
<td>58.44</td>
<td>3022</td>
<td>2</td>
</tr>
<tr>
<td>Sucrose*</td>
<td>–</td>
<td>342.30</td>
<td>STP670</td>
<td>2</td>
</tr>
<tr>
<td>Aprotinin</td>
<td>Bovine lung</td>
<td>6500</td>
<td>058K7024</td>
<td>2</td>
</tr>
<tr>
<td>α-lactalbumin</td>
<td>Bovine milk</td>
<td>14178</td>
<td>107K7027V</td>
<td>3</td>
</tr>
<tr>
<td>Lysozyme</td>
<td>Chicken egg white</td>
<td>14307</td>
<td>K40380581</td>
<td>3</td>
</tr>
<tr>
<td>Trypsin inhibitor</td>
<td>Glycine max</td>
<td>20100</td>
<td>010M73531</td>
<td>3</td>
</tr>
<tr>
<td>Ovalbumin</td>
<td>Hen egg white</td>
<td>44287</td>
<td>040M7001V</td>
<td>3</td>
</tr>
<tr>
<td>Albumin*</td>
<td>Bovine serum</td>
<td>66776</td>
<td>089K1438</td>
<td>3</td>
</tr>
<tr>
<td>Phosphorylase b</td>
<td>Rabbit muscle</td>
<td>97200</td>
<td>124K7405</td>
<td>2</td>
</tr>
</tbody>
</table>

the solution preparation to avoid possible coagulation or ageing.

In order to create a one-dimensional field, the binary solution was first injected in the diffusion cell. Then, pure water was injected with the SID to create a concentration gradient and initiate the diffusion process. Since each experiment requires at least 500 µl of solution, the mass diffusion coefficient for 2 mg/ml difference diffusion experiments could be determined with at least 1 mg of solute. This is actually the maximum quantity that could be purchased for aprotinin, which is a very expensive protein sold by the milligram.

As explained in Chapter II §3, the experimental setup can manage concentration differences of at least 1 mg/ml. However, a 2 mg/ml concentration difference is preferable in order to obtain a better accuracy by increasing the number of fringes and reducing the turbulence due to similar densities. The influence that the concentration difference has on the accuracy of the measurement is discussed in detail in Chapter II §3.2.

**Transient concentration profiles of biomolecules**

Figure 3.1 shows the phase-shifted data for (a) NaCl, (b) aprotinin, (c) α-lactalbumin, (d) trypsin, (e) bovine serum albumin (BSA), and (f) phosphorylase, at different times. As
Figure 3.1: Phase-shifted data (modulo $2\pi$) for the six aqueous solutions. The solutes are (a) NaCl, (b) aprotinin, (c) $\alpha$-lactalbumin, (d) trypsin, (e) BSA, and (f) phosphorylase b at $t = 100$ s, 300 s, 500 s, 900 s, 1400 s, and 2000 s. See Table 3.1 for the concentration $C_{\text{high}}; C_{\text{low}} = 0$ mg/ml.
indicated, the gravity force is from right to left, meaning that the solution containing the solute of interest is in the left part while pure water is in the right part of the phase-shifted data. These data were acquired every $\Delta t = 100$ s; some of these snapshots are shown in Fig. 3.1. The concentration difference in experiments (a), (b), and (f) is 2 mg/ml, while in experiments (c), (d), and (e) it is 3 mg/ml. Diffusion cells of different width and thickness were used. In experiments (a), (b), (c), and (d), the width of the cell is 2 mm, while in experiments (e) and (f) the width is 5 mm (the phase-shifted data shown in (e) and (f) have a width of about 1 mm). Moreover, the scale of the observation zone in experiments (a) and (f) differs from the one in (b), (c), (d), and (e). This scale was adjusted in each experiment based on an estimate of the diffusion coefficient of the substance. For example, in the case of NaCl, its diffusion coefficient in liquids is expected to be higher than for the other substances since its molecular size is small; so in this case a larger scale and a shorter time difference between snapshots was chosen.

From this phase-shifted data, it is clear that different substances with different molecular mass diffuse at different rates. Here, the general trend is that the bigger the molecular mass is, the slower it diffuses, as predicted by Stokes-Einstein equation. However, this is only a qualitative description. Therefore, a quantitative analysis based on the determination of mass diffusion coefficients is conducted.

Figure 3.2 shows the transient concentration distributions for the same binary solutions as in Fig. 3.1. The ordinate is the position $z$ [mm] and the abscissa is the concentration $C$ [mg/ml]. From these figures, a different diffusion rate for the binary solutions can be observed. Moreover, for the cases of $\alpha$-lactalbumin (c), trypsin (d), and BSA (e), no values for the concentration profiles at $t_{ini} = 100$ s could be measured due to dense fringe pattern in the phase-shifted data, as shown in the corresponding phase-shifted data in Fig. 3.1. In the case of aprotinin (b), an asymmetrical diffusion between $t = 100$ s and 200 s is observed. The main cause for this asymmetry could be due to the fact that the diffusion process that is taking place inside the 2 mm width diffusion cell has not yet reached a one-dimensional state. Another cause might be the concentration dependence
Figure 3.2: Transient concentration profiles for the six aqueous solutions whose phase-shifted data is shown in Fig. 3.1. The profiles for (a) NaCl, (b) aprotinin, (c) α-lactalbumin, (d) trypsin, (e) BSA, and (f) phosphorylase b are shown at different times.
of the diffusion coefficient within this small concentration difference, e.g. for NaCl as shown in Fig. 2.36(a). This can be clearly seen in Figs. 3.1(b-d) at $t = 100$ s. In the case of NaCl (a), even though the width of the cell was 2 mm, the diffusion rate is larger so the disturbance disappears almost entirely at $t = 100$ s, as shown in Fig. 3.1(a).

For a clearer comparison between the diffusion process of the proteins, the concentration profiles and corresponding phase-shifted data for $\alpha$-lactalbumin, trypsin inhibitor, ovalbumin, and BSA at $t = 800$ s are shown in Fig. 3.3. The initial conditions are almost the same due to the automatic injection by using the SID. From this figure, it is clear that different proteins exhibit different diffusive behaviour. Molecules with larger molecular mass generally diffuse slower than those with smaller mass, as described by the Stokes-Einstein equation:

$$D = \frac{k_B T}{6\pi\mu r_0},$$

(3.1)

where $k_B$ is Boltzmann’s constant, $T$ is the temperature, $\mu$ is the solvent viscosity, and $r_0$ is the radius of the solute molecules. Equation (3.1) predicts the diffusion coefficient in the dilute region, i.e. no interaction exists between the solute molecules. In this equation,
Figure 3.4: Results for the isothermal mass diffusion coefficient. The abscissa is the reference time $t$ and the ordinate indicates the determined mass diffusion coefficient $D_{opt}$.

The solute molecules are assumed as hard spheres with a size much larger than the solvent molecules. This assumption is roughly valid for the lysozyme molecules whose molecular size is $45 \times 30 \times 30$ Å, as reported by Blake et al. [25]. On the other hand, the BSA molecules exhibit a more prominent prolate ellipsoid whose size is $140 \times 40 \times 40$ Å, as reported by Sorensen et al. [187].

**Binary diffusion coefficient of protein aqueous solutions**

Figure 3.4 shows the determined diffusion coefficients for some protein solutions (NaCl also included) as a function of the reference time $t$ from the transient concentration profiles shown in Fig. 3.2. The abscissa is the reference time $t$ of the experimental concentration distribution $C_{exp}(z,t)$ used in the calculation of the mass diffusion coefficient (see the objective function in Eq. (2.14)), and the ordinate is the calculated mass diffusion coefficient $D_{opt}$ for which the objective function is minimum. In an ideal measurement, where
the diffusion coefficient is constant, the determined diffusion coefficient is independent of $t$, i.e. horizontal profiles should be obtained in Fig. 3.4. Nonetheless, our results indicate that the determined diffusion coefficient varies significantly only for $t$ close to $t_{ini}$, i.e. in all cases the calculated mass diffusion coefficient reaches a nearly constant value beyond some values of the reference time. The large difference in the calculated mass diffusion coefficients for early reference times is due to closely packed concentration profiles, as those shown in Figs. 3.2(e,f). If the profiles are too dense, the errors in the measurement system affect the calculation accuracy in a much higher degree than with curves that are more distant. Therefore, in the case of NaCl, where the diffusion is fast, the calculated mass diffusion coefficient reaches a nearly constant value just at the first reference time, i.e. $t = 200$ s, as shown in Fig. 3.4.

Another reason for the strong variations of the calculated mass diffusion coefficient when the reference time is chosen close to $t_{ini}$, is that for small mass diffusion coefficients it takes a longer time for the one-dimensional concentration profile to form. When the high and low concentration solutions become in contact during the injection process with the SID, weak mixing occurs due to the initial surface tension effects. In a small width diffusion cell, the high concentration solution first introduced climbs along the sidewalls due to the surface tension, forming U-shaped initial concentration profiles. This can be observed in the phase-shifted data of Figs. 3.1(b-d) at $t = 100$ s, where a 2 mm width diffusion cell was used. In the case of NaCl shown in Fig. 3.1(a), there is no U-shaped profile at $t = 100$ s because the diffusion process is fast and the initial high concentration zones near the walls quickly disappear. In contrast, the effects of the initial disturbance still remain in the first stages of the experiment in the case of macromolecules. For aprotinin, a one-dimensional diffusion is reached at $t \approx 300$ s; in the case of $\alpha$-lactalbumin, it is reached at $t \approx 500$ s; and in the case of trypsin it is reached at $t \approx 900$ s. This two-dimensional diffusion process clearly compromises the calculated values of diffusion coefficients that are obtained through a model based on a one-dimensional calculation. Nevertheless, the calculated values of the mass diffusion coefficient do reach a certain
Table 3.2: Determined diffusion coefficient for two inorganic and seven protein solutions. The reference values available are also listed. * indicates that the binary solution was measured at pH 8.0. $C_m$ is the mean concentration of the diffusion experiment.

<table>
<thead>
<tr>
<th>Name</th>
<th>Molecular Mass [Da]</th>
<th>$C_m$ [mg/ml]</th>
<th>$D$ (Reference) [$m^2/s \times 10^{-10}$]</th>
<th>Standard deviation [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>58.44</td>
<td>1.0</td>
<td>15.10 (15.45 [21])</td>
<td>0.167 (1.1)</td>
</tr>
<tr>
<td>Sucrose</td>
<td>342.30</td>
<td>1.0</td>
<td>5.17 (5.22 [21])</td>
<td>0.114 (2.2)</td>
</tr>
<tr>
<td>Aprotinin</td>
<td>6500</td>
<td>1.0</td>
<td>2.54</td>
<td>0.136 (5.3)</td>
</tr>
<tr>
<td>α-Lactalbumin</td>
<td>14178</td>
<td>1.5</td>
<td>2.10</td>
<td>0.123 (5.9)</td>
</tr>
<tr>
<td>Lysozyme</td>
<td>14307</td>
<td>1.5</td>
<td>4.48</td>
<td>0.176 (3.9)</td>
</tr>
<tr>
<td>Trypsin inhibitor</td>
<td>20100</td>
<td>1.5</td>
<td>2.03</td>
<td>0.011 (0.5)</td>
</tr>
<tr>
<td>Ovalbumin</td>
<td>44287</td>
<td>1.5</td>
<td>3.40</td>
<td>0.004 (0.3)</td>
</tr>
<tr>
<td>Albumin (BSA)</td>
<td>66776</td>
<td>1.5</td>
<td>0.77 (0.59* [13])</td>
<td>0.040 (5.2)</td>
</tr>
<tr>
<td>Phosphorylase b</td>
<td>97200</td>
<td>1.0</td>
<td>1.61</td>
<td>0.036 (2.2)</td>
</tr>
</tbody>
</table>

A constant value after enough time has passed, as shown in Fig. 3.4. These are the values that are averaged and reported in this study.

In this study, the diffusion coefficient of the binary system is taken as the average diffusion coefficient when the standard deviation of five consecutive values is less than 6.0%. The determined diffusion coefficients with their correspondent standard deviation for NaCl, sucrose, and seven protein solutions are listed in Table 3.2. The reference values for NaCl, sucrose, and BSA [13,21] are also included. Notice that the diffusion coefficient for BSA is reported in the literature for pH 8.0 [13]. A good agreement with the literature values is obtained, validating the measurement method for biomolecules, such as BSA. The small standard deviation in Table 3.2 indicates the high accuracy of the measurement.

**DISCUSSION**

Figure 3.5 shows the plotted values of Table 3.2, i.e. the molecular mass dependence of the diffusion coefficient at pH 7.0. This is the pH of distilled water containing a very diluted protein. The results exhibit the general trend which is that the diffusion coefficient is inversely proportional to the molecular mass. If the diffusing molecules are taken as hard spheres with density $\rho$, Eq. (3.1) can be rewritten as:
Figure 3.5: Experimental results for the diffusion coefficient of different proteins plotted as a function of the molecular mass $M$ at pH 7.0. The values of NaCl and sucrose are also included for comparison. The solid line is the fit of Eq. (3.2). A rough agreement with the Stokes-Einstein equation was obtained.

$$D = \xi M^{-1/3},$$

where

$$\xi = \frac{k_B T}{6\pi \mu} \left(\frac{4\pi \rho}{3}\right)^{1/3}.$$  \hspace{1cm} (3.3)

The curve fitting based on the objective function for these experimental values is shown by the solid line in Fig. 3.5. This demonstrates that even though the molecules have different molecular structure and isoelectric point, the trend for the dependence of the diffusion coefficient with molecular mass can be roughly predicted by the Stokes-Einstein equation. Furthermore, since the coefficient $\xi$ is only a function of the molecular density $\rho$ at constant temperature for the same solvent, one could predict an average molecular density for the proteins from the experimental data. Substituting the fitted experimen-
tal value $5 \times 10^{-9}$ [Da$^{1/3}$ m$^2$/s] for $\xi$, and taking the viscosity of water at $T = 25^\circ$C as $8.9 \times 10^{-4}$ [Pa·s] in Eq. (3.3), the molecular density is estimated to be $2.03 \times 10^3$ kg/m$^3$. However, a direct calculation of the molecular density of lysozyme and BSA using the molecular mass listed in Table 3.2, leads to the values of $1.40 \times 10^2$ kg/m$^3$ and $1.18 \times 10^2$ kg/m$^3$, respectively. This overestimation of the molecular density based on the Stokes-Einstein equation suggests that the solute molecules are hydrated, and therefore the radius $r_0$ is rather a measure of the solute-water complex.

**ADVANTAGES**

The advantages of the proposed method to measure isothermal diffusion coefficients in biological systems are the following:

1. **Small quantity of sample.** Less than 1 mg of solute and 1 ml of solvent are required to determine the mass diffusion coefficient of the substance. The cost is a limiting factor in the determination of expensive proteins, such as aprotinin.

2. **Short-time measurement.** The time required for the determined mass diffusion coefficient to become constant is less than 30 min, as shown in Fig. 3.4. This is a short measurement time in comparison to those reported for similar measurement techniques [192].

3. **Accurate measurement.** As indicated in Table 3.2, the standard deviation for most of the measurements is within 5%.

4. **Simple determination procedure.** The experimental concentration profiles are compared with profiles obtained by a simple one-dimensional numerical calculation.

The mass diffusion coefficients in the binary mixtures were determined for a very dilute concentration, i.e. $C_m = 1-2$ mg/ml, and thus their values could be considered
constant. This is suggested by the small standard deviation of the measurements. However, the measurement of the concentration dependence of mass diffusion coefficients is essential since these values are required to predict phenomena in highly concentrated environments, such as in crystal growth processes. This is discussed in the next section.

2.2 CONCENTRATION DEPENDENCE OF ISOThERMAL DIFFUSION: LYSOZYME AND ALBUMIN

Figure 3.6 shows the determined concentration dependence of the diffusion coefficients of lysozyme and BSA. The experimental procedure is the same as that explained in Chapter II §2. The vertical bars in Fig. 3.6 indicate the standard deviation of the measurements for different $t$. In Fig. 3.5, the diffusive behaviour for different infinitely dilute solutes in a common solvent was shown, uncovering interactions between the solute and solvent

![Figure 3.6: Concentration dependence of the isothermal diffusion coefficient for BSA (right ordinate) and lysozyme (left ordinate). Notice that the order of magnitude in the ordinate axes is different. The concentration dependence for BSA is consistent with those predicted by hard-sphere models, whereas the concentration dependence for lysozyme is consistent with those predicted by soft-sphere models [195].](image-url)
molecules. In contrast, in Fig. 3.6 the solute-solvent system is fixed but considered at different solute concentrations. Hence, the molecular interactions within the solute are expected to play a role. As in the dilute case, the diffusion coefficient of BSA is about one order of magnitude smaller than that of lysozyme throughout the examined concentration range: this is mainly due to the larger molecular mass of BSA. However, both proteins have a different dependence of the mass diffusion coefficient with concentration. For BSA, the diffusion coefficient does not vary significantly from 0 to 80 mg/ml. This indicates a very weak intermolecular interaction, i.e. the diffusion process is almost the same as in the infinite dilute region. In contrast, the diffusion coefficient of lysozyme exhibits a considerable drop for the same concentration range. Therefore, interaction between molecules occurs even at relatively low concentrations, such as 30 mg/ml.

This difference in the concentration dependence of the mass diffusion coefficients has recently been studied by molecular dynamics (MD) simulations by Tokuyama et al. [195]. They reported that for molecules modelled as hard spheres the long-time self-diffusion coefficient has a weak dependence on the concentration in the dilute region, and that there is a sudden drop when the concentrated region is reached. In contrast, the soft-core potential model induces a steeper drop of the self-diffusion coefficient in the dilute region than that obtained with the hard sphere model. We can notice that this contrast of behaviours is observed in Fig. 3.6.

It is also important to acknowledge that the binary diffusion coefficients reported in this study are close to the self-diffusion coefficient of the solute [55], since the chemical potential gradient throughout the diffusion field is kept small. From the MD results of Tokuyama et al. [195] and the experimental results reported in Fig. 3.6, it is inferred that BSA behaves as a hard sphere, whereas lysozyme has a soft-sphere-like diffusive characteristic. The hard sphere behaviour of BSA has previously been reported by Nesmelova et al. [136]. Nonetheless, lysozyme (studied at different pH values) was also taken as a hard sphere, even though its diffusion coefficient does not experience a sudden drop in value beyond a certain concentration.
3 ISOHERMAL DIFFUSION IN DILUTE TERNARY SOLUTIONS

In §2, Fickian diffusion in binary solutions, which is the most basic form of mass diffusion, was investigated. However, all the diffusion processes that occur in nature take place in a multicomponent environment. A binary system is just an approximation of an ideal system where only two species exist, i.e. there are no impurities whatsoever. Furthermore, solvents that are merely composed of pure water, as those studied in §2, are rarely encountered in biological systems. Most of the solvents are mixtures of many components that interact with each other, as well as with the diffusing species. A pseudo-binary diffusion may be assumed to estimate the diffusion rate in some systems, such as the ones studied in §2. Nevertheless, when the concentration of the various species is not negligible, an additional assessment concerning the interaction between the species is required. Detailed evaluation of multicomponent diffusion is of particular interest in processes that occur in saturated conditions, such as crystal growth.

Moreover, chromatography is one of the most important tools in bioengineering and it has become essential to the analysis of mixtures. Chromatography is based on the measurement of the different diffusion rates for different species within a gel or porous medium, i.e. hindered diffusion in a multicomponent system. This hindered diffusion is a very slow process. In order to reduce the analysis time, techniques such as high-performance liquid chromatography (HPLC) were developed. An alternative to HPLC, where an absorbent is used to cause the hindered diffusion leading to the separation of the species, could be the use of an optical technique that analyses the free diffusion of a multicomponent solution. Free diffusion is a much faster process than hindered diffusion and can be used with less amount of sample.

In this section, a ternary system with the phase-shifting interferometric technique developed in Chapter II was investigated. The ternary system is a dilute NaCl-lysozyme-
buffer solution, where the buffer is a solvent used to fix the pH of the mixture. First, an experimental investigation of the cross-term effect is conducted in diluted systems. Then, the inverse analysis proposed in Chapter II is developed for multicomponent systems. Finally, the inverse analysis is applied to the ternary system to obtain the diffusion coefficients. The system is studied at $T_{room} = 25^\circ C$.

### 3.1 MATERIALS

The ternary system NaCl-lysozyme-buffer aqueous solution was examined in a set of experiments. NaCl (58.5 Da) and lysozyme (14307 Da) from chicken egg-white were used as solutes, while a Britton-Robinson type buffer was used as solvent. Lysozyme (one of the proteins studied in §2) is a small enzyme which can be found in the tears of humans and in the chicken egg-white. It protects us from the ever-present danger of bacterial infection by attacking the protective cell walls of bacteria. Therefore, due to its importance it was chosen in this diffusion study. Many research groups have studied it under isothermal and non-isothermal conditions [15] [34] [111] [112] [206]. Binary and ternary diffusion coefficients have been reported [7] [9] [10] [101]; solubility values in NaCl solutions are also known [11] [33] [83] [216].

A Britton-Robinson type buffer was used to control the pH of the solution [156]. The pH of this buffer is set by combining a $\chi$ ml volume of a mixture consisting of boric acid
Table 3.3: pH values of the Britton-Robinson buffer in function of $\chi$ [156]. $\chi$ is the volume in [ml] of a mixture consisting of boric acid 0.2 M and citric acid 0.05 M; $(200 - \chi)$ ml of trisodium phosphate is added to this mixture.

<table>
<thead>
<tr>
<th>pH</th>
<th>$\chi$</th>
<th>pH</th>
<th>$\chi$</th>
<th>pH</th>
<th>$\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>195</td>
<td>5.5</td>
<td>125</td>
<td>9.0</td>
<td>69</td>
</tr>
<tr>
<td>2.5</td>
<td>184</td>
<td>6.0</td>
<td>118</td>
<td>9.5</td>
<td>60</td>
</tr>
<tr>
<td>3.0</td>
<td>176</td>
<td>6.5</td>
<td>109</td>
<td>10.0</td>
<td>54</td>
</tr>
<tr>
<td>3.5</td>
<td>166</td>
<td>7.0</td>
<td>99</td>
<td>10.5</td>
<td>49</td>
</tr>
<tr>
<td>4.0</td>
<td>155</td>
<td>7.5</td>
<td>92</td>
<td>11.0</td>
<td>44</td>
</tr>
<tr>
<td>4.5</td>
<td>144</td>
<td>8.0</td>
<td>85</td>
<td>11.5</td>
<td>33</td>
</tr>
<tr>
<td>5.0</td>
<td>134</td>
<td>8.5</td>
<td>78</td>
<td>12.0</td>
<td>17</td>
</tr>
</tbody>
</table>

Table 3.4: Ternary solutions of NaCl-lysozyme-buffer prepared for the isothermal diffusion experiment. Two sets of solutions with the solute concentration of 30 and 40 mg/ml were prepared (pH 3.9).

<table>
<thead>
<tr>
<th>Solution</th>
<th>$C = 30$, 40 mg/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lysozyme:NaCl</td>
<td>1:1</td>
</tr>
<tr>
<td>NaCl [%]</td>
<td>50</td>
</tr>
<tr>
<td>Lysozyme [%]</td>
<td>50</td>
</tr>
</tbody>
</table>

0.2 M and citric acid 0.05 M with $(200 - \chi)$ ml of trisodium phosphate, as shown in Table 3.3. The pH is known to influence the solubility of the solutes as well as the values of mass diffusion coefficients. Figure 3.7(b) shows how clusters of lysozyme appear with time in a lysozyme-buffer solution at a high concentration (80 mg/ml) and at pH 6.9. In order to avoid solutal coagulation, the pH of the buffer was set to pH 3.9 and the lysozyme concentration was limited to 30 and 40 mg/ml, taking into account the lysozyme solubility in NaCl-water solutions reported by Howard et al. [83].

Variations in pH levels can alter the shape of the protein molecules, resulting in significant changes in the values of the mass diffusion coefficient as predicted by the Stokes-Einstein equation, i.e. Eq. (3.1). From this equation, it can also be predicted that the small NaCl molecules will diffuse faster than the large molecules of lysozyme. Actually, the large size of lysozyme molecules impedes its use as a useful drug. It can be applied topically, but cannot rid the entire body of disease, because it is too large to travel between cells.
Table 3.4 shows the concentration ratios of the ternary solutions that were prepared. Here, four binary solutions of 30 and 40 mg/ml were prepared for NaCl and lysozyme. By mixing these binary solutions with the concentration ratios listed in Table 3.4, a total of eight ternary solutions with different solute composition, of concentration 30 and 40 mg/ml, were prepared. The different concentration rates were chosen to change the number of fringes in the phase-shifted data and, thus, modify the accuracy of the measurement with the optical system. The percentage [%] of the concentration ratio for each solution is also listed.

In order to assess the magnitude of the cross-term in these ternary solutions, the transient concentration profiles of binary experiments are compared to those of the ternary experiments. The mass diffusion coefficient also depends on the pH of the solution, so the results obtained for binary systems in §2 cannot be used for comparison (in those experiments distilled water was used as solvent). Here, binary diffusion experiments are conducted with the same solutions used in the ternary experiments. Finally, these two results are compared to assess any possible interaction between the diffusing species.

### 3.2 ASSESSMENT OF CROSS-TERM DIFFUSION

**Binary diffusion experiments with buffered solution**

For these experiments, a buffer solution at \( C_{low} = 0 \) mg/ml is injected above the binary solution at \( C_{high} \), determining a concentration difference \( \Delta C = C_{high} \) and a mean concentration \( C_m = C_{high}/2 \). Figure 3.8 shows the phase-shifted data (modulo \( 2\pi \)) for the binary systems of NaCl-buffer and lysozyme-buffer at \( C_m = 15 \) and 20 mg/ml for \( t = 100 \) s, 225 s, 400 s, 625 s, 900 s, and 1225 s. These measurement times were selected in order to ease the comparison (instead of using \( \Delta t = 100 \) s as in §2). Notice that since the concentration difference in (b) and (d), i.e. 40 mg/ml, is about 30% higher than in (a) and (c), i.e. 30 mg/ml, there are about 30% more fringes in the former than in the latter. This results in a higher measurement accuracy for the local concentration. However, as shown in Fig.
Chapter 4

Chapter 3 cannot be used since the solvent of these experiments was pure water. Instead, binary diffusion experiments are also conducted with the same solutions used to do the ternary experiments. Finally, these two are compared to qualitatively verify if there is any interaction between the solutes.

4.1.1 Preliminary Binary Experiments

Figure 4.2 shows the phase-shifted data for the binary systems of 30 mg/ml NaCl-Buffer and Lysozyme-Buffer at 100s, 225s, 400s, 625s, 900s, and 1225s. These times were selected, in contrast to the 100s time difference in Chapter 3, in order to simplify the comparison. The transient concentration distributions obtained from these phase-shifted data are shown in Fig. 4.3. Again, the diffusion of the ionized NaCl in the buffer solution seems to obey Fick’s law anddiffuses faster than Lysozyme. These results are the same reported in Chapter 3 for the case of water as solvent. The effects of the buffer solution on the diffusing species can be detected by determining the mass diffusion coefficient in each case. From Fig. 4.3(b), it can be seen that the profiles at 1225s are waved. This is due to instabilities in the laser caused by a long operation time. The instability was reduced by attaching black cooling fins to the laser, as well as by turning off the laser between snapshots.

The transient concentration distributions obtained from the phase-shifted data shown in Fig. 3.8(a,b) are shown in Fig. 3.9. Again, the diffusion of NaCl and lysozyme can be compared: the former species diffuses faster than the latter. The same occurs when using water as solvent (see Fig. 3.5). From Fig. 3.9(b), it can be seen that the profiles at t = 1225 s are waved. This is due to instabilities in the laser caused by a long operating time. The instability was reduced by attaching black cooling fins to the laser (see Fig. 2.3), as well as by turning off the laser between snapshots. Furthermore, in the NaCl concentration profiles (b) a gradient of concentration at the boundaries for t = 900 s and 1225 s is observed, indicating there is a mass flux through the boundaries. This means 3.8(c), the fringes for lysozyme with \( C_{\text{high}} = 40 \text{ mg/ml} \) at \( t = 100 \) and 225 s are too dense, so that the phase-shifted data could not be successfully unwrapped and the corresponding concentration profiles were not obtained from these phase-shifted data.

Figure 3.8: Phase-shifted data (modulo \( 2\pi \)) for the binary experiments using a buffer solution (pH 3.9). The binary solution at high concentration \( C_{\text{high}} \) is first placed inside the cell. A buffer solution at \( C_{\text{low}} = 0 \text{ mg/ml} \) (solutal concentration) is injected from above with the SID.

3.8(c), the fringes for lysozyme with \( C_{\text{high}} = 40 \text{ mg/ml} \) at \( t = 100 \) and 225 s are too dense, so that the phase-shifted data could not be successfully unwrapped and the corresponding concentration profiles were not obtained from these phase-shifted data.

The transient concentration distributions obtained from the phase-shifted data shown in Fig. 3.8(a,b) are shown in Fig. 3.9. Again, the diffusion of NaCl and lysozyme can be compared: the former species diffuses faster than the latter. The same occurs when using water as solvent (see Fig. 3.5). From Fig. 3.9(b), it can be seen that the profiles at \( t = 1225 \text{ s} \) are waved. This is due to instabilities in the laser caused by a long operating time. The instability was reduced by attaching black cooling fins to the laser (see Fig. 2.3), as well as by turning off the laser between snapshots. Furthermore, in the NaCl concentration profiles (b) a gradient of concentration at the boundaries for \( t = 900 \text{ s} \) and 1225 s is observed, indicating there is a mass flux through the boundaries. This means
that the boundary conditions that were given to the connected phase-shifted data profile are no longer accurate. This must be taken into account when these profiles are analysed. The effects of the buffer solution on the diffusive properties can be quantified with the mass diffusion coefficient (as in §2).

Before conducting the ternary diffusion experiments, the effects of the concentration of each species on the refractive index must be measured. This is the same process as that explained in Chapter II §4.3.

In spite of conducting the same phase-shifting processing, the quantities extracted from the interference patterns for the phase-shifted data corresponding to diffusion in the binary and ternary mixtures are essentially different. In the case of a conventional Mach-Zehnder interferometer, the fringe pattern reflects an optical phase difference between reference and objective beams and can be expressed as:

\[ \Delta \phi(y, z) = \phi(y, z) - \langle \phi(y, z) \rangle = \frac{2\pi L}{\lambda_{\text{beam}}} [n(y, z) - n_0] \]  

(3.4)

where \( \langle \phi(y, z) \rangle \) is the phase value averaged over the full field of view and \( n_0 \) is the refractive index. 

Figure 3.9: Transient concentration profiles for two buffered binary solutions at \( C_{\text{high}} = 30 \text{ mg/ml.} \) (a) lysozyme, and (b) NaCl. See Figs. 3.8(a,b) for the corresponding phase-shifted data.
tive index of a mixture with concentration averaged over the full cell volume. In this case, the phase difference extracted from the interferogram is straightforwardly transformed into the refractive index.

In a binary mixture, the relation between the refractive index and concentration is easily expressed. This was seen in Chapter II §4.3 when measuring the contrast factor for such mixtures, which is an essential step for the measurement of Soret coefficients.

In a ternary mixture, however, two concentration variations contribute to the variation of the refractive index of the fluid:

\[
\frac{\partial n}{\partial C_i} C_i(z,t) + \frac{\partial n}{\partial C_j} C_j(z,t) = \n(\gamma, z) - n_o = \left( \frac{\partial n}{\partial C_1} \right)_{C_2, T} [C_1(z,t) - C_1^0] + \left( \frac{\partial n}{\partial C_2} \right)_{C_1, T} [C_2(z,t) - C_2^0]
\]

where \( \frac{\partial n}{\partial C_i} \) are the contrast factors (see Chapter II §4.3), \( C_i(z,t) \) is the spatial distribution of \( i \)-th component and \( C_i^0 \) is its mean value over the cell. In our ternary system the component (1) is NaCl and the component (2) is lysozyme. Notice however that the number of fringes in Fig. 3.8 is about the same for each concentration, regardless of the kind of species. This brings us to the most important assumption in the following set of experiments. We assume that the contrast factor for both solutes is approximately the same.

**Ternary Diffusion Experiments with Buffered Solution**

The phase-shifted data and the corresponding concentration profile for the ternary system NaCl-lysozyme-buffer at \( C_{high} = 30 \) mg/ml are shown in Fig. 3.10. The results for \( C_{high} = 40 \) mg/ml are very similar to those shown in Fig. 3.10 (these are omitted for the sake of clarity). It is interesting to notice that there is a difference between the binary and the ternary concentration profiles shown in Figs. 3.9 and 3.10, respectively. The ternary profiles seem not to exhibit the same Gaussian pattern observed in the binary case, as described by the analytical solution for binary systems.
Figure 3.10: Phase-shifted data and concentration profiles in the ternary system NaCl-lysozyme-buffer at $C_{\text{high}} = 30$ mg/ml and $t = 100$ s, 225 s, 400 s, 625 s, 900 s, and 1225 s for the lysozyme-NaCl concentration ratios of (a) 1:1, (b) 1:2, and (c) 1:3.
Determination of Mass Diffusion Coefficients in Multicomponent Solutions

species has closer value, is reported in Appendix B. Furthermore, it is important to note that in these systems there is only one ionized component. Therefore, the interaction that occurs between ionized components due to the electrostatic force does not take place between the NaCl and Lysozyme molecules. It has been reported that electrostatic interactions between ionized solutes, even at dilute concentrations, have a considerable effect and cannot be neglected [4.5].

The results for the 40mg/ml regime shown in Fig. 4.8 indicate the same behavior as for the 30mg/ml regime. Both solutes are moving independently to some extent. Figure 4.9 shows several ternary concentration profiles for different volume ratios. In spite that the concentration profiles at $t=100s$ in this regime could not be obtained because the fringes were too close together, the effects of the ternary diffusion can be clearly observed from the fringe patterns as shown in Fig. 4.9(a). The fringes are more tightly packed in the center of the phase-shifted data as the concentration ratio of Lysozyme increases, as opposed to apparent equidistant fringes in the binary phase-shifted data.

(a)  
(b)

Figure 3.11: Comparison of the concentration profiles at $t=625s$ for the solutions $C_{high}=30$ mg/ml at different solutal mass ratios, lysozyme:NaCl (L:N). (a) Phase-shifted data and (b) concentration profile.

\[
C(z) = \frac{C_{high} + C_{low}}{2} - \frac{C_{high} - C_{low}}{2} \exp \left( -\frac{z^2}{4Dt} \right), \quad (3.6)
\]
as in Eq. (2.12) in Chapter II.

The effect of varying the mass, or concentration, ratios for the different components is shown in Fig. 3.11 for $C_{high}=30$ mg/ml at $t=625s$. Here two ternary and two binary concentration profiles at $t=625s$ for different concentration ratios are shown. A higher concentration of lysozyme, which is the slower solute in the mixture, not only makes the overall ternary diffusion slower but also changes the curve characteristics, as shown by the cases with lysozyme at 75% and 25% (see Fig. 3.11). These results might suggest that the molecules of each solute are diffusing almost independently inside the solution, as opposed to the diffusion of aqueous NaCl (with Na$^+$ and Cl$^-$ ions) where the electrostatic forces induce the species to move together resulting in a Fickian diffusion for a quasi-binary system. It has been reported that electrostatic interactions between ionized solutes, even at dilute concentrations, have a considerable effect and cannot be neglected [210]. Moreover, as reported in §2, the mass diffusion coefficient of NaCl is an
order of magnitude larger than that of lysozyme and, hence, a ternary diffusion effect is expected to be easily identified.

Figure 3.12 shows the ternary concentration profiles at $t = 625$ s for $C_{\text{high}} = 40$ mg/ml and four concentration ratios. The phase-shifted data in Fig. 3.12(a) are denser than in Fig. 3.11(a) and, therefore, the accuracy is higher. Nevertheless, the profiles at $t = 100$ s in this regime could not be obtained because the fringes were too dense. Furthermore, the fringes are more tightly packed in the center of the phase-shifted data as the concentration ratio of lysozyme increases, as opposed to the somewhat equidistant fringes in the binary phase-shifted data.

**Comparison between experiments for cross-term assessment**

The results shown in Figs. 3.11 and 3.12 suggest that there is an additive effect in the ternary diffusion from the binary diffusion of the different species. It is also evident that the diffusion of this ternary system is not as in the case of the ionized NaCl, where the cations and anions move as a whole due to the electrostatic interactions. However, the
cross-term diffusion effect ought to be present among the diffusive species, as stated in Onsager’s generalized Fick’s law [140]

\[ j_i = - \sum_k D_{ik} \nabla C_k, \tag{3.7} \]

where \( j_i \) is the mass flux per unit area of the species \( i \), and \( D_{ik} \) is the constant of proportionality between \( j_i \) and the concentration gradient of species \( k \). For \( k \neq i \), \( D_{ik} \) is called the cross-term diffusion between species \( i \) and \( k \) representing their mutual interaction. For \( k = i \), \( D_{ik} \) represents the mass diffusion coefficient of the species \( i \) due to its own concentration gradient, just as in the binary case discussed in §2.1. The assessment of this cross-term diffusion for NaCl-lysozyme mixtures at different concentration values is the main interest in this section.

In order to assess the cross-term diffusion of ternary systems, the preliminary binary experimental results and the ternary experimental results are compared. We will assume that the interaction between the solutes is negligible, i.e. the molecules of NaCl and lysozyme move independently, and see from the experimental results whether this assumption is plausible or not. This could be the case because the concentration levels are low and because there are no strong electrostatic forces. With this assumption, the cross-terms \( D_{ij} \) (with \( i \neq j \)) described in Eq. (3.7) are taken as zero. In this case, the one-dimensional multicomponent concentration profiles could be written as a function of the concentration distribution of each solute and their concentration ratio in the form

\[ C_{M,exp}(z,t) = \sum_i v_i C_i(z,t), \tag{3.8} \]

where \( C_{M,exp}(z,t) \) is the concentration distribution of a multicomponent system, \( C_i(z,t) \) is the concentration distribution in the binary case for the \( i \)-th species at \( C_m = 30 \text{ mg/ml} \) (not the concentration distribution in the ternary solution), and \( v_i \) is the concentration ratio of the \( i \)-th component. Note that in Eq. (3.8), the cross-term diffusion is taken as zero. For a ternary system, Eq. (3.8) becomes
The concentration difference is defined as $\delta C = |C_{M,\text{exp}} - C_{\text{derived}}|$.

$$C_{T,\text{exp}}(z,t) = \nu_L C_{L,\text{exp}}(z,t) + \nu_N C_{N,\text{exp}}(z,t),$$

(3.9)

where the subscript T, L, and N denote ternary system, lysozyme, and NaCl, respectively. The binary experimental results for lysozyme and NaCl shown in Fig. 3.9 can then be substituted in Eq. (3.9), and the obtained $C_{T,\text{exp}}(z,t)$ compared with the ternary experimental results shown in Fig. 3.10. The difference between the derived ternary profile and the experimental ternary profile would give us an insight into the strength of the cross-term diffusion. On the other hand, if the difference between these two profiles is small, we could then infer that our assumption was valid and that the cross-term effects are negligible.

In this section, only the results for $C_{\text{high}} = 30 \text{ mg/ml}$ are presented for the sake of
clarity, but the same results are obtained for $C_{\text{high}} = 40 \text{ mg/ml}$. Figure 3.13 shows the comparison at $t = 900 \text{ s}$ between the derived profile using Eq. (3.9) and the experimental profile for the NaCl-lysozyme-buffer system for a concentration ratio of $L:N = 1:3$. Notice that in a ternary system the concentration of each solute is taken with respect to the solvent. In Fig. 3.13, the solid lines indicate the experimental results (except for the solid line indicating the difference), and the dashed line indicates the ternary profile derived from the binary diffusion experiments (see Fig. 3.9) using Eq. (3.9). The maximum difference between the two ternary profiles is $0.75 \text{ mg/ml}$, which corresponds to only $2.5\%$ of the maximum concentration. This means that there is almost an exact match between the derived profile and the ternary experimental results. Therefore, the solutes in this solution can be considered as diffusing independently and the super-position principle for this system would apply within a $2.5\%$ error.

The maximum discrepancy between the derived ternary concentration profiles and the experimental ternary concentration profiles is obtained around $x = 0$, as shown in Fig. 3.13. This discrepancy might be due to slight differences in the location of the mean concentration point $C_m$ for the experiments which are being compared. Another reason for such discrepancy might be the interactions between the diffusing solute molecules in the region where the concentration gradient, and thus the flux, reaches its maximum. High mass fluxes might result in an increment of the interaction between solute molecules since, the higher speed the molecules have, the higher the possibility they have to collide. In this region with a high concentration gradient, the generalized Fick’s law proposed by Onsager may become inaccurate considering that the mass diffusion coefficients might also be dependent on the concentration gradient. Remember that the mass diffusion coefficient itself is a function of the concentration (see Chapter II §3.3), but taking the mass diffusion coefficient as a function of the concentration gradient might be more proper in the case of multicomponent solutions. This suggestion is summarized as follows

$$|j_i| = -\sum_k D_{ik} \left( \frac{\partial C_k}{\partial z} \right) \nabla C_k, \quad k \neq i. \quad (3.10)$$
Equation (3.10) considers that the concentration gradient of the \( k \)-th species, i.e. \( \frac{\partial C_k}{\partial z} \), increases even further the mass flux of the \( i \)-th species. This can be seen as an additional "pushing" effect, which is not considered for \( k = i \).

Figure 3.14 shows the comparison between the derived concentration profiles from binary diffusion experiments and the experimental concentration profiles directly measured in a ternary diffusion experiment for the concentration ratio of \( L:N = 1:3 \). The solid and dashed lines indicate the experimental and derived results, respectively, at \( t = 100 \) s, \( 400 \) s, and \( 1225 \) s. The binary experimental results for lysozyme and NaCl shown in Fig. 3.9 are used to derive the dashed lines in Fig. 3.14. Moreover, the right ordinate indicates the difference between these two curves, as in Fig. 3.13, showing a maximum difference of 1.8 mg/ml at \( t = 400 \) s. This small difference, only about 5% of the maximum concentration, indicates that the superposition principle for lysozyme and NaCl in the buffer solution is valid to a good approximation for the current concentration levels.
Figure 3.15: Superposition of concentration profiles in ternary systems. Experimental (solid lines) and derived (dashed lines) ternary concentration profiles (from the binary diffusion experiments) are shown for the concentration ratios of lysozyme:NaCl of (a) 1:1, (b) 1:2, and (c) 1:3.
The same analysis described above was applied to all ternary experiments. Figures 3.15 (a), (b), and (c) show the comparison between experimental and derived ternary concentration profiles for the concentration ratios L:N = 1:1, 1:2, and 1:3, respectively. For all the cases, the super-position principle was valid within a 5% error. The results obtained for the concentration ratio L:N = 3:1 were the same, i.e. the super-position principle is valid. The assessment of the cross-term diffusion for other ternary systems such as NaCl-sucrose-water and sucrose-lysozyme-water, in which the diffusive properties of the solutes are more similar, was also conducted. It was confirmed that the super-position principle is applicable in dilute solutions where there is no electrolyte interaction.

Finally, experiments that follow the same procedures described in this section but at higher concentration levels were performed for the ternary system NaCl-sucrose-water at $C_m = 290$ mg/ml. It was confirmed that at this high mean concentration the super-position principle is no longer valid.

### 3.3 Measurement of Pseudo-Binary Diffusion Coefficients

#### Inverse Analysis in Dilute Ternary Systems

The inverse analysis in dilute multicomponent systems consists of finding the pseudo-binary mass diffusion coefficient and the concentration ratio of each solute. In order to do this, the multicomponent transient diffusion fields are compared with a numerical solution, similar to the inverse analysis proposed in Chapter II. In this case, however, not only the mass diffusion coefficients but also the concentration ratios are unknown. As described by Eq. (3.9), these two parameters characterize the multicomponent diffusion fields. Therefore, the fitting process of the numerical curve to the experimental curve should be able to give information about the mass diffusion coefficients and concentration ratios. If the number of solutes increases, or if the mass diffusion coefficient of the solutes is very similar, then the accuracy of the measurement performed with the inverse analysis would decrease.
The experimental results reported above show that the super-position principle can be applied within 5% error, i.e. the cross-term diffusion effect can be neglected for dilute solutions. However, it is important to remember that the cross-term diffusion effects might exceed this margin for the case where there are more than two ionized solutes. By using this super-position principle, the multicomponent numerical profile can be defined as

\[ C_{M,cal}(z,t,D_{i,cal}, v_{i,cal}) = \sum_{i=1}^{N} v_{i,cal} C_{i,cal}(z,t,D_{i,cal}), \]  

(3.11)

where \( C_{M,cal} \) is the numerical concentration distribution of the multicomponent system, the subscripts \( i, cal \) refer to the numerical binary profile for the \( i \)-th species, and \( N \) is the total number of solutal species in the solution. This means that the profile we want to obtain \( C_{M,cal} \) is also a function of the binary mass diffusion coefficient and the concentration ratio of each component. Furthermore, the concentration ratios satisfy

\[ \sum_{i=1}^{N} v_{i,cal} = 1. \]  

(3.12)

For a ternary system, Eq. (3.11) becomes

\[ C_{T,cal}(z,t,D_{A,cal}, D_{B,cal}, v_{A,cal}, v_{B,cal}) = v_{A,cal} C_{A,cal}(z,t,D_{A,cal}) + v_{B,cal} C_{B,cal}(z,t,D_{B,cal}), \]  

(3.13)

where \( C_{T,cal}, C_{A,cal}, \) and \( C_{B,cal} \) denote the numerical or analytical concentration profiles for the ternary system, solute A, and solute B, respectively. The symbols \( v_{A,cal} \) and \( v_{B,cal} \) are the concentration ratios of solutes A and B, respectively. Since there are only two solutes in the solution, Eq. (3.12) becomes

\[ v_{A,cal} + v_{B,cal} = 1. \]  

(3.14)

Hence, by substituting \( v_{B,cal} \) in Eq. (3.13), the numerical or analytical ternary profile
becomes

\[ C_{T,\text{cal}}(z,t;D_{A,\text{cal}},D_{B,\text{cal}},v_{A,\text{cal}}) = v_{A,\text{cal}} C_{A,\text{cal}}(z,t;D_{A,\text{cal}}) + (1 - v_{A,\text{cal}}) C_{B,\text{cal}}(z,t;D_{B,\text{cal}}). \]  \( (3.15) \)

From this equation, we know that the numerical concentration at a given point and time is a function of the numerical diffusion coefficients \( D_{A,\text{cal}}, D_{B,\text{cal}}, \) and the numerical concentration ratio \( v_{A,\text{cal}}. \) Therefore, if a concentration profile defined by Eq. \( (3.15) \) matches a measured multicomponent concentration profile, the mass diffusion coefficients of solute A and B, as well the their concentration ratio could be determined.

In Chapter II, a numerical calculation was used to obtain the mass diffusion coefficients with a good accuracy. As most of the methods reported in the literature use analytical solutions, using here also a numerical calculation would increase the accuracy of the measurement. Nevertheless, as described in Eq. \( (3.15) \), the ternary concentration profile depends on the concentration profile of both solutes. That is, even if the initial concentration profile of the ternary solution is experimentally obtained, the initial concentration profile for each species remains unknown. Therefore, the initial conditions cannot be introduced in the numerical calculations and an analytical solution, which has a step-wise initial concentration profile, has to be used.

Fick’s second law for the \( i \)-th species is

\[ \frac{\partial C_{i,\text{cal}}}{\partial t} = D_{i,\text{cal}} \frac{\partial^2 C_{i,\text{cal}}}{\partial z^2}. \]  \( (3.16) \)

An isothermal one-dimensional diffusion is assumed, and the mass diffusion coefficient of the \( i \)-th species is taken as constant. The non-dimensional analytical solution for Eq. \( (3.16) \), whose dimensionless concentration \( C^* \) is between 0 and 1, is written as follows
\[ C_{i,\text{cal}}^*(z, t, D_{i,\text{cal}}) = \frac{1}{2} \text{erfc} \left( \frac{z}{2\sqrt{D_{i,\text{cal}}t}} \right), \]  \hspace{1cm} (3.17)

where, \( \text{erfc}(\cdot) \) is the complementary error function defined as
\[
\text{erfc}(\xi) = 1 - \frac{2}{\sqrt{\pi}} \int_{0}^{\xi} \exp(-\gamma^2) d\gamma.
\]  \hspace{1cm} (3.18)

Since the mass diffusion coefficient is assumed to be constant for all concentration values, the choice of a non-dimensional solution does not affect the analytical results. Furthermore, working with non-dimensional concentration profiles not only simplifies the mathematical work but also eliminates the requirement of knowing the boundary conditions of the concentration, i.e., the boundary conditions of 0 [-] and 1 [-] are applied to the unwrapped phase-shifted data \( \psi(y, z) \). This is a great advantage for analysing solutions whose concentration \( C_m \) is unknown.

By replacing Eq. (3.17) in Eq. (3.11) the general non-dimensional analytical solution for the multicomponent concentration profile in dilute solutions is written as
\[
C_{M,\text{cal}}^*(z, t, D_{i,\text{cal}}, \nu_{i,\text{cal}}) = \sum_{i=1}^{N} \nu_{i,\text{cal}} \frac{1}{2} \text{erfc} \left( \frac{z}{2\sqrt{D_{i,\text{cal}}t}} \right).
\]  \hspace{1cm} (3.19)

Therefore, for a dilute ternary system with solutes A and B, the non-dimensional analytical solution becomes
\[
C_{T,\text{cal}}^*(z, t, D_{A,\text{cal}}, D_{B,\text{cal}}, \nu_{A,\text{cal}}) = \frac{\nu_{A,\text{cal}}}{2} \text{erfc} \left( \frac{z}{2\sqrt{D_{A,\text{cal}}t}} \right) + \\
\frac{(1 - \nu_{A,\text{cal}})}{2} \text{erfc} \left( \frac{z}{2\sqrt{D_{B,\text{cal}}t}} \right). \hspace{1cm} (3.20)
\]

If values for \( D_{A,\text{cal}}, D_{B,\text{cal}} \), and \( \nu_{A,\text{cal}} \) are found such that the analytical concentration profile fits the experimental concentration profile, then the mass diffusion coefficients
of each solute, as well as the concentration ratio, can be determined. In order to do this, in analogy with the inverse analysis explained in Chapter II, an objective function is defined as the area between the experimental concentration profile and the analytical concentration profile

$$
\delta(D_{A,cal}, D_{B,cal}, \nu_{A,cal}) = \int_{z_{\text{min}}}^{z_{\text{max}}} |C_{T,exp}^*(z) - C_{T,cal}^*(z, D_{A,cal}, D_{B,cal}, \nu_{A,cal})| dz, \quad (3.21)
$$

where $C_{T,exp}^*(z)$ [-] is the non-dimensional ternary experimental concentration distribution at reference time $t$ [s], and $\delta$ [mm] is the objective function. Notice that the units of $\delta$ are [mm] since both concentration have been normalized. By minimizing Eq. (3.21), the analytical solution curve is fitted to the experimental profile.

In Chapter II, only one variable was considered when minimizing the objective function, so only a simple one-dimensional search (Golden Section Method) was enough to determine the binary mass diffusion coefficients. However, when dealing with a number $i$ of species in a solvent, the number of variables increases to $(2i - 1)$. This is the number of mass diffusion coefficients and concentration ratios (minus one) determined from Eq. (3.12). When dealing with a ternary system, i.e. $i = 2$, there are three variables that have to be used in the optimization of Eq. (3.21).

There are many optimization techniques for multi-variable problems. The technique to be chosen depends on the kind of problem that is being dealt with. For example, when the objective function is not smooth, i.e. there are many local minimums or maximums, the Genetic Algorithm (GA) [67] is the most suitable for finding the global minimum or maximum. When the objective function is smooth enough, a gradient-driven technique, such as the Steepest Descent Method (SDM) or the Conjugate Gradient Method (CGM) [205], can be used. In some problems, a combination of these two kinds of techniques (e.g. GA and CGM) is used. Taking into account the convergence characteristics of these methods, CGM was finally chosen as the optimization algorithm to analyse the ternary...
transient diffusion fields.

3.4 RESULTS AND DISCUSSION

DETERMINATION OF PSEUDO-BINARY DIFFUSION COEFFICIENTS

As mentioned in the previous subsection, an increase number of variables used in the optimization process decreases the accuracy of the method. Therefore as a first step in this subsection, only the mass diffusion coefficients of solutes A and B are determined, i.e. the experimental volume fraction $\nu_{A,exp}$ is known. In this case, the objective function at a reference time $t$ becomes

$$\delta(D_{A,cal}, D_{B,cal}) = \int_{z_{min}}^{z_{max}} |C^*_T,exp(z) - C^*_T,cal(z, D_{A,cal}, D_{B,cal})|dz, \quad (3.22)$$

where $C^*_T,cal(z)$ is the non-dimensional analytical ternary concentration profile, which can be rewritten by using Eq. (3.20) as

$$C^*_T,cal(z, D_{A,cal}, D_{B,cal}) = \frac{\nu_{A,exp}}{2} \text{erfc} \left( \frac{z}{2 \sqrt{D_{A,cal} t}} \right) + \frac{(1 - \nu_{A,exp})}{2} \text{erfc} \left( \frac{z}{2 \sqrt{D_{B,cal} t}} \right). \quad (3.23)$$

The symbol $\nu_{A,exp}$ is the experimental concentration ratio of solute A, which is known.

Figure 3.16 shows two sets of analytical results for ternary concentration profiles $C^*_T,cal$. In Fig. 3.16(a), $D_{A,cal} = 5 \times 10^{-9}$ m$^2$/s, $D_{B,cal} = 10^{-10}$ m$^2$/s were chosen to calculate two pseudo-binary concentration profiles at $t = 500$ s, i.e. $C_{A,cal}$ and $C_{B,cal}$, whereas in Fig. 3.16(b) $D_{A,cal}$ and $D_{B,cal}$ were set to $5 \times 10^{-10}$ and $2.5 \times 10^{-9}$, respectively. The concentration ratio is equal to $\nu_{A,exp} = 75\%$. From this figure, it is clear that there is an area delimited by the ternary experimental and analytical profiles that changes
Figure 3.16: Comparison between two analytical ternary profiles with the experimental ternary profile at $t = 500$ s for $\nu_{A,\text{exp}} = 75\%$. (a) $D_{A,\text{cal}} = 5 \times 10^{-9}$ m$^2$/s, $D_{B,\text{cal}} = 10^{-10}$ m$^2$/s. (b) $D_{A,\text{cal}} = 5 \times 10^{-10}$ m$^2$/s, $D_{B,\text{cal}} = 2.5 \times 10^{-9}$ m$^2$/s.

depending on the values of $D_{A,\text{cal}}$ and $D_{B,\text{cal}}$. This area is quantified by the objective function in Eq. (3.22).

Figure 3.17 shows the values of the objective function at the reference time $t = 900$ s in terms of the mass diffusion coefficients of each solute, $D_{A,\text{cal}}$ and $D_{B,\text{cal}}$, when $\nu_{A,\text{exp}} = 75\%$. From this plot we can identify the minimum value of the objective function. This minimum was initially identified by a preliminary zero-order dimensional search which was carried out to estimate the mass diffusion coefficient of both solutes, as shown in Fig. 3.18. Furthermore, CGM was also used as first-order optimization method to effectively determine the mass diffusion coefficient of solutes A and B. The minimum $\delta$ for $\nu_{A,\text{exp}} = 75\%$ and $t = 900$ s was found to be $\delta_{\text{opt}} = 0.023$ mm. The optimum parameters, i.e. the optimum mass diffusion coefficients of each solute, corresponding to $\delta_{\text{opt}}$ are

$$D_{A,\text{cal}} = 1.68 \times 10^{-10} \text{ m}^2/\text{s}, \quad (3.24a)$$

$$D_{B,\text{cal}} = 1.37 \times 10^{-9} \text{ m}^2/\text{s}. \quad (3.24b)$$
Figure 3.17: Contour map of the objective function $\delta$ at $t = 900$ s in terms of the mass diffusion coefficients $D_{A,\text{cal}}$ and $D_{B,\text{cal}}$, when $\nu_{A,\exp} = 75\%$. A minimum value is clearly observed.

Figure 3.18: Minimization of the objective function $\delta$ by a zero-order method. The mass diffusion coefficient of each solute could be determined.
Figure 3.19: Optimization results for binary diffusion coefficients. Britton-Robinson buffer at pH 6.9 was used as solvent. The determined mass diffusion coefficients $D_{opt}$ are shown for (a) lysozyme-buffer and (b) NaCl-buffer. The left ordinate is $D_{opt}$, the right ordinate is $\delta$, while the abscissa indicates the reference time $t$.

By comparing these results with data of binary mass diffusion coefficients, we are able to identify the type of solute, or at least estimate its molecular mass by using the Stokes-Einstein equation, i.e. Eq. (3.1). However, since the values of the mass diffusion coefficient also depend on the pH of the solution, the results for the binary systems determined in §2, which use water as solvent (pH 7.0), cannot be used for comparison in this ternary system. Therefore, the binary mass diffusion coefficients corresponding to the preliminary experiments reported in §3.2 (see Figs. 3.8 and 3.9) must be determined.

In order to do this, $\nu_{A,exp}$ in Eq. (3.23) is set to 1 and the resulting objective function $\delta(D_{A,cal})$ is optimized by the GSM algorithm since there is only one variable.

Figure 3.19 shows the optimization results for the two binary systems. The right ordinate indicates the minimized objective function, i.e. $\delta_{opt}$, while the left ordinate indicates the determined mass diffusion coefficients $D_{opt}$ for which this objective function becomes minimum at a given reference time $t$; the abscissas indicate $t$. In the case of NaCl, the boundary conditions are no longer met at $t = 1225$ s, so a drastic drop in the values of the mass diffusion coefficient can be observed in Fig. 3.19(b). Furthermore, since an analyti-
cal solution (instead of a numerical calculation) is used in the inverse analysis, the effect of the initial concentration distribution, which is characteristic in each experiment and not taken into account, would increase the error of the determined diffusion coefficient. This error is more prominent for shorter reference times. In contrast, the inverse analysis performed with a numerical calculation (see Chapter §3.4), instead of the analytical solution, take into account the characteristic initial concentration distribution for each experiment. To compare both approaches, the values of the optimum parameters obtained by using a numerical calculation in the objective function are included in Fig. 3.19(b) with red dots. In both approaches, a drop in the mass diffusion coefficient of NaCl is observed at long reference times due to the error in the boundary conditions (which are fixed in this case) but a small standard deviation is obtained for the $D_{opt}$ obtained with the inverse analysis using the numerical calculation.

In this set of binary diffusion experiments, only the optimized values obtained from the analytical solution between $t = 400$ s and 1225 s in the case of lysozyme, and between $t = 400$ s and 900 s in the case of NaCl are considered. The average binary mass diffusion coefficients are

$$D_{\text{lysozyme}} = 1.62 \times 10^{-10} \text{ m}^2/\text{s},$$

$$D_{\text{NaCl}} = 1.43 \times 10^{-9} \text{ m}^2/\text{s}. $$

(3.25a)

(3.25b)

In comparison with the values reported when water was used as solvent (see Table 3.2), a large difference (about 65% decrease) for the values of the mass diffusion coefficient of lysozyme was observed. In contrast, the mass diffusion coefficient for NaCl does not vary significantly with respect to the values determined in §2.1, i.e. $D_{\text{NaCl}}(C_m = 1 \text{ mg/ml}) = 1.51 \times 10^{-9} \text{m}^2/\text{s}$. This demonstrates that the mass diffusion coefficient of proteins is highly dependent on the pH levels. Based on measurement results for pH 7.0 (distilled water) and pH 3.9 (buffer), we can discuss the probable causes for the variation
of the mass diffusion coefficient. The strong dependence on pH of the mass diffusion coefficient of lysozyme may be due to the attachment of H\(^+\) and OH\(^-\) when the pH is decreased. This small pH has two effects: (1) the lysozyme molecules become hydrated, increasing in size and thus resulting in slower diffusion as predicted by the Stokes-Einstein equation, and (2) the lysozyme molecules become ionized resulting in electrostatic forces that have a damping effect on the diffusion process.

Now that the mass diffusion coefficients of the binary systems in the buffer solution have been determined, as given by Eq. (3.25), the results obtained for the ternary systems at \(\nu_{A,\text{exp}} = 75\%\) and \(t = 900\ \text{s}\) using Eq. (3.24) can be compared with these values. The results are striking: it is clear that solute A is lysozyme and solute B is NaCl, with a margin of error of 3.6\% and 4.2\%, respectively.

In a mixture where the components are unknown, the concentration ratio is usually unknown as well. Therefore, the concentration ratio \(\nu_{A,\text{cal}}\) must also be included in the inverse analysis for achieving a complete analysis of a ternary mixture which is dilute and non-electrolytic (the ions of Na\(^+\) and Cl\(^-\) are considered as a single species).

**Determination of diffusion coefficients and concentration ratio**

The mass diffusion coefficient of each solute and their concentration ratio are now determined by minimizing Eq. (3.21), i.e. all the three optimization parameters are considered. The experimental ternary results that are analysed are shown in Fig. 3.10. Only the results at \(C_{\text{high}} = 30\ \text{mg/ml}\) are analysed, since similar results are obtained for \(C_{\text{high}} = 40\ \text{mg/ml}\).

Two optimization methods were employed: a zero-order and a first-order method. The zero-order method consists in a systematic evaluation of the objective function for a given range of the parameters. The results of this method are used to plot the graphs that follow in this section. However, since zero-order methods are usually inefficient, a smarter search based on CGM first-order method was developed to minimize the objective function in order to determine the optimum diffusion coefficients and the concentration ratio from a ternary diffusion experiment. Although CGM can make the calculations more efficient, it
Figure 3.20: Objective function $\delta$ for different parameter values for the experimental ternary concentration distribution shown in Fig. 3.10(a) at $t = 625$ s.

was not used for the results presented in this section.

Figure 3.20 shows the values of the objective function $\delta$ for the ternary concentration profiles shown in Fig. 3.10(a) at the reference time $t = 625$ s. The plotted points in this figure correspond for a given concentration ratio $\nu_A$ to the optimum values of $D_A$ and $D_B$ for which $\delta$ reaches its minimum value, as shown in Fig. 3.18. In this way, the two parabolic-like curves thus obtained give at their minimum the optimum concentration ratio as well as the optimum diffusion coefficients. From these results, it is clear that solute A is lysozyme, solute B is NaCl, and that the concentration ratio of lysozyme is about 50%. This means that the mass diffusion coefficients of each solute and their concentration ratio were successfully determined from only one phase-shifted data at a reference time $t$. In other words, the analysis of the ternary mixture is possible with only one phase-shifted data.

Figure 3.20 shows the optimum values for which $\delta$ becomes minimum at a given
reference time. If we consider all the phase-shifted data acquired in a ternary diffusion experiment, then a chronological analysis for the substance can be obtained. Figure 3.21 shows the analysis results for all the concentration profiles (obtained at different times) shown in Fig. 3.10(a). As mentioned above, the effect(s) of the initial concentration distribution is (are) not taken into account with the analytical solution and, hence, a larger error is expected for early reference times. However, for longer reference times, the effects of the initial disturbance is decreased, resulting in a smaller temporal variation, e.g. between \( t = 900 \) s and \( t = 1225 \) s, for the values obtained for both diffusion coefficients \( (D_A \) and \( D_B) \) and the concentration ratio \( (v_A) \). Remember that an ideal measurement would yield the exact same values for mass diffusion coefficients and concentration ratios at any \( t \).

Considering the results shown in Fig. 3.21, the averaged mass diffusion coefficient of each solute and their concentration ratio are the following:

![Figure 3.21: Optimum values of \( D_A, D_B, \) and \( v_A \) with respect to the objective function \( \delta \) for the fit of the experimental profiles shown in Fig. 3.10(a), where the concentration ratio is \( L:N = 1:1 \) \( (v_{A,\text{exp}} = 50\%) \). The reference time \( t \) is the time at which these profiles were obtained.](image-url)
In order to reduce the effects of the initial disturbance at \( t = 225 \text{ s} \) and the errors of the boundary conditions at \( t = 1225 \text{ s} \), only the values for \( t = 400 \text{ s}, 625 \text{ s}, \) and \( 900 \text{ s} \) are averaged. Moreover, by comparing these results with the binary results (3.25), it can be inferred that component A is lysozyme, component B is NaCl, and the concentration ratio of component A is 55.3\% within an uncertainty of 7.4\%, 16.1\%, and 10.6\%, respectively (these margins are given relatively to the values of the binary case).

Figure 3.22 shows the analytical results for the ternary transient concentration profiles shown in 3.10(c), where the concentration ratio is L:N = 1:3 (\( \nu_{A,\text{exp}} = 25\% \)). The average values of the optimized parameters for \( t = 400 \text{ and } 625 \text{ s} \) are

\[
D_A = 1.50 \times 10^{-10} \text{ m}^2/\text{s}, \quad (3.26a)
\]
\[
D_B = 1.66 \times 10^{-9} \text{ m}^2/\text{s}, \quad (3.26b)
\]
\[
\nu_A = 55.3\%. \quad (3.26c)
\]

Again, these results predict the mass diffusion coefficient for each solute within a 4.9\% margin of uncertainty, as well as the concentration ratio within a 8.0\% margin of uncertainty. In Fig. 3.22(b), a more efficient convergence was obtained in comparison to the results for the L:N = 1:1 system shown in Fig. 3.21. This is due to the well defined minima in the curve for the objective function profiles shown in Fig. 3.22(a), which is an indication of the accuracy of the measurement.

From these results, it is clear that the mass diffusion coefficient and the concentration
Figure 3.22: Optimization results for $\delta$, $D_A$, $D_B$, and $\nu_A$ for the fit of the experimental profiles shown in Fig. 3.10(c), where the concentration ratio is L:N = 1:3 ($\nu_{A,\exp} = 25\%$). The reference time $t$ is the time at which $\delta$ was evaluated. (a) Objective function $\delta$ for different parameter values at $t = 625$ s. (b) Optimum values of $D_A$, $D_B$, and $\nu_A$ at different reference times.
ratio of each component in a dilute non-electrolytic ternary system can be determined accurately from the transient concentration profiles. Let us remember the two important assumptions:

1. **Equal contrast factors for each component.** For ternary systems where the contrast factors for each component largely differ, e.g. Fontainebleau benchmark mixtures [178], a more detailed analysis is required [121].

2. **Negligible cross-term effect.** This is only valid for non-electrolytic dilute mixtures. For a more detailed analysis that considers the cross-term see [7] [121].

The error in the measurement, i.e. for the results shown in Eqs. (3.26) and (3.27), can be attributed to:

i. **Errors in the optical apparatus.** These errors might be attributed to a poor alignment of the optical elements as well as to defects in these elements, e.g. the Soret cell without perfectly parallel quartz walls as shown by the distorted phase map in Fig. 2.20. See Chapter II for more details.

ii. **Use of an analytical solution in the inverse analysis.** This analytical solution is used instead of a numerical solution as in §2. A numerical solution cannot be used because the initial concentration profile of the different species is unknown.

iii. **Validity of the assumptions** (1)(2).

4 **THERMOPHORESIS IN DILUTE PROTEIN AQUEOUS BINARY SOLUTIONS**

In §2 and §3 the focus was on Fickian diffusion of biomolecules in isothermal systems. In this section, thermodiffusion in protein aqueous solutions (usually called thermophoresis in biological systems) is discussed as an application of the measurement technique
4.1 CONTRAST FACTORS

The phase-shifted data acquired during the binary diffusion experiments reported in §2 can be used to determine the contrast factor $\eta$. This phase-shifted data is shown in Fig. 3.1 for various protein-aqueous solutions. In this section, we are interested in the lysozyme-water and aprotinin-water binary solutions. Figure 3.23 shows the isothermal diffusion experiments for aprotinin-water and lysozyme-water (both at $C_m = 1 \text{ mg/ml}$) which are used to determine $\eta$. See Chapter II §4.3 for details on the determination procedure.

The results for contrast factors of aprotinin-water and lysozyme-water binary solutions are shown in Table 3.5. The solutal concentration is used as the reference to calculate $\eta$. 

Figure 3.23: Experimental transient concentration profiles of the protein aqueous solutions of (a) aprotinin-water, and (b) lysozyme-water, at $C_m = 1 \text{ mg/ml}$ used to determine the contrast factors. The OP is 20 mm. The phase-shifted data (modulo $2\pi$) corresponding to the initial and final concentration profiles are shown in the insets. The diffusion process starts at $t = 0 \text{ s}$. 

The aim of this section is to verify whether thermophoresis of macrobiomolecules can be observed and measured with OPSI. Therefore, in this set of experiments, no extra measures are taken to fix the ionic strength of the solution or its pH level, i.e. the protein is used as solute without any further purification and dissolved in distilled water at $T = 25^\circ\text{C}$.
Table 3.5: Values of the contrast factor $\eta$ measured for two protein aqueous solutions at mean concentration $C_m$. $\eta$ is related to the protein concentration.

<table>
<thead>
<tr>
<th>Binary solution</th>
<th>aprotinin-water</th>
<th>lysozyme-water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean concentration, $C_m$ [mg/ml]</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Contrast factor, $\eta$ [(g/l mm)$^{-1}$]</td>
<td>$0.29\pi$</td>
<td>$-0.51\pi$</td>
</tr>
<tr>
<td>$(\frac{\partial n}{\partial C})_{(p,T)} \times 10^{-2}$</td>
<td>$-3.07$</td>
<td>6.01</td>
</tr>
</tbody>
</table>

4.2 VISUALIZATION OF THERMOPHORESIS

Figure 3.24 shows the phase-shifted data obtained during two thermodiffusion experiments for a dilute aprotinin-water ($C_m = 3$ mg/ml) binary solution: at $\Delta T = 5$ K (higher temperature at the top), $T_m = 25^\circ$C, and $\Delta T = 10$ K, $T_m = 30^\circ$C. The height of the cell was shortened from $h = 2.0$ mm in the experiments reported in the validation (see Chapter II §4.4) to $h = 1.5$ mm in this experiment. This is to reduce the measurement time that is expected to be longer for protein molecules, such as aprotinin (see Eq. (3.1)), than for the Fontainebleau benchmark mixtures. The visualization width for $L1$ is shorter than for $L2$. Optical defects prevent us from achieving the isophase (infinite fringe) condition with $L2$ at $t = 0$ s, even though the solution is in a homogenous state (i.e. $\Delta T = 0$ K and $\Delta C = 0$ mg/ml). Finding the deformed wavefront (see Fig. 2.20) and then subtracting it from the unwrapped data at time $t$ can correct this optical problem.

The first experimental run at $\Delta T = 5$ K, which is shown in Fig. 3.24(a), was conducted in accordance with the temperature ranges chosen in the validation experiments (see Chapter II §4.4). However, very few fringes were observed in the steady state at $t = 12000$ s and at the beginning of the isothermal diffusion phase at $t = 12200$ s. The number of fringes is proportional to the resolution of the concentration measurement. Therefore, a second experiment run, which is shown in 3.24(b), was conducted at a higher temperature difference, $\Delta T = 10$ K, in an attempt to increase the resolution of the measurement by obtaining more fringes in the phase-shifted data. The mean temperature within the cell and room temperature were set to $T_m = 30^\circ$C and $T_{room} = 27^\circ$C, respec-
Thermophoresis in dilute protein aqueous binary solutions

Figure 3.24: Phase-shifted data for two thermodiffusion experiments of a dilute aprotinin-water ($C_m = 3$ mg/ml) binary solution inside a Soret cell of $h = 1.5$ mm. (a) First experimental run: $\Delta T = 5$ K, $T_m = 25$ °C; (b) second experimental run: $\Delta T = 10$ K, $T_m = 30$ °C. The fringes observed at $t = 0$ s are due to optical defects of the quartz walls. The fringes due to thermophoresis are clearly observed in the thermodiffusion and isothermal diffusion phases. The beam deflection problem becomes more prominent in (b) for $\Delta T = 10$ K and OP $L = 20$ mm.
tively; these temperature values enable us to use more effectively the surrounding air as heat sink for the Peltier modules. As shown in Fig. 3.24(b), the thermophoretic-induced concentration gradients inside the protein aqueous solution are clearly observed at the end of the thermodiffusion phase at $t = 3600$ s and the beginning of the isothermal diffusion phase at $t = 3680$ s. However, the high temperature difference $\Delta T$ between the walls increases the beam deflection problem described in Fig. 2.50. This jeopardizes the ability to measure the Soret coefficient only from the thermodiffusion phase since the exact concentration value at the boundaries becomes unknown. On the other hand, the isothermal data does not have the beam deflection problem and, thus, they can be used to determine the thermodiffusion and isothermal diffusion coefficients.

At this point, we can determine whether the aprotinin molecules ($6.5 \text{ kDa}$) dissolved in water ($C_m = 3 \text{ mg/ml}$) are thermophobic or thermophilic by observing the phase-shifted data in the isothermal phase shown in Fig. 3.24. In the preliminary experiments shown in Fig. 3.23, we observed that the phase-shift $\phi$ increases with increasing concentration of aprotinin molecules (positive contrast factor $\eta$). In the isothermal phase, on the other hand, we observe that the phase-shift $\phi$ increases with the position $z$ from the lower wall, indicating that the concentration increases with $z$ and, thus, we can infer that the aprotinin molecules have moved to the upper heated wall during the thermodiffusion phase. Therefore, the aprotinin molecules in pure water ($C_m = 3 \text{ mg/ml}$) are thermophilic, i.e. the Soret coefficient $S_T$ is negative for this species.

Figure 3.25 shows the transient concentration profiles in the isothermal diffusion phase for the second experimental run of the aprotinin-water binary solution (see Fig. 3.24(b)). Here, the contrast factor $\eta$ for aprotinin-water at $C_m = 1 \text{ mg/ml}$ and at $T = 25^\circ C$ (see Table 3.5) was used to determine the concentration profiles at $C_m = 3 \text{ mg/ml}$, i.e. we assume that the contrast factor does not change significantly within these temperature and concentration ranges. The thermophilic nature of the aprotinin molecules is evident due to a higher concentration of these molecules that have accumulated near the upper hot boundary after the thermodiffusion phase. Furthermore, a quasi-linear profile is detected
Figure 3.25: Transient concentration profile during the isothermal diffusion phase of the second experimental run of the aprotinin-water binary solution. The height of the cell is \( h = 1.5 \) mm, and the temperature difference applied during the thermodiffusion phase is \( \Delta T = 10 \) K. Three phase-shifted data at \( t = 3690 \) s, 3740 s, and 6000 s are shown in the insets. The aprotinin molecules exhibit a thermophilic behavior (\( S_T < 0 \)) within the aqueous surrounding.

at the beginning of the isothermal diffusion phase at \( t = 3690 \) s. In contrast, a linear profile was not observed at the beginning of the isothermal phase for the ethanol-water solution (see Fig. 2.46) due to the higher diffusion coefficient of this liquid pair. We can thus use the linear profile at \( t = 3690 \) s, shown in Fig. 3.25, to estimate the concentration difference \( \Delta C \) between the plates obtained at the end of the thermodiffusion phase. We obtain \( \Delta C = 0.4 \) mg/ml for this experiment where \( C_0 = 3 \) mg/ml and \( \Delta T = 10 \) K. In order to obtain the Soret coefficient from Eq. (2.20), we first need to change the units of concentration from [mg/ml] to [wt%]. This is done by assuming that the density of water at \( T_m = 30^\circ \)C is \( \rho = 0.9956 \) g/ml. Then, the mean concentration and concentration difference become \( C_0 = 0.3 \) wt% and \( \Delta C = 0.04 \) wt%. Substituting these values in Eq. (2.20) yields the Soret coefficient \( S_T = -1.34 \times 10^{-2} \) K\(^{-1}\), which has a negative value.

Figure 3.26 shows some concentration profiles for the thermodiffusion phase of a lysozyme-water binary solution (\( C_m = 3 \) mg/ml) and the phase-shifted data correspond-
Figure 3.26: Concentration profiles for the thermodiffusion phase of a lysozyme-water binary solution ($C_m = 3$ mg/ml). The temperature difference is set to $\Delta T = 5$ K between the liquid/copper boundaries separated by $h = 2$ mm. The concentration difference $\Delta C$ is too small to obtain a reliable measurement of the Soret coefficient. Nevertheless, the thermophobic nature ($S_T > 0$) of the lysozyme molecules is evident from this experimental result.

The distance between the walls was set to $h = 2$ mm (the same as in the validation experiments), the temperature difference to $\Delta T = 5$ K, and the mean temperature to $T_m = 25\,^\circ$C. The beam deflection problem is not clearly visible with this temperature difference, but still, the data near the upper and lower copper/liquid boundaries could not be retrieved. Furthermore, the concentration difference $\Delta C$ between the upper and lower boundaries is too small to obtain a reliable measurement of the Soret coefficient. The temporal fluctuation of $\Delta C$ with only one fringe in the phase-shifted data is too large, so the linear concentration profile expected at large times is not reliable and hence this result is not included in Fig. 3.26. Therefore, the Soret coefficient is nearly zero at $C_m = 3$ mg/ml and $T_m = 25\,^\circ$C. We can however observe that the lysozyme molecules (14.3 kDa) are thermophobic ($S_T > 0$) in this dilute aqueous solution because they migrate from the upper hot region to the lower cold region. This result is in accordance with those reported by Piazza et al. [160] where the Soret coefficient is nearly zero, but positive, for
a dilute lysozyme solution \((C_m = 10 \text{ mg/ml})\) at \(T = 25^\circ\text{C}\) and pH 7.1 in the presence of 100 mM NaCl (which is used to screen the electrostatic effects at lower ionic strengths).

5 CONCLUDING REMARKS

In this chapter, the optical system developed in Chapter II was applied to mass diffusion measurements in several biological systems. In §1 the importance of Fickian diffusion and thermodiffusion in biological systems was discussed. The challenges to study these systems were also presented. The focus of this chapter is biomolecular Fickian diffusion in binary and dilute ternary systems, as well as thermophoresis.

In §2, the mass diffusion coefficients of seven different types of macromolecules (and two inorganic compounds) were determined at infinite dilute concentration. These experiments were conducted in order to investigate the solvent-solute interactions. Here, the same solvent, i.e. distilled water (pH 7.0), is used in all solutions. Less than 500 µg of protein was required in each measurement. The experiments were conducted at \(T = 25^\circ\text{C}\). The results show that the diffusion coefficient decreases with molecular mass, as predicted by the Stokes-Einstein equation. It was found that the diffusion coefficient is proportional to the molecular mass to the power \(-1/3\) by assuming a constant molecular density for the proteins studied. Nevertheless, the deduced values of protein density were not always accurate. This might be due to a possible hydration and other intermolecular effects not considered in the Stokes-Einstein equation. Furthermore, the concentration dependence of lysozyme and BSA was determined (pH 7.0, \(T = 25^\circ\text{C}\)). A qualitative comparison between molecular dynamics calculations reported in the literature and the present measurement results was conducted. It was shown that BSA has a hard-sphere-like diffusion behaviour, whereas lysozyme exhibits a soft sphere characteristic.

In §3, a dilute ternary system consisting of NaCl-lysozyme-buffer \((C = 30 \text{ mg/ml})\) was studied. A buffer solution was used to fix the acidity of the solution to pH 3.9. It was experimentally proven that, for the dilute ranges of concentration considered in this study,
the cross-term effect between the diffusion species is negligible. A general formulation for the inverse analysis in dilute multicomponent systems was then proposed. It was found that from a ternary concentration profile the isothermal diffusion coefficient of each substance and their concentration ratio can be determined. These diffusion coefficients were determined within a 8.0% margin of uncertainty. This method could be an alternative to conventional chromatography methods where hindered diffusion through a gel is used to analyse the diffusion properties of the mixture.

In §4, the measurement technique was then applied to study thermodiffusion in two dilute protein aqueous solutions at $C_m = 3$ mg/ml: aprotinin-water and lysozyme-water. It was found that the aprotinin molecules have a thermophilic behaviour ($S_T < 0$) in its highly dilute form, whereas lysozyme molecules have a thermophobic behaviour ($S_T > 0$) at the same concentration level. In order to bring the concentration field to a value that could be measured by using our optical apparatus, a higher temperature difference was applied to the aprotinin-water solution. It was shown, however, that the increment of the temperature difference also worsens the beam deflection problem, making unfeasible the measurement of Soret coefficient values only from the thermodiffusion phase. Then, the isothermal diffusion phase was used to estimate the concentration difference in the steady state of the thermodiffusion phase and, thus, a reliable Soret coefficient for the aprotinin molecules was determined in the aqueous solution ($C_m = 3$ mg/ml). In contrast, the concentration difference for the lysozyme-water binary solution ($C_m = 3$ mg/ml) was too small to measure the Soret coefficient of the lysozyme component, i.e. the Soret coefficient was almost zero. This result is in accordance with that reported by Piazza \textit{et al.} [160] where the Soret coefficient of lysozyme in a dilute solution ($C_m = 10$ mg/ml) at $T = 25^\circ$C and pH 7.1 was found to be almost zero. In spite of the weak thermodiffusion effect, our results show that the thermophobic or thermophilic behavior of the protein molecules could be determined by using phase-shifting interferometry.

The proposed optical technique described in Chapter II was used to visualize for the first time thermodiffusion of protein molecules. This optical method can then be used in
the future as a tool to deepen our understanding of thermodiffusion in biological systems, and specifically of thermophoresis of protein and DNA molecules.

Some of the methods and results presented in this chapter were published in [198,199].
IV

THREE-DIMENSIONAL CONTINUATION METHOD TO STUDY CONVECTION IN BOXES
OVERVIEW

In Chapter II, an optical method to study mass and heat transport in enclosures was developed. An experimental technique to study isothermal diffusion and thermodiffusion was proposed and the method was validated by measuring Fickian and Soret coefficients of benchmark mixtures. In Chapter III, the optical technique was used to study isothermal diffusion and thermodiffusion of various biomolecules, which are difficult to predict with the available models. The same optical system can be used to study natural convection by measuring two-dimensional temperature fields (see Chapter VI).

A numerical study of natural convection is also possible since the flows can be modelled (to a very good approximation) with the Navier-Stokes equations. As mentioned in Chapter I, we can impose a tilt to a cavity which is differentially heated to modify its heat transfer characteristics. The purpose of this chapter is to develop a numerical method capable of investigating convective heat transfer of steady natural convection in tilted enclosures.

In §1, a brief background of natural convection in enclosures is presented and the goals of the current study are stated. In §2, the mathematical model, the numerical techniques, and the continuation method are described. In §3, the method is then validated by comparing with the numerical results of other authors. In Chapter V, the method is used to study in depth steady natural convection in a tilted truncated square duct and a tilted cubical cavity.

1 INTRODUCTION

STEADY NATURAL CONVECTION IN ENCLOSURES

Since the pioneering studies of Bénard [19, 20] and Rayleigh [175], the Rayleigh-Bénard convection has been extensively studied. The first interest for these studies was to analyse...
pattern formation, which was an intriguing phenomenon. This problem, involving both fluid mechanics and heat transfer, is also of great interest in practical applications, as for example crystal growth (see Lappa [102, 103], Wilcox [214], and Tsukada et al. [88, 117, 203]) and thermal convection in the earth’s mantle (see Baumgardner [16]). The first studies rather concerned infinitely extended layers for which analytical derivations could be performed, but studies in confined enclosures have also developed in connection with practical applications and with the progress in numerical computing [120]. Rayleigh-Bénard convection is an interesting problem for the dynamics of the flows which develop from the motionless conductive solution [27]. A critical Rayleigh number $Ra_c$ has to be reached for the onset of flows, and subsequent flow bifurcations can occur before a chaotic state is reached. The dynamics are particularly rich in confined situations where geometry effects and boundary conditions play an important role and where symmetry considerations are involved [48].

Numerical linear stability analyses have first been carried out to determine the variation of $Ra_c$ with the aspect ratio of the cavity, as those of Catton [40, 41] for rectangular parallelepipedic cavities and Charlson and Sani [43] for cylindrical cavities. These linear stability studies were also able to identify the flow patterns that developed at values of the Rayleigh number, $Ra$, slightly above $Ra_c$, but cannot give information about further flow transitions occurring at larger $Ra$. Nonlinear analyses were thus needed. The numerical methods using parameter continuation and bifurcation methods [179], which were recently developed in the case of three-dimensional situations [168], prove to be very efficient for such studies. In the cylindrical situation, we can mention the work on the influence of a free surface by Touihri et al. [201], where complex bifurcation diagrams have been obtained. In the parallelepipedic situation, very interesting results are reported by Puigjaner et al. [168–171]. Detailed bifurcation diagrams give the development of the steady flow patterns inside a cubical cavity heated from below with either adiabatic or conducting lateral walls and filled either with air ($Pr = 0.71$) or silicone oil ($Pr = 130$). Different flow patterns are found to be stable in the same $Ra$ range. These bifurcation
diagrams allow to explain the transitions between different steady flow patterns observed experimentally by Pallares et al. [149] in a cubical cavity filled with silicone oil. Pallares et al. [150, 151] also studied such transitions in a cubical cavity by three-dimensional direct numerical simulations. They obtain different flow structures and identify transitions between them, but cannot give precise bifurcation diagrams due to the lack of a continuation method.

OBJECTIVES

In this chapter, a continuation method developed from a spectral finite element code is used to study the three-dimensional flows in a tilted rectangular enclosure. The fluid is considered to be pure, i.e. there is no mass diffusion. The continuation method is validated by reproducing the work of Puigjaner et al. [168] for natural convection in a horizontal cubical cavity with adiabatic sidewalls and heated from below. An accuracy assessment is also conducted by comparing with the benchmark solutions proposed by Wakashima et al. [208] for a cubical cavity with adiabatic sidewalls and heated from the sides.

This numerical technique is a first step to a continuation method in which binary mixtures with their mass diffusive properties, e.g. Fickian and Soret coefficients, are also considered.

2 Mathematical model and numerical techniques

2.1 Mathematical model

The mathematical model consists of a rectangular parallelepiped cavity filled with a fluid and differentially heated. The cavity has aspect ratios $A_z = L^*/h^*$ and $A_y = l^*/h^*$, where $L^*$ is the length of the cavity (along $z^*$), $h^*$ is its height (along $x^*$), and $l^*$ is its width (along $y^*$). Note that the superscript * denotes the dimensional quantities, contrary to the convention in Chapters II and III. The origin of the system of coordinates is placed at the
center of the cavity and its axes are parallel to the edges of the cavity. The coordinates $(x^*, y^*, z^*)$ shown in Fig. 4.1 are then normalized by $h^*$ to obtain $(x, y, z)$. The two walls corresponding to $yz^*$-planes at $x^* = -h/2$ and $x^* = h/2$ (lower and upper walls, respectively, in the case without inclination) are isothermal. They are held at different temperatures, $T_H^*$ for the wall at $x^* = -1/2$ and $T_C^*$ for the wall at $x^* = 1/2$, with $T_H^* > T_C^*$, whereas the other sidewalls are adiabatic. The cavity is tilted by an angle $\theta$ around the $-z^*$ axis. $\theta$ is defined as the angle between the horizontal plane and the hot wall ($yz$-plane at $x = -1/2$) and is given in degrees throughout the text (the superscript $*$ is omitted). The fluid is assumed to be Newtonian with constant physical properties (kinematic viscosity $\nu^*$, thermal diffusivity $\kappa^*$, density $\rho^*$), except that, according to the Boussinesq approximation, the fluid density is considered as temperature dependent in the buoyancy term with a linear law $\rho^* = \rho_m^*(1 - \beta^*(T^* - T_m^*))$, where $\beta^*$ is the thermal expansion coefficient and $T_m^*$ is a reference temperature taken as the mean temperature $(T_H^* + T_C^*)/2$. The convective motions are then modeled by the Navier-Stokes equations coupled to an energy equation.
Using \( h^* \), \( h^*/\kappa^* \), \( \kappa^*/h^* \), \( \rho^* \kappa^2/h^2 \) and \( (T_H^* - T_C^*) \) as scales for length, time, velocity, pressure and temperature, respectively, these equations take the following form:

\[
\nabla \cdot \mathbf{u} = 0, \quad (4.1a)
\]

\[
\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} = -\nabla p + Pr \nabla^2 \mathbf{u} + Pr Ra T (\cos(\theta) \mathbf{e}_x + \sin(\theta) \mathbf{e}_y), \quad (4.1b)
\]

\[
\frac{\partial T}{\partial t} + (\mathbf{u} \cdot \nabla) T = \nabla^2 T, \quad (4.1c)
\]

with boundary conditions given by \( T = 1/2 \) on \( x = -1/2 \) and \( T = -1/2 \) on \( x = 1/2 \), \( \partial T/\partial z = 0 \) on \( z = -A_z/2 \), \( A_z/2 \) and \( \partial T/\partial y = 0 \) on \( y = -A_y/2 \), \( A_y/2 \), and \( \mathbf{u} = 0 \) on all the boundaries. The dimensionless variables are the velocity vector \( \mathbf{u} = (u,v,w) \), the pressure \( p \), and the temperature \( T = (T^* - T_m^*)/(T_H^* - T_C^*) \). \( \mathbf{e}_x \) and \( \mathbf{e}_y \) are the unit vectors in the \( x \) and \( y \) directions, respectively, and the non-dimensional parameters are the Rayleigh number, \( Ra = \beta^* (T_H^* - T_C^*) gh^3 / \kappa^* \nu^* \) and the Prandtl number, \( Pr = \nu^* / \kappa^* \). \( g \) is the gravitational acceleration. We can also define the Nusselt number \( Nu \), which expresses the actual heat transfer through \( yz \)-planes compared to the diffusive heat transfer. Due to the adiabatic sidewalls, \( Nu \) is the same for all \( yz \)-planes. It can be calculated easily at the boundaries \( x = \pm 1/2 \). In our case, \( Nu \) is calculated on the boundary at \( x = 1/2 \) (\( \mathbf{u} = 0 \)) and can be simply expressed as

\[
Nu = \int_{-A_y/2}^{A_y/2} \int_{-A_z/2}^{A_z/2} -\left( \frac{dT}{dx} \right)_{x=1/2} dydz. \quad (4.2)
\]

\[\text{2.2 Numerical Techniques}\]

The governing equations of the model, i.e. Eqs. (4.1), are solved in the three-dimensional domain using a spectral element method, as described in [18]. The spatial discretisation is obtained through Gauss-Lobatto-Legendre points distributions; the time discretisation is carried out using a semi-implicit splitting scheme where, as proposed by Karniadakis
et al. [90], the non-linear terms are first integrated explicitly, the pressure is then solved through a pressure equation enforcing the incompressibility constraint (with a consistent pressure boundary condition derived from the equations of motion), and the linear terms are finally integrated implicitly. This time integration scheme is used for transient computations with the third-order accurate formulation described in [90]. But, in its first-order formulation, it is also used for steady state solving [114], eigenvalue and eigenvector calculation, and determination of bifurcation points [22, 159] through a Newton method. These methods, which are essential in this study to determine bifurcation diagrams, are described in the following.

We first consider steady state solving. The first order time scheme can be written in the abbreviated form

\[
\frac{X^{(n+1)} - X^{(n)}}{\Delta t} = \mathcal{N}(X^{(n)}, Ra) + \mathcal{L} X^{(n+1)},
\]

where \( X \) denotes all of the spatially discretised fields \((u, v, w, T)\), and \( \mathcal{N} \) and \( \mathcal{L} \) are the spatially discretised nonlinear and linear operators. For the purpose of the Newton solver, this time scheme can be slightly modified and expressed as

\[
X^{(n+1)} - X^{(n)} = -\mathcal{L}^{-1} \left[ \mathcal{N}(X^{(n)}, Ra) + \mathcal{L} X^{(n)} \right],
\]

Now we consider the steady-state problem

\[
\mathcal{N}(X, Ra) + \mathcal{L} X = 0,
\]

and solve it with a Newton method. Each Newton step can be written as

\[
[\mathcal{N}_X(X, Ra) + \mathcal{L}] \delta X = -[\mathcal{N}(X, Ra) + \mathcal{L} X],
\]

\[
X \leftarrow X + \delta X,
\]

where \( \mathcal{N}_X(X, Ra) \) is the Jacobian of \( \mathcal{N} \) with respect to \( X \) evaluated at \( X \) and \( Ra \). In
order to improve the convergence of the iterative inversion, we rather solve

$$\mathcal{L}^{-1} \left[ N_X(X,Ra) + \mathcal{L} \right] \delta X = -\left( \mathcal{L}^{-1} \right) \left[ N(X,Ra) + \mathcal{L} X \right], \quad (4.7)$$

where the operator $-\mathcal{L}^{-1}$ serves as a preconditioner (i.e. approximate inverse for $N + \mathcal{L}$). If we solve the linear system (4.7) by an iterative conjugate gradient method, we need only provide the right-hand-side and the action of the matrix-vector product constituting the left-hand-side. Referring to Eq. (4.4), we see that the right-hand-side of Eq. (4.7) can be obtained by carrying out a time step, and the matrix-vector product by carrying out a linearised version of the same time step. The Jacobian matrix is thus never constructed or stored. The GMRES algorithm from the NSPCG software library [142] is generally used as iterative solver, as it was found to be more robust than the biconjugate gradient squared algorithm (BCGS) previously used [201]. Note that the system (4.7) is only appropriate for solving the steady state problem at constant $Ra$. At a saddle node, where $X$ ceases to be a function of $Ra$, a new algorithm is therefore needed to follow a solution branch. When any component $X_l$ varies faster than some threshold, we treat this as an imminent saddle node by fixing $X_l$ and allowing $Ra$ to vary. One Newton step for solving (4.5) becomes

$$\begin{bmatrix} N_X(X,Ra) + \mathcal{L} & \mathcal{N}_{Ra}(X,Ra) \\ e_l^T & 0 \end{bmatrix} \begin{bmatrix} \delta X \\ \delta Ra \end{bmatrix} = -\begin{bmatrix} N(X,Ra) + \mathcal{L} X \\ 0 \end{bmatrix}, \quad (4.8)$$

$$X \leftarrow X + \delta X,$$

$$Ra \leftarrow Ra + \delta Ra.$$
solution branch.

When computing steady solutions along a branch, we are interested in determining whether the solutions are stable or unstable. For that, we need to calculate the leading eigenvalues - those with the largest real part and thus responsible for initiating instability - and their corresponding eigenvectors. One possibility is to evaluate a set of those eigenvalues (for example the ten leading ones) with an Arnoldi method, which gives a large overview of the stability changes. To do so, we use Arnoldi’s method from the ARPACK library [107] and follow the ideas of Mamun and Tuckerman [114], i.e. the action of the Jacobian is obtained by time-stepping the linearised equations of the problem (linearised version of Eq. (4.4)) with a small time step equal to $10^{-5}$. In this way, we are able to calculate the exponential of the leading eigenvalues through Arnoldi’s method with a good accuracy (the first ten real or complex leading eigenvalues and their corresponding eigenvectors are generally computed). Such Arnoldi calculation is, however, costly and cannot be done at each continuation step. Another possibility, using the fact that the eigenvalue spectrum usually does not change drastically when following a solution branch on a given range of the continuation parameter, is to follow a specific eigenvalue (generally the largest stable eigenvalue, which is expected to become soon unstable) at each continuation step through a Newton method. This calculation follows the same ideas as for steady-state solving. For a known steady solution $X$, to calculate the eigenvalue $\lambda$ associated with a given eigenvector $h$ whose $l$-th component is normalized to a given value $q$, we have to solve

$$
\begin{align*}
[\mathcal{M}_X (X, Ra) + \mathcal{L}] h - \lambda h &= 0, \\
h_l - q &= 0.
\end{align*}
$$

One Newton step for solving the system (4.9) is

$$
\begin{bmatrix}
\mathcal{M}_X (X, Ra) + \mathcal{L} - \lambda & -h \\
e^T_l & 0
\end{bmatrix}
\begin{bmatrix}
\delta h \\
\delta \lambda
\end{bmatrix}
= -
\begin{bmatrix}
[\mathcal{M}_X (X, Ra) + \mathcal{L}] h - \lambda h \\
0
\end{bmatrix},
$$

(4.10)
\[ h \leftarrow h + \delta h, \]
\[ \lambda \leftarrow \lambda + \delta \lambda. \]

Preconditioned as in Eq. (4.7), this system can still be solved by conjugate gradient iterations, the different terms being obtained by minor modifications of the first-order time integration scheme. Note that $\lambda$ and $h$ are real quantities in case of steady eigenvalue calculation, but they are complex quantities in case of oscillatory eigenvalue calculation. In this last case, we will rather write two real equations, respectively associated with the real part $h_r$ and imaginary part $h_i$ of the eigenvector.

Once we have identified a $Ra$ range where a bifurcation point exists (the real part of an eigenvalue has been found to change its sign in this $Ra$ range), we proceed to determine the precise location of this bifurcation point, i.e. find the corresponding critical Rayleigh number. This direct calculation of the bifurcation points is more complex than steady state solving but follows the same rationale. We will consider a steady bifurcation point. At this bifurcation point, $X$ is a solution to Eq. (4.5), and the Jacobian is singular, with a null vector $h$ whose $l$-th component will be normalized to $q$:

\[ \mathcal{N}(X,Ra) + \mathcal{L} X = 0, \]
\[ [\mathcal{N}_X(X,Ra) + \mathcal{L}] h = 0, \]
\[ h_l - q = 0. \]  

(4.11)

One Newton step for solving Eq. (4.11) is

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\[
\begin{bmatrix}
N_X(X, Ra) + L & 0 & N_{Ra}(X, Ra) \\
N_{X,Ra}(X, Ra) h & N_X(X, Ra) + L & N_{X,Ra}(X, Ra) h \\
0 & e^T_i & 0
\end{bmatrix}
\begin{bmatrix}
\delta X \\
\delta h \\
\delta Ra
\end{bmatrix}
= \\
\begin{bmatrix}
N(X, Ra) + L X \\
[N_X(X, Ra) + L] h \\
0
\end{bmatrix}, \quad (4.12)
\]

\[
X \leftarrow X + \delta X, \\
h \leftarrow h + \delta h, \\
Ra \leftarrow Ra + \delta Ra.
\]

Note that for a primary bifurcation point, \( X \) is the known conductive solution, and the Newton step is reduced to

\[
\begin{bmatrix}
N_X(X, Ra) + L & N_{Ra}(X, Ra) \\
e^T_i & 0
\end{bmatrix}
\begin{bmatrix}
\delta h \\
\delta Ra
\end{bmatrix}
= \\
\begin{bmatrix}
[N_X(X, Ra) + L] h \\
0
\end{bmatrix}, \quad (4.13)
\]

\[
h \leftarrow h + \delta h, \\
Ra \leftarrow Ra + \delta Ra.
\]

In the case of a Hopf bifurcation point, the null vector \( h \) is complex and associated with an angular frequency \( \omega \). To express the singularity of the Jacobian, we choose to write two real equations involving the real part \( h_r \) and imaginary part \( h_i \) of the eigenvector. The system we have to solve is
\[
N(X, Ra) + \mathcal{L} X = 0,
\]
\[
[\mathcal{N}_X(X, Ra) + \mathcal{L}] h_r + \omega h_i = 0,
\]
\[
[\mathcal{N}_X(X, Ra) + \mathcal{L}] h_i - \omega h_r = 0,
\]
\[
(h_r)_l - q_r = 0,
\]
\[
(h_i)_l - q_i = 0,
\]
(4.14)

and each Newton step is given by

\[
\begin{bmatrix}
\mathcal{N}_X(X, Ra) + \mathcal{L} & 0 & 0 & \mathcal{N}_{Ra}(X, Ra) & 0 \\
\mathcal{N}_{X,X}(X, Ra) h_r & \mathcal{N}_X(X, Ra) + \mathcal{L} & \omega & \mathcal{N}_{X,Ra}(X, Ra) h_r & h_i \\
\mathcal{N}_{X,X}(X, Ra) h_i & -\omega & \mathcal{N}_X(X, Ra) + \mathcal{L} & \mathcal{N}_{X,Ra}(X, Ra) h_i & -h_r \\
0 & e^T_1 & 0 & 0 & 0 \\
0 & 0 & e^T_1 & 0 & 0
\end{bmatrix} \times
\begin{bmatrix}
\delta X \\
\delta h_r \\
\delta h_i \\
\delta Ra \\
\delta \omega
\end{bmatrix} =
\begin{bmatrix}
\mathcal{N}(X, Ra) + \mathcal{L} X \\
[\mathcal{N}_X(X, Ra) + \mathcal{L}] h_r + \omega h_i \\
[\mathcal{N}_X(X, Ra) + \mathcal{L}] h_i - \omega h_r \\
0 \\
0
\end{bmatrix},
\]
(4.15)

\[
X \leftarrow X + \delta X,
\]
\[
h_r \leftarrow h_r + \delta h_r,
\]
\[
h_i \leftarrow h_i + \delta h_i,
\]
\[
Ra \leftarrow Ra + \delta Ra,
\]
\[
\omega \leftarrow \omega + \delta \omega.
\]

In the systems (4.12), (4.13), and (4.15), \( \mathcal{N}_{Ra} \) is the Jacobian of \( \mathcal{N} \) with respect to \( Ra \),
$N_{X,X}$ is the double Jacobian of $N$ with respect to $X$, and $N_{X,Ra}$ is the Jacobian of $N$ with respect to both $X$ and $Ra$. Preconditioned as (4.7), these systems can still be solved by conjugate gradient iterations. As before, the different terms of the right-hand-side and of the matrix-vector product are obtained through slightly adapted first order normal or linearised time steps.

2.3 CONTINUATION

Our first objective is to compute the global bifurcation diagrams associated with our physical system. For that, a continuation procedure has been developed, which organizes the different steps of the calculation. Note that we have first to define the range of $Ra$ values over which we want to follow the solution branches.

We can take the non-inclined situation, where a diffusive solution exists, as an example. In that case, the leading eigenvalues of the diffusive solution are first calculated for increasing $Ra$ in order to detect the steady primary bifurcations. We alternate an expensive step using Arnoldi’s method allowing the calculation of the ten leading eigenvalues and several cheaper steps based on the solution of the system (4.10) allowing to follow a specific, well chosen eigenvalue. When the real part of an eigenvalue changes sign as $Ra$ is increased, this is an indication that a bifurcation just occurred. The corresponding eigenvector is thus used as an initial guess in the direct calculation of the bifurcation point, which is performed by solving the Newton system (4.13). The critical Rayleigh number, $Ra_c$, and the critical eigenvector are then stored. Once the limit $Ra$ number is reached, a new sequence begins.

For each primary bifurcation point, successively, a branching algorithm uses the critical eigenvector as a predictor in order to jump to the steady solution branch emerging at this point. This branching algorithm is based on the solution of the system (4.8) so as to be able to catch both supercritical and subcritical branches. The new branch is then followed by continuation, using either (4.6) or (4.8), up to the limit $Ra$ number. For each steady solution calculated along the branch, some leading eigenvalues are calculated, in
the same way as for the diffusive solution branch. This allows to detect the secondary steady bifurcation points, which, once detected, will be precisely calculated using (4.12), with an initial guess corresponding to the solution and the transitional eigenvector at the detection point. The steady branches emerging at the steady secondary bifurcation points can, in turn, be reached using the branching algorithm, with a predictor built on the critical solution perturbed by the critical eigenvector. These branches can then be followed by continuation up to the limit $Ra$ number.

The direct calculation of the bifurcation points by Newton method can also be used independently. When a bifurcation point has been found to play an important role in the dynamics of our system, it could be interesting to follow its evolution as we vary other parameters of the problem (for example, the inclination angle or the Prandtl number). In that case, the critical Rayleigh number, solution and eigenvector at the reference value of the parameter are used as initial guess, and the parameter is varied with a small increment. When the convergence of the Newton system, e.g. Eqs. (4.13) or (4.12), at a given value of the parameter is reached, new critical values are obtained, which, in turn, are used as initial guess for the next step at a slightly modified value of the parameter. We generally choose a constant increment value for the parameter, but this value is further decreased if difficulties of convergence are encountered. Stability maps can thus be obtained, which may improve the understanding of our physical situation by extending the results obtained with the bifurcation diagrams at given parameter values to larger parameter ranges.

Note that, in spite of the continuation procedure, it is difficult to calculate a complex bifurcation diagram in a single run of the code. The fact that, at each continuation step, we do not use Arnoldi’s method, but rather follow a selected eigenvalue, makes it possible to miss some of the bifurcations. We can indeed follow an eigenvalue, which seemed to be a good candidate for transition, while another eigenvalue evolves more quickly and is eventually the first to become unstable. Sometimes, this transition can be detected at the next Arnoldi step. In any case, an a posteriori careful reading of the output file will reveal any missed bifurcations, and a specific calculation will then be conducted to determine
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Table 4.1: Nusselt number $Nu$ in a cubical cavity filled with air ($Pr = 0.71$) differentially heated between two opposite vertical sidewalls ($\theta = 90^\circ$) at high values of $Ra$. Comparisons between our results and the benchmark results proposed by Wakashima et al. [208].

<table>
<thead>
<tr>
<th>$Ra$</th>
<th>This study, $Nu$</th>
<th>Wakashima et al. [208], $Nu$</th>
<th>Difference, $\Delta Nu$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^4$</td>
<td>2.0551</td>
<td>2.0624</td>
<td>0.0073 (0.35)</td>
</tr>
<tr>
<td>$10^5$</td>
<td>4.3370</td>
<td>4.3665</td>
<td>0.0295 (0.68)</td>
</tr>
<tr>
<td>$10^6$</td>
<td>8.6394</td>
<td>8.6973</td>
<td>0.0579 (0.67)</td>
</tr>
</tbody>
</table>

them precisely.

3 VALIDATION

The validation and accuracy of the code is conducted in three steps. First, the primary instability threshold in a cubical cavity for $Ra \leq 8000$ and $Pr = 1$ are determined. These results are compared with those of Puigjaner et al. [169] for $Pr = 130$. Notice that the primary instability thresholds do not depend on the Prandtl number. Second, an accuracy assessment is conducted determining the Nusselt number in a cubical cavity filled with air, i.e. $Pr = 0.71$, and heated from the sides. These results are compared to those of Wakashima et al. [208], who proposed a benchmark solution for steady natural convection inside a cubical cavity. In Chapter V, natural convection inside a truncated square duct is investigated, so a comparison with the work of Mallinson and Davis [113] is also included in this validation section. Third, the code is used to reproduce the work of Puigjaner et al. [168] where a complete bifurcation diagram for a cubical cavity filled with air ($Pr = 0.71$) heated from below is given for the range $Ra \leq 1.5 \times 10^5$. Here, primary and secondary steady bifurcations, as well as Hopf bifurcations, are determined.

3.1 NUSSELT NUMBER IN A CAVITY HEATED FROM THE SIDES

In order to assess the accuracy of the code at higher $Ra$, as well as the feasibility of the calculation when the cavity is heated from the side, we ran the code for the well-known case
Table 4.2: Nusselt number $Nu$ in a truncated square duct with aspect ratios $A_y = 1$ and $A_z = 2$ filled with air ($Pr = 0.71$) and differentially heated from two opposite vertical sidewalls ($\theta = 90^\circ$) at high values of $Ra$. Comparisons between our results and the benchmark results proposed by Mallinson and Davis [113].

<table>
<thead>
<tr>
<th>$Ra$</th>
<th>This study, $Nu$</th>
<th>Mallinson and Davis [113], $Nu$</th>
<th>Difference, $\Delta Nu$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^4$</td>
<td>2.15</td>
<td>2.20</td>
<td>0.05 (2.27)</td>
</tr>
<tr>
<td>$3 \times 10^4$</td>
<td>3.05</td>
<td>3.18</td>
<td>0.13 (4.08)</td>
</tr>
<tr>
<td>$6 \times 10^4$</td>
<td>3.78</td>
<td>4.00</td>
<td>0.22 (5.50)</td>
</tr>
<tr>
<td>$1.5 \times 10^5$</td>
<td>5.01</td>
<td>5.14</td>
<td>0.13 (2.52)</td>
</tr>
<tr>
<td>$3 \times 10^5$</td>
<td>6.16</td>
<td>6.53</td>
<td>0.37 (5.67)</td>
</tr>
<tr>
<td>$5 \times 10^5$</td>
<td>7.16</td>
<td>7.43</td>
<td>0.27 (3.63)</td>
</tr>
</tbody>
</table>

of a cubical cavity filled with air ($Pr = 0.71$) differentially heated between two opposite vertical sidewalls ($\theta = 90^\circ$) with the remaining walls set adiabatic. A benchmark for this situation was proposed by Wakashima et al. [208]. They computed the Nusselt number $Nu$ in this cubical cavity with a finite difference method having a fourth-order accuracy. Table 4.1 compares the Nusselt number obtained by our continuation method to the benchmark values. We used a $31 \times 31 \times 31$ grid with a Gauss-Lobatto-Legendre point distribution (see Fig. 4.3(e)) while Wakashima et al. [208] used a uniform $120 \times 120 \times 120$ grid. As expected, the differences between the benchmark values and our results increase at higher values of $Ra$. Nevertheless, the percent difference is within 0.7% even at values of $Ra$ as high as $10^6$.

Mallinson and Davis [113] were the first to conduct a numerical study for a cavity with aspect ratios $A_y = 1$ (square $xy$ cross section) and $A_z = 2$ which is heated from the sides. Their study was conducted in 1977 and, hence, it has less accuracy than the numerical work of Wakashima et al. [208] for cubical cavities. Nevertheless, it is useful to compare their results with ours in order to see the order of magnitude of the Nusselt numbers that we have in such cavities. Here, we used a $27 \times 27 \times 41$ grid with a Gauss-Lobatto-Legendre point distribution. This is the same mesh used in Chapter V for the tilted truncated square duct (see refinement tests in Chapter V §2.1). Table 4.2 shows the calculation results obtained in this study, listed next to those of Mallinson and Davis [113].

In the literature used for the accuracy assessment [113, 208], discrete values of the
This study
Wakashima et al. (2004)

This study
Mallinson and Davis (1977)

(a)  
N\nu

1
10
10^2 10^3 10^4 10^5 10^6

Ra

(b)  
N\nu

1
10
10^2 10^3 10^4 10^5 10^6

Ra

Figure 4.2: Calculations performed for the accuracy assessment of the code. The cavities are filled with air ($Pr = 0.71$) and differentially heated between two opposite vertical sidewalls ($\theta = 90^\circ$). The other walls are set adiabatic. Results for (a) the cubical cavity studied by Wakashima et al. [208]; (b) a truncated square duct studied by Mallinson and Davis [113]. See tables 4.1 and 4.2 for the literature values.

average Nusselt number $N\nu$ were computed. However, continuation methods can vary the continuation parameter, e.g. $Ra$, in order to obtain a broader description of the system. This is actually one of the advantages of the continuation methods. Figures 4.2 (a) and (b) show $N\nu$ as a function of $Ra$ for the benchmark solution calculations [208] and for those of Mallinson and Davis [113]. The results are plotted in log-scale. Notice the small increment of $N\nu$ in the low Rayleigh number range $Ra < 10^3$. Furthermore, there are no bifurcations for this solution branch in this range. This is because the cavity is heated from the sides.

### 3.2 Primary Bifurcations in a Cubical Cavity

In contrast to the case where the cavity is heated from the sides, complex bifurcation diagrams are expected when the cavity is heated from below [149], i.e. in the Rayleigh-Bénard convection. The validation of the method for this case cannot be done with any aspect ratio, as few results are available for such cavities. The case that has been the most studied is the case of convection inside a cubical cavity with adiabatic sidewalls. We then
Table 4.3: Critical Rayleigh numbers $Ra_c$ for the first three primary bifurcation points ($P_1$, $P_2$, and $P_3$) in a horizontal cubical cavity heated from below ($\theta = 0^\circ$). Three different meshes are listed to assess the calculation accuracy. The Prandtl number in the calculations is set to $Pr = 1$. The results of Puigjaner et al. [169] are listed for comparison ($Pr = 130$).

<table>
<thead>
<tr>
<th>Primary threshold</th>
<th>This work, $Pr = 1$</th>
<th>Puigjaner et al. [169] $Pr = 130$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_1$</td>
<td>3388.521</td>
<td>3389</td>
</tr>
<tr>
<td>$P_2$</td>
<td>5900.429</td>
<td>5902</td>
</tr>
<tr>
<td>$P_3$</td>
<td>7456.133</td>
<td>7458</td>
</tr>
</tbody>
</table>

choose this case, which was also recently studied by Puigjaner et al. [169]. Table 4.3 shows the critical Rayleigh number, $Ra_c$, obtained for the first three primary bifurcations inside a cubical cavity ($A_y = 1$, $A_z = 1$) heated from below. The calculations were conducted for $Pr = 1$ and for three different numbers of grid points. We first see the good convergence of the results with the refinement of the grid. The critical Rayleigh number obtained for the same primary bifurcation points by Puigjaner et al. [169] inside a cubical cavity for $Pr = 130$ are also given for comparison. (Note that $Ra_c$ corresponding to a primary threshold does not depend on $Pr$.) A good agreement is obtained between the different results.

### 3.3 Bifurcation Diagram for a Cubical Cavity Heated from Below: $Ra \leq 1.5 \times 10^5$ and $Pr = 0.71$

**Accuracy assessment**

Our results concern the cavity shown in Fig. 4.1 but for a cubic shape and $\theta = 0^\circ$. Figure 4.3 shows the Gauss-Lobatto-Legendre point distribution on a side plane of the cavity for $N = 11, 17, 21, 27, 31$, and $37$; here, $N$ is the number of grid points on each edge of the cubical cavity. The mesh is shown in Fig. 4.3 for one face of the cubical cavity. Notice that an odd number is chosen for $N$, so that there are points on the axes of symmetry.

The same refined mesh comprising $31 \times 31 \times 31$ grid points (see Fig. 4.3(e)) was cho-
Table 4.4: Mesh refinement test of the numerical accuracy based on calculation results of steady bifurcations ($Pr = 0.71$). The calculated critical Rayleigh numbers $Ra_c$ for the first three primary bifurcations ($P_1$, $P_2$, $P_3$) and the first secondary destabilizing bifurcation ($S_1B_1$) are listed for different meshes. $N$ is the number of grid points on each edge of the cubical cavity. The total number of grids points is then $N^3$. The last column shows the relative difference $\Delta$ between $N = 37$ and $N = 31$, i.e. $\Delta_{37-31} = |N(37) - N(31)| \times 100/N(37)$.

<table>
<thead>
<tr>
<th>$N$</th>
<th>11</th>
<th>17</th>
<th>21</th>
<th>27</th>
<th>31</th>
<th>37</th>
<th>$\Delta_{37-31}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_1$</td>
<td>3388.328</td>
<td>3388.507</td>
<td>3388.520</td>
<td>3388.525</td>
<td>3388.526</td>
<td>3388.527</td>
<td>2.95 x 10^{-3}</td>
</tr>
<tr>
<td>$P_2$</td>
<td>5899.894</td>
<td>5900.382</td>
<td>5900.423</td>
<td>5900.442</td>
<td>5900.446</td>
<td>5900.449</td>
<td>5.08 x 10^{-5}</td>
</tr>
<tr>
<td>$P_3$</td>
<td>7455.518</td>
<td>7456.098</td>
<td>7456.129</td>
<td>7456.143</td>
<td>7456.150</td>
<td>7456.149</td>
<td>1.34 x 10^{-5}</td>
</tr>
<tr>
<td>$S_1B_1$</td>
<td>65267.559</td>
<td>66240.768</td>
<td>65762.379</td>
<td>65821.829</td>
<td>65818.898</td>
<td>65820.775</td>
<td>2.85 x 10^{-3}</td>
</tr>
</tbody>
</table>

Figure 4.3: Gauss-Lobatto-Legendre point distribution for different grid points. $N$ is the number of grid points on each edge of the cubical cavity. The mesh is shown for one face of the cubical cavity. $N$ for (a), (b), (c), (d), (e), and (f) is 11, 17, 21, 27, 31, and 37, respectively.
sen for all $Ra$ in the calculations of the validation that follows ($\theta = 90^\circ$), as well as for all $\theta$ and $Ra$ in the calculations concerning a cubical enclosure in Chapter V §3. This point distribution gives a very good precision for the threshold calculations in the horizontal case, as indicated by the precision tests shown in Table 4.4. The accuracy of the calculation is expected to decrease when the intensity of the flow increases, i.e. $Ra$ becomes larger. This is confirmed by the larger drop in accuracy for the calculation corresponding to the secondary bifurcation point $S_1B_1$, as shown in Table 4.4. Nevertheless, for the mesh chosen in this study, the error is below 0.003% even at $Ra$ as high as 65 000.

**Bifurcation diagram calculation**

The stability of steady natural convection inside a horizontal cubical cavity heated from below and filled with air ($Pr = 0.71$) is now discussed. This Rayleigh-Bénard configuration has been reported in detail in the literature [168]. These results are used as validation of the numerical methods employed in this study to determine bifurcation diagrams with primary, secondary, and Hopf bifurcations.

Figure 4.4 shows the bifurcation diagram determined for a horizontal cubical cavity filled with air in the range $Ra \leq 20000$. The Nusselt number, $Nu$, is plotted as a function of $Ra$. The solutions belonging to the same flow pattern that evolve from a pitchfork bifurcation have the same $Nu$ at a given $Ra$ and, thus, we can plot these solutions by using a single branch. In the bifurcation diagrams presented in this thesis, the solid lines, dashed lines, and dotted lines represent stable solutions, unstable solutions with one positive eigenvalue, and unstable solutions with two or more positive eigenvalues, respectively. The encircled numbers within some bifurcation diagrams indicate the number of eigenvalues with a positive real part for the solutions on a dotted segment of branch. The solid points, open points, and open squares, represent pitchfork, saddle-node, and Hopf bifurcations, respectively. In Fig. 4.4, the branches initiated at secondary and tertiary bifurcations are omitted for the sake of clarity, except for the branch $B_3$ ($B_{31}$, $B_{32}$, and $B_{311}$ are plotted), which is of special interest because the solution is stabilized at $S_1B_3$. Here, $S$ stands for
Figure 4.4: Bifurcation diagram for air ($Pr = 0.71$) inside a horizontal cubical cavity in the range $Ra \leq 20000$. The Nusselt number $Nu$ is plotted as a function of the Rayleigh number $Ra$. Here and in all subsequent bifurcation diagrams, stable solutions are depicted with solid lines, unstable solutions by dashed lines when they have one unstable eigenmode and by dotted lines when they have two or more unstable eigenmodes. The number of eigenvalues with positive real part is encircled for the dotted segments. The solid points denote pitchfork bifurcation points. Branches initiated at secondary and tertiary bifurcations are omitted, except for $B_{31}, B_{32},$ and $B_{311}$. The flows obtained at $Ra = 20000$ are shown in Table 4.5.

*secondary* bifurcation point (on non-trivial solutions) and $B$ for *branch*; $P$ stands for *primary* bifurcation point. Furthermore, the branches are systematically named $B_{ijk}$, where $i$, $j$, and $k$ indicate the primary, secondary, and tertiary bifurcation points, respectively, from which the branch is initiated. Figure 4.4 shows the level of detail in which the bifurcation diagrams are determined with the numerical method explained in §2.3.

Figure 4.5 shows several ways of representing a stable transverse solution $B_1$ at $Ra = 20000$. Figures 4.5(a,b) show two possible three-dimensional representation of the flow. In Fig. 4.5(a), the magnitude of the velocity, i.e. $V = (u^2 + v^2 + w^2)^{1/2}$, is plotted on the mean isothermal surface, i.e. $T = 0$. The roll characteristic of the flow is evident.
Figure 4.5: Three-dimensional (a,b) and two-dimensional (c,d) representation of a stable transverse roll solution $B_1$ at $Ra = 20000$ ($Pr = 0.71$). (a) The magnitude of the velocity, i.e. $V = (u^2 + v^2 + w^2)^{1/2}$, is plotted on the isothermal surface $T = 0$. (b) $T$ is plotted on the isosurface for the velocity magnitude $V = 22$; the mesh at the mid-horizontal $yz$ plane is shown. (c) and (d) The vertical velocity $u$ is plotted in this plane ($x = 0$). In (c), the contours are shown in color in the cubical cavity. In (d), the contours are shown in black & white in two-dimensions; the solid and dashed lines represent positive and negative values of $u$. The plot shown in (d) is the most convenient to represent the flow pattern. Notice that the coordinate system represents the orientation of the axes but not its origin, which coincides with the center of the cavity.
IV Three-dimensional continuation method to study convection in boxes

Figure 4.6: Solutions with the same flow pattern $B_1$ at $Ra = 20000$. The vertical velocity $u$ on the horizontal midplane ($x = 0$) is shown with solid and dashed lines for positive and negative values, respectively. These solutions have the same $Nu$ but different roll orientation. They are labelled with the direction of the rotation vector that represents each roll. So from left to right, these solutions are named $B_y$ (same solution as in Fig. 4.5), $B_{-z}$, $B_{-y}$, and $B_z$.

Moreover, note that this roll has its axis of rotation in the $y$ direction. In Fig. 4.5(b), the temperature $T$ is plotted on an isosurface for the magnitude of the velocity, $V = 22$. The maximum $V$ in the cavity is $V_{max} = 32.23$. The mesh at the mid-$yz$ plane is shown. Here, we can see the heat (indicated by the high temperature surface) moving upwards. Figures 4.5(c) and (d) show the vertical velocity $u$ in this midplane ($x = 0$). In Fig. 4.5(c), the contours are shown in color in the cubical cavity. In Fig. 4.5(d), the contours are shown in black & white in two-dimensions; the solid and dashed lines represent positive and negative values of $u$. The plot shown in Fig. 4.5(d) is the most convenient to represent the flow of this kind of flow patterns.

Figure 4.7: Solutions with the same flow pattern $B_2$ at $Ra = 20000$. The vertical velocity $u$ on the horizontal midplane ($x = 0$) is shown with solid and dashed lines for positive and negative values, respectively. They are labelled with the direction of the rotation vector that represents each roll.
Figure 4.6 shows the four stable solutions at $Ra = 20000$ that belong to the flow pattern $B_1$. Notice that, since these solutions are symmetrical to each other by some rotation around the vertical $x$ axis, they have the same heat transfer characteristics, i.e. the same $Nu$. However, their velocity fields have different orientations and, hence, we should unambiguously name each solution. In this study, we label the solutions by using the direction of the rotation vector that represents each roll (following the right-hand rule). So the solutions shown in Fig. 4.6 are called from left to right: $B_y$ (the same solution as in Fig. 4.5), $B_{-z}$, $B_{-y}$, and $B_z$. The same logic applies to the four unstable diagonal solutions $B_2$ shown in Fig. 4.7, which belong to the same flow pattern and are named (from left to right in Fig. 4.7) $B_{y+z}$, $B_{y-z}$ (the same inset as in Table 4.5), $B_{-y+z}$, and $B_{-y-z}$. These solutions still have the same heat transfer characteristics, i.e. the same average Nusselt number $Nu$, as they are also related to each other by rotations around the vertical $x$ axis.

Figure 4.8 shows several ways of representing a stable four-roll solution $B_3$ at $Ra = 20000$. The same as in Fig. 4.5, an isothermal surface (a), isovelocity surface (b), and vertical velocity contours in a mid-horizontal plane (d) are plotted. In Fig. 4.5(c), the vectors corresponding to the vertical velocity $u$ are plotted from the mid-horizontal plane. Again, plot (d) is the simplest to represent such flows. Figure 4.9 shows the two stable solutions that belong to the flow pattern $B_3$. Again, these solutions have the same $Nu$ as their velocity field is rotated by $\pi/2$ about the vertical $x$ axis. In Chapter V, more details about the solutions that belong to the same flow pattern are presented, with a special focus on the effects of a tilt on the stability of these solutions.

The bifurcation diagram shown in Fig. 4.4 is extended to the range $Ra \leq 150000$. The results are plotted in Fig. 4.10. These calculations show that for $Ra \leq 150000$, the stable branch $B_1$ is destabilized at $S_1 B_1$ giving rise to a new stable branch $B_{11}$, whereas the twice unstable branch $B_3$, which is stabilized at $S_1 B_3$, remains stable in the $Ra$ range studied.

Table 4.5 shows the ranges of stability for the branches shown in Fig. 4.10. The flow structure is also shown by the vertical velocity contours in the horizontal midplane ($x = 0$) at $Ra = 20000$, 100000 and 150000. The literature values (see Puigjaner et al. [168]) are
Figure 4.8: Three-dimensional (a-c) and two-dimensional (d) representation of a stable four-roll solution $B_3$ at $Ra = 20000$ $(Pr = 0.71)$. (a) $V$ is plotted on the isothermal surface $T = 0$. (b) $T$ is plotted on the isosurface for the velocity magnitude $V = 20$. (c) The vectors corresponding to the vertical velocity $u$ are plotted from the mid-horizontal plane $(x = 0)$. The mesh at this plane is shown for (a-c). (d) The contours of the vertical velocity $u$ are shown in black & white in the mid-horizontal plane; the solid and dashed lines represent positive and negative values of $u$. This plot is the most convenient to represent the flow pattern.
Table 4.5: Flow structures for the main steady solutions initiated at the first five primary bifurcation points in the case of convection inside a horizontal cubical cavity filled with air ($Pr = 0.71$). The flow is depicted at $Ra = 20000, 100000$ and $150000$. The vertical velocity $u$ on the horizontal midplane ($x = 0$) is shown with solid and dashed lines for positive and negative values, respectively. The flows are all unstable, except for those which are labelled stable. The brackets give the name of each branch and the range(s) of stability or (and) instability reported by Puigjaner et al. [168].

<table>
<thead>
<tr>
<th>Primary bifurcation</th>
<th>Branch</th>
<th>Flow pattern, $u$ on $x = 1/2$</th>
<th>Range of stability</th>
<th>Range of instability</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_1$</td>
<td>$B_1$</td>
<td>$[S1]$</td>
<td>$3388.5 – 65 818.9$</td>
<td>$65 818.9 – [66 200 –]$</td>
</tr>
<tr>
<td></td>
<td>$B_{11}$</td>
<td>$[S7]$</td>
<td>$65 818.9 – 174 714$</td>
<td>$174 714 –$</td>
</tr>
<tr>
<td></td>
<td>$B_2$</td>
<td>$[S2]$</td>
<td>$8270.4 – 267 378$</td>
<td>$8270.4 – [8300 –]$</td>
</tr>
<tr>
<td></td>
<td>$B_{31}$</td>
<td>$[S5]$</td>
<td>$5900.4 – 8270.4$</td>
<td>$5900.4 – 8270.4 – [5901 – 8300]$</td>
</tr>
<tr>
<td></td>
<td>$B_{32}$</td>
<td></td>
<td>$–$</td>
<td>$8270.4 –$</td>
</tr>
<tr>
<td>$P_2$</td>
<td>$B_3$</td>
<td>$[S5]$</td>
<td>$8270.4 – 267 378$</td>
<td>$8270.4 – [8300 –]$</td>
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<tr>
<td></td>
<td>$B_{31}$</td>
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<td>$8270.4 –$</td>
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<td></td>
<td>$B_{32}$</td>
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<td>$8270.4 –$</td>
</tr>
<tr>
<td>$P_3$</td>
<td>$B_4$</td>
<td>$[S4]$</td>
<td>$–$</td>
<td>$7456.1 – [7456 –]$</td>
</tr>
<tr>
<td>$P_4$</td>
<td>$B_5$</td>
<td>$[S8]$</td>
<td>$–$</td>
<td>$8601.1 – [10 000 –]$</td>
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<td>$B_6$</td>
<td></td>
<td>$–$</td>
<td>$12 998.0 –$</td>
</tr>
<tr>
<td></td>
<td>$B_7$</td>
<td></td>
<td>$–$</td>
<td>$12 998.0 –$</td>
</tr>
</tbody>
</table>
Figure 4.9: Solutions with the same flow pattern $B_3$ at $Ra = 20000$. The vertical velocity $u$ on the horizontal midplane ($x = 0$) is shown with solid and dashed lines for positive and negative values, respectively. These solutions have the same $Nu$. They are labelled as $B_{R4-}$ (same solution as in Fig. 4.8) and $B_{R4+}$.

included for comparison. A very good agreement with the published work is obtained, except for $B_5$. Our results indicate that this branch is triggered at the primary bifurcation $P_4$ at $Ra_c \approx 8601.1$, whereas Puigjaner et al. [168] designate this branch as secondary and commencing at $Ra_c \approx 10000$. The calculation was run multiple times (with different Rayleigh number increment $\Delta Ra$) in order to confirm that the stability threshold for $P_4$ is really at $Ra_c \approx 8601.1$ (the branch $B_5$ initiated at $P_4$ is clearly depicted in Fig. 4.4). Furthermore, we notice from Table 4.5 that the discrepancies between our results and the literature values increase at larger $Ra$. This is expected because the accuracy drops at higher $Ra$, as indicated in Table 4.4 for $S_1B_1$. Our accuracy assessment demonstrates, however, that the stability thresholds calculated by our method at high $Ra$ remain very accurate.

Concerning the complementary calculations for this system, it was found that the stable branch $B_{11}$ becomes oscillatory unstable after the Hopf bifurcation $H_1B_{11}$ at $Ra_c \approx 174714$, and that the stable four-roll solution $B_3$ becomes twice unstable at $Ra_c \approx 267378$. The unstable branches, $B_{31}, B_{32}, B_6,$ and $B_7$ were additionally calculated in an attempt to find the disconnected stable branch reported by Puigjaner et al. [168]. This attempt was however unsuccessful. Furthermore, the stabilization of the diagonal-roll solutions $B_2$ at higher $Ra$ could have been expected, following the results of Puigjaner et al. [169] for $Pr = 130$. However, we found that for $Pr = 0.71$ the branch $B_2$ encounters a destabilizing
Figure 4.10: Extension of the bifurcation diagram shown in Fig. 4.4 (Pr = 0.71) to the range $Ra \leq 150000$. Secondary and tertiary unstable bifurcation branches are omitted for the sake of clarity, except for $B_{11}$, $B_{31}$, and $B_{32}$. The stable branches are indicated with bold letters (solid lines). Refer to Table 4.5 to see the stability ranges of these branches and the vertical velocity contours in the horizontal midplane obtained at $Ra = 20000$, 100000, and 150000.

Hopf bifurcation $H_1B_2$ at $Ra_c \approx 154282$, showing the different stability characteristics encountered for different Prandtl numbers.

**DISCUSSION**

The stable solutions are the main focus of this study because they determine the flow in a real physical situation. Based on the results for $Pr = 0.71$ (Fig. 4.10) and $Pr = 130$ (reported in [169]), we can expect the following types of stable solution branches for
Rayleigh-Bénard convection in a cubical cavity:

(i) no-flow (trivial) solutions before $P_1$.
(ii) $B_1$, transverse rolls from $P_1$ to $S_1B_1$.
(iii) $B_{11}$, transverse rolls with a broken symmetry after $S_1B_1$.
(iv) $B_{111}$, asymmetric transverse rolls after $S_1B_{11}$.
(v) $B_3$, four-roll solutions after $S_1B_3$.
(vi) $B_2$, diagonal rolls stabilized after $S_1B_2$.

For $Pr = 0.71$, (iv) and (vi) do not apply. As already seen, for the flow pattern $B_1$ (denoted as transverse rolls), there are four types of solutions that have the same average Nusselt number $Nu$. Note that the unstable solutions with one or two positive eigenvalues are also important because they might yield stable solutions after sufficiently increasing $Ra$, such as for $B_2$ [169] and $B_3$ (see Fig. 4.4). For these solutions, in the same way as for the transverse solutions $B_1$, there are dynamically equivalent solutions, four for the diagonal-roll solutions $B_2$ (see Fig. 4.6) and two for the four-roll solution group $B_3$ (see Fig. 4.9). Moreover, for $B_3$, two sets of four equivalent unstable branches emerge at the secondary bifurcation $S_1B_3$ on both primary branches (see Fig. 5.20). The multiple solutions that arise at these bifurcations in the horizontal case are discussed in more detail in Chapter V §3.2.

Finally, the bifurcation diagram depicted in Fig. 4.10 was calculated with the continuation procedure described in §2.3. It is known, however, that other disconnected solutions might exist [179]. In the case discussed for the validation ($Pr = 0.71, \theta = 0^\circ$), Puigjaner et al. [168] reported a disconnected stable branch in the range $76,800 < Ra < 86,500$ with its secondary stable branch in the range $86,500 < Ra < 94,800$. They first calculated a solution on this branch by using a fourth-order finite-difference solver, and then employed their continuation method to follow the branch. Chances to detect these isolated branches are very small indeed. Therefore, in this study, we choose not to look for disconnected branches in the horizontal case. We rather focus on the family of solutions that can be directly calculated with the continuation method, and extend this calculation procedure to
find the multiple disconnected branches that are expected to exist for tilted enclosures.

4 CONCLUDING REMARKS

In this chapter, a continuation method was developed from a three-dimensional spectral finite element code. This method is particularly well suited for the studies involving complex bifurcation diagrams of three-dimensional convection in rectangular parallelepiped cavities.

This continuation method allows the calculation of solution branches, the stability analysis of the solutions along these branches, the detection and precise direct calculation of the bifurcation points, and the jump to newly detected stable or unstable branches, all this being managed by a simple continuation algorithm. This can be used to calculate the bifurcation diagrams describing the convection in tilted cavities (see Chapter V).

An accuracy assessment of the code was performed by comparing with the work of Wakashima et al. [208]. They proposed benchmark solutions for natural convection of air ($Pr = 0.71$) in a cubical cavity heated from the sides using a finite difference method having a fourth-order accuracy. The percent difference on the calculated Nusselt number between their results and our results (computed with the mesh used in all our study on a cubical cavity) is within 0.7%. The case studied by Mallinson and Davis [113] was then reproduced with a higher accuracy. Here, natural convection inside a truncated square duct, with its length two times the length of the square side, and heated from the sides was studied.

The code for calculating the solution branches and bifurcation points was validated by reproducing the work of Puigjaner et al. [168]. Here, detailed bifurcation diagrams were determined for a cubical cavity with adiabatic sidewalls and heated from below. Air was used as working fluid. A very good agreement with their work was obtained, validating the developed continuation method.

Some of the methods and results presented in this chapter were published in [197].
V

Bifurcation analysis of steady natural convection in tilted rectangular enclosures
OVERVIEW

In Chapter IV, a continuation method was developed to calculate solution branches in steady natural convection in parallelepiped cavities. The stability analysis of the solutions along these branches, the detection and precise direct calculation of the bifurcation points, and the jump to newly detected stable or unstable branches are all managed by a single continuation algorithm. In this chapter, this continuation method is used to investigate the effects of a tilt on the stability of the flow in a parallelepiped cavity heated from its lower side.

In this chapter we consider two kinds of parallelepiped cavities: a truncated square duct and a cubical cavity. The truncated square duct has its length equal to two times the side of its square cross-section. This aspect ratio was chosen to clarify the effect of the tilt on the transverse and longitudinal rolls that have been observed in experiments [148] and predicted by numerical calculations [1]. The cubical cavity is studied in more detail because it has a richer dynamics due to many symmetry properties (see Chapter IV), and it has been studied in detail in the horizontal case but never in the tilted case. Understanding the inclination effect is of great importance because in real applications it is common that the rectangular enclosure is tilted by a large inclination angle, e.g. in the case of solar collectors [100]. Moreover, even in cases where the cavity is intended to be horizontally placed, there is always a slight tilt due to unavoidable imperfections in the physical setup.

In §1, a brief introduction that includes the most relevant literature on the problem is presented. In §2, the influence of the tilt on a truncated square duct tilted around its longer axis is clarified. Here, special attention is given to the bifurcations around the first instability thresholds for a fluid of Prandtl number $Pr = 1$. In §3, the focus is turned to a cubical cavity heated from below and tilted around a lower horizontal edge. Here, the stability of steady natural convection is investigated for the range of inclination $0^\circ \leq \theta \leq 90^\circ$, Rayleigh number $Ra \leq 150000$, and Prandtl number $0.71 \leq Pr \leq 130$, clarifying all the transitions from the basic steady state solution to the periodic solutions.
1 INTRODUCTION

Rayleigh-Bénard convection is a more complex phenomenon than natural convection heated from the sides [66] (see the validation of the code in Chapter IV §3), and is one of the most studied problems in fluid mechanics in both extended layers and confined cavities. It has been extensively studied during the course of a century since the pioneering studies of Bénard [19, 20] and Rayleigh [175]. In this type of fluid motion, the buoyancy forces must overcome the viscous forces for convection to set in. This occurs at a critical Rayleigh number, after which flow patterns with a given type of symmetry usually arise. The critical Rayleigh number as a function of the aspect ratio is well-known [41]. The lateral walls increase the critical Rayleigh number due to the additional shear stress exerted to the system. Depending on the roll orientation with respect to the axes of a non-cubical cavity, these stable solutions are usually called transverse or longitudinal rolls. From the different aspect ratios that have been studied, the cubical cavity is the most fundamental geometry. Pallares et al. [149] conducted experiments that show various convective flow patterns in such cubical enclosure.

1.1 CONVECTION IN THREE-DIMENSIONAL HORIZONTAL CAVITIES

Puigjaner et al. [168–171] have conducted a thorough bifurcation analysis of Rayleigh-Bénard convection in a cubical cavity filled with air and silicone oil (Prandtl numbers $Pr = 0.71$ and 130, respectively) for perfectly insulating and conducting lateral sidewalls. Their results are summarized in detailed bifurcation diagrams where the different stable and unstable branches are depicted for the Rayleigh number range $Ra \leq 1.5 \times 10^5$.

- In their first paper [168], air in a cubical cavity with adiabatic sidewalls was studied. Their results are used as a benchmark in Chapter IV for the numerical methods implemented in this study.
- In their second paper [169], the cubical geometry with adiabatic sidewalls was kept
but they now focused on a higher value of the Prandtl number by using silicone oil as the working fluid. It was shown that the first stable branch, which consists of one-roll structures aligned with the sidewalls, gives rise to secondary and tertiary stable bifurcated branches which eventually become unstable after a Hopf bifurcation, whereas only a secondary bifurcation was detected on this branch in the previous study for air in the same range $Ra \leq 1.5 \times 10^5$.

- In their third paper [170], they expand their study to air and silicone oil in a cubical cavity with conducting sidewalls. For both working fluids, the bifurcation diagrams were more complex than those previously reported for adiabatic sidewalls.

All these studies yield important results that clarify the stability behaviour of natural convection in a cubical enclosure heated from below. See Chapter IV for details on the bifurcation diagrams and flow patterns for the case of $Pr = 0.71$.

### 1.2 Convection in Tilted Cavities

In practical applications, it is common that the cavity is tilted. Even when the cavity is intended to be placed horizontally, a very slight inclination exists in a real physical situation. Then, two fundamental questions arise:

- What is the effect of a slight inclination on the stability of the system?
- What happens during the transition from Rayleigh-Bénard convection to the heated-from-the-sides configuration?

In spite of the importance of natural convection in tilted cavities, there is no complete bifurcation analysis that addresses these questions in a realistic three-dimensional configuration, such as in the literature reviewed in §1.1.

Rayleigh-Bénard flows can be disturbed by small uncontrolled perturbations, coming for example from thermal defects or a small inclination of the cell (by an angle $\theta$). The
inclination effect is particularly interesting as it induces a flow at any value of $Ra$ and, thus, prevents the existence of the no-flow conductive state found in the horizontal case. Changes of flow symmetries will also occur and modifications of the bifurcation diagrams are expected. Rather few studies are related to this inclination effect in Rayleigh-Bénard situations.

Cliffe and Winters [47] calculated the bifurcation diagram for a tilted two-dimensional square cavity. They show that the primary pitchfork bifurcation, which is found in the horizontal case, disappears and that the diagram predicts a leading solution (convective roll generated by the inclination) which develops smoothly from zero Rayleigh number and an anomalous solution (with opposite sense of rotation) on a disconnected branch initiated at a saddle-node point. The saddle-node critical Rayleigh number is also predicted as a function of the inclination angle of the cell. In their review paper on the Rayleigh-Bénard convection, Bodenschatz et al. [27] mention different studies concerned by the inclination effect. Most of these studies have considered extended layers and they analyze how the shear flow induced by the inclination modify the transitions to transverse or longitudinal rolls. One of the studies by Kirchartz and Oertel [92] considers more confined layers, with aspect ratios 10:4:1 and 4:2:1. Using both experiments and numerical calculations, the authors obtain very interesting results showing the influence of the inclination angle, the Rayleigh number and the Prandtl number on the different flow patterns. More recently, Pallares et al. [151] give some information on the influence of very small inclinations ($\theta \leq 1^\circ$) on the flow patterns obtained in a cubical cavity. At given values of $Ra$, they show that some of the solutions obtained without inclination are still present with a small inclination, whereas other solutions are no longer observed and replaced by a solution with a different structure. They cannot, however, explain why these transitions occur.

Finally, two rather old papers by Ozoe et al. [146, 148] and a quite recent paper by Adachi [1], consider the natural convection in an inclined square channel or duct. In these papers, the inclination is due to a rotation around the longitudinal axis of the chan-
nel. Ozoe et al. [148] performed both two-dimensional simulations in the cross-section of the square channel and experiments in a convection channel with dimensions 15 mm × 15 mm × 270 mm. They focused on the heat transfer properties of natural convection expressed in terms of the Nusselt number. Both theoretically and experimentally, the maximum heat transfer is found to occur at about 50 degrees of inclination and is associated with a longitudinal roll. This longitudinal roll is obtained experimentally for inclinations $\theta > 10^\circ$. For $\theta < 10^\circ$, more complex flow structures are obtained, suggesting the presence of multiple stationary modes. Hence, a minimum heat transfer was found at an inclination of about 10 degrees. Finally, when the square duct was kept almost horizontal ($\theta < 1^\circ$), a series of side-by-side two-dimensional roll-cells was eventually established.

Adachi [1] considers the stability of natural convection in an inclined square duct. He does not perform three-dimensional simulations, but considers that the duct has an infinite length and calculates the stability of the two-dimensional basic flows in the square cross-section of the duct with regard to three-dimensional perturbations. He can thus obtain information on the longitudinal one-roll solution and on its stability, but cannot calculate the transverse roll solution, which is the first to appear without inclination, and cannot obtain the mixed mode solutions that are expected with inclination. We thus see that there is a need for three-dimensional simulations on such Rayleigh-Bénard problems involving tilted confined cavities, and that continuation methods would be the appropriate tool for these studies.

1.3 Objectives

The former studies of Ozoe et al. [148] and Adachi [1] on tilted square ducts with a large length are extended to a three-dimensional truncated square duct. Furthermore, the former studies of Puigjaner et al. [168,169] are investigated for the inclined situation. The objectives of this chapter are the following.

1. Investigate the flow transition from the trivial solution to transverse or longitudinal rolls in a horizontal ($\theta = 0^\circ$) truncated square duct.
Figure 5.1: Dimensionless geometry of a truncated square duct titled by an angle $\theta$. The $xy$ cross section of the cavity is a square of dimensions $(l \times h) = (1 \times 1)$ and its length is $L = 2$. The two walls corresponding to $yz$-planes at $x = -1/2$ and $x = 1/2$ are isothermal and held at $T_H = 1/2$ and $T_C = 1/2$, respectively. The other sidewalls are adiabatic. The cavity is tilted by an angle $\theta$ (expressed in degrees) around the $-z$ axis.

2. For steady natural convection in the three-dimensional duct, clarify the influence of the inclination on the stability of the system. Here, stability diagrams are presented for Rayleigh numbers in the range $Ra \leq 25000$. A working fluid of Prandtl number $Pr = 1$ is considered.

3. For steady natural convection in a cubical cavity, clarify the influence of the inclination on the stability of the system. Here, stability diagrams are presented for $Pr = 5.9$, $Ra \leq 150000$, and $0^\circ \leq \theta \leq 90^\circ$. The critical angles that limit the existence range of the stable solutions are then investigated for $0.71 \leq Pr \leq 130$. 

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2 NATURAL CONVECTION IN A TRUNCATED SQUARE DUCT TILTED AROUND ITS LONGEST AXIS

Initially, a rectangular enclosure with a length equal to two times the size of the square cross-section is considered. We focus on the truncated (or finite-length) square duct shown in Fig. 5.1. This cavity has a reasonable length for three-dimensional computing, it avoids the solution degeneracy of the strongly symmetric cubical cavity and, as in the duct with infinite length, the first transition is expected to be to transverse rolls and to occur before the transition to the longitudinal roll. The thermal boundary conditions on the sidewalls are chosen as adiabatic, as in the work of Ozoe et al. [148].

On this problem, we first present the precise bifurcation diagram obtained in the horizontal situation. We then put into light all the subtle modifications induced in the bifurcation diagram around the first primary and secondary bifurcations by applying a slight tilt to the cavity. We finally determine the domains of existence for the different stable solutions in the $Ra-\theta$ parameter space, and conclude with comparisons with previous works.

2.1 MESH REFINEMENT TESTS

For the calculations in the parallelepiped cavity with $A_y = 1$ and $A_z = 2$ shown in Fig. 5.1, the same refined mesh comprising $27 \times 27 \times 41$ points (in the $x$, $y$, and $z$ directions,
respectively) was chosen for all the calculations in this section. This mesh is shown in Fig. 5.2. It gives a very good precision for the calculation of the different bifurcation points, as indicated by the precision tests given in Table 5.1. The bifurcation points used in these mesh refinement tests are presented in §2.3. The precision slightly decreases for inclined cavities when the variation of the critical Rayleigh number with \( \theta \) is very steep. The test done on the saddle-node point \( N \pm \) for \( \theta = 4^\circ \), however, shows that the value of \( Ra_c \) changes by less than 0.01% when the mesh is further refined. The calculation of the solutions by Newton method is less difficult, so that the chosen mesh also gives a good precision for the solutions in the whole parameter range studied (\( 0 \leq Ra \leq 25000, 0^\circ \leq \theta \leq 90^\circ \)).

### 2.2 Symmetries

In such confined convective situations, the flow states have different symmetries which play an important role as they are often involved in the different bifurcations. Indeed, at a bifurcation point, a symmetry of the solution is generally broken by the critical eigenvector (pitchfork bifurcation) and the solutions on the new branch bifurcating at this point will have lost this symmetry. Checking the symmetries is then not only important to characterize the different flow states, but also to check the coherence of the bifurcation diagram and sometimes to guess the new solutions which must be obtained (for example, when a tilt of the cavity is imposed).
Under the approximation of the model, the basic diffusive no-flow solution in the
horizontal situation (which is simply \( T = -x \) and \( u = 0 \)) presents different symmetries. In
the case of a cavity with \( A_y \neq A_z \), these symmetries are the reflection symmetries \( S_{P_x}, S_{P_y}, \)
and \( S_{P_z} \) with respect to the three middle planes (longitudinal \( yz \)-plane at \( x = 0 \), longitudinal
\( xz \)-plane at \( y = 0 \), and transverse \( xy \)-plane at \( z = 0 \), respectively), which, by combination,
induce \( \pi \)-rotational symmetries \( S_{A_x}, S_{A_y}, \) and \( S_{A_z} \) about the three middle axes (\( x \)-, \( y \)-,
and \( z \)-axes, respectively). These symmetries belong to a \( Z_2 \times Z_2 \times Z_2 = Z_2 \times D_2 \) group. As an
example, we define two of these symmetries, \( S_{P_z} \) and \( S_{A_z} \), and the others can be obtained
by circular permutation:

\[
S_{P_z} : \quad (x, y, z, t) \rightarrow (x, y, -z, t), \quad (u, v, w, T) \rightarrow (u, v, -w, T), \quad (5.1)
\]

\[
S_{A_z} : \quad (x, y, z, t) \rightarrow (-x, -y, z, t), \quad (u, v, w, T) \rightarrow (-u, -v, w, -T). \quad (5.2)
\]

The symmetry \( S_C \) with respect to the center point of the cavity can also be obtained by
combination of the previous symmetries. When the flow is triggered, at least the up-down
\( S_{P_z} \) symmetry is broken. The effective symmetries of the flow will depend on the flow
configuration triggered. The symmetries for a cavity with \( A_y = A_z \) will be presented in
\( \S 3.1 \) giving results for the cubic cavity.

When the cavity is tilted around the longitudinal \(-z\) axis, there is no motionless state
for \( Ra \neq 0 \) and the convection first induced corresponds to a single longitudinal roll with
the \(-z\) axis as axis of rotation and the same sense of rotation as the inclination angle. The
original symmetries of this inclined case independent of the aspect ratios of the cavity are
those of the longitudinal roll, which are the \( S_{P_z}, S_{A_z}, \) and \( S_C \) symmetries. These symme-
tries belong to a \( Z_2 \times Z_2 = D_2 \) group. In both the horizontal and tilted situations, when
increasing \( Ra \), bifurcations to new flow states (steady or oscillatory) will occur, at which
some of the symmetries will usually be broken.
Table 5.2: Critical Rayleigh numbers $Ra_c$ for the first ten primary bifurcation points ($P_1$ to $P_{(10)}$) in a horizontal $1 \times 1 \times 2$ cavity heated from below ($Pr = 1$).

<table>
<thead>
<tr>
<th></th>
<th>$P_1$</th>
<th>$P_2$</th>
<th>$P_3$</th>
<th>$P_4$</th>
<th>$P_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>2726.53</td>
<td>2818.78</td>
<td>3443.54</td>
<td>3498.72</td>
<td>4504.21</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$P_6$</th>
<th>$P_7$</th>
<th>$P_8$</th>
<th>$P_9$</th>
<th>$P_{(10)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>4717.45</td>
<td>6161.47</td>
<td>6819.74</td>
<td>7198.32</td>
<td>8693.36</td>
</tr>
</tbody>
</table>

2.3 Horizontal square duct

In the case of the horizontal cavity, where a diffusive solution exists and where convection sets in beyond primary bifurcation points, the entire continuation algorithm described in Chapter IV §2 was used to calculate the bifurcation diagram. All the solutions emerging from the first ten primary bifurcation points (denoted as $P_1$ to $P_{(10)}$) and within the range $0 \leq Ra \leq 10000$ were calculated. The onset of convection, at the first primary bifurcation point $P_1$, occurs at $Ra_c = 2726.53$. The critical values for the other nine primary bifurcation points can be found in Table 5.2. All these primary bifurcations are pitchforks, as they at least break the up-down symmetry.

The critical eigenvectors at these primary bifurcation points are plotted in Figs. 5.3 and 5.4. The vertical velocity contours in the horizontal midplane ($x = 0$) for these eigenvectors are shown in Fig. 5.3, whereas the velocity vector field in the vertical $xz$-plane (at $y = 0$) for the eigenvectors at the primary bifurcations $P_3$ and $P_5$ is plotted in Fig. 5.4. As shown in Fig. 5.3, the eigenstructures can be characterized by their number $n_T$ of counter-rotating transverse rolls (with axis along $y$) and their number $n_L$ of counter-rotating longitudinal rolls (with axis along $z$), and can then be denoted as $(n_T, n_L)$ structures. They also have characteristic symmetries which can be related to the parity of $n_T$ or $n_L$: odd values correspond to symmetries with respect to axes and even values correspond to symmetries with respect to planes. We thus see that the critical eigenstructures at $P_1$ [(2,0) structure], $P_7$ [(4,0) structure] and $P_9$ [(0,2) structure] have the $S_{P_z}$ and $S_{P_y}$ symmetries, those at $P_2$
Figure 5.3: Vertical velocity contours in the horizontal midplane ($x = 0$) for the critical eigenvectors at the first ten primary bifurcation points ($P_1$ to $P_{(10)}$) for a horizontal $1 \times 1 \times 2$ cavity heated from below ($Pr = 1$). The positive and negative vertical velocities are indicated by solid and dashed lines, respectively. The eigenstructures can be characterized by their number $n_T$ of counter-rotating transverse rolls (with axis along $y$) and their number $n_L$ of counter-rotating longitudinal rolls (with axis along $z$) ($n_T, n_L$ structures). They have also characteristic symmetries: $S_{P_1}$ and $S_{P_2}$ at $P_1$ ((2,0) structure), $P_7$ ((4,0) structure) and $P_8$ ((0,2) structure), $S_{P_6}$ and $S_{A_2}$ at $P_2$ ((0,1) structure) and $P_5$ ((2,1) structure), $S_{A_1}$ and $S_{P_2}$ at $P_3$ ((3,0) structure), $P_9$ ((1,0) structure) and $P_{(10)}$ ((1,2) structure), and $S_{A_1}$ and $S_{A_2}$ at $P_4$ ((1,1) structure) and $P_8$ ((3,1) structure).
Figure 5.4: Velocity vector field in the vertical $xz$-plane (at $y = 0$) for the critical eigenvectors at the primary bifurcation points $P_3$ and $P_5$ for a horizontal $1 \times 1 \times 2$ cavity heated from below ($Pr = 1$).

$P_3$ and $P_5$ have the symmetries, those at $P_3$ [(3,0) structure], $P_5$ [(1,0) structure] and $P_{(10)}$ [(1,2) structure] have the $S_{A_x}$ and $S_{P_z}$ symmetries and those at $P_4$ [(1,1) structure] and $P_8$ [(3,1) structure] have the $S_{A_y}$ and $S_{A_z}$ symmetries. Figure 5.4 gives some precisions for the flow structures at $P_3$ and $P_5$, which, according to Fig. 5.3, have some similarities. We see that the structure at $P_3$ corresponds to three transverse counter-rotating rolls, the central roll being dominant, whereas the structure at $P_5$ corresponds to a long-scale transverse circulation embedding two co-rotating transverse cells.

The complete calculation of the bifurcation diagram in the range $0 \leq Ra \leq 10000$ was not performed in a single run of the code. The number of stored secondary bifurcation points, further used for branching, was limited to 10, and that was not enough to account for the numerous secondary branches emerging from the ten primary branches. Moreover, the fact that, at each continuation step, we do not use Arnoldi’s method, but rather follow a selected eigenvalue, makes it difficult not to miss some of the bifurcations. We can indeed follow an eigenvalue, which seemed to be a good candidate for transition, while another eigenvalue evolves more quickly and is eventually the first to become unstable. Sometimes, this transition can be detected at the next Arnoldi step. In any case, an a posteriori careful reading of the output file will reveal any missed bifurcations, and a specific calculation will then be conducted to determine them precisely.
Figure 5.5: Bifurcation diagram in the case of a horizontal $1 \times 1 \times 2$ cavity heated from below ($Pr = 1$). The abscissa indicates the Rayleigh number $Ra$ and the ordinate the maximum absolute value of the vertical velocity inside the cavity. The stability of each branch is indicated by using the notation $n - p$, where $n$ is the number of unstable real eigenvalues and $p$ is the number of couples of unstable complex conjugate eigenvalues (when $p = 0$, only $n$ is given). (a) The solution branches obtained in the range $2600 \leq Ra \leq 4000$ and initiated from the first four primary bifurcations are plotted. This diagram was calculated during a single run of the code. (b) The solution branches obtained in the range $2000 \leq Ra \leq 10000$ and initiated from the first six primary bifurcations are plotted. Insets are vertical velocity contours in the horizontal midplane ($x = 0$) for different solutions.
In Fig. 5.5(a), we give the first part of the bifurcation diagram, for \( Ra \leq 4000 \), which was calculated in a single run of the code. In this plot, the range \( Ra < 2600 \) was omitted since only the no-flow diffusive solution exists for this range. The maximum absolute value of the vertical velocity \( |u|_{\text{max}} \) is plotted as a function of the Rayleigh number \( Ra \). Precisions on the stability of each branch are given using the notation \( n - p \), where \( n \) is the number of unstable real eigenvalues and \( p \) is the number of couples of unstable complex conjugate eigenvalues. Thus the number of unstable eigenvalues is \( n + 2p \). For simplicity, when \( p = 0 \) only \( n \) is given. Solid circles indicate steady bifurcation points. In this first calculation (2600 \( \leq Ra \leq 4000 \)), four primary bifurcations were detected on the diffusive branch and precisely calculated. From these primary bifurcations, thanks to the branching algorithm, four primary branches were calculated and followed up to \( Ra = 4000 \). Three secondary bifurcation points were then detected and precisely calculated on these primary branches, and the secondary branches emerging from these points were eventually calculated. We choose to denote the different primary, secondary and tertiary branches as \( B_i, B_{ij} \) and \( B_{ijk} \), respectively, where \( i \) is the index of a primary branch, \( j \) is the index of a secondary branch on this primary branch, and \( k \) is the index of a tertiary branch on this secondary branch. If an index has more than two digits, then we use parentheses to indicate the numeral, e.g. \( P_{i(10)} \). Likewise, the secondary bifurcation points on these branches (say \( B_m \)) will be denoted as \( S_lB_m \), where \( l \) indicates the \( l \)th secondary bifurcation point.

The results shown in Fig. 5.3 indicate that the first primary branch \( B_1 \), which corresponds to two transverse rolls, is stable in the calculated range of \( Ra \). The second primary branch \( B_2 \), which corresponds to a single longitudinal roll, is unstable at its onset, but stabilized at a secondary bifurcation point (\( Ra_c = 3213.62 \)). The critical eigenvector at this bifurcation point is a transverse two-roll structure, similar to the primary eigenvector at \( P_1 \) (see Fig. 5.3). The bifurcated branch \( B_{21} \), which is one time unstable, corresponds to a kind of two-oblique-roll structure which has kept the reflection symmetry with respect to the \( xy \)-plane, as shown in the inset in Fig. 5.5(a). The insets in Fig. 5.5, and in all
subsequent figures, are vertical velocity contours in the midplane \((x = 0)\) for different solutions, the same as those shown in Fig. 5.3. The third primary branch \(B_3\) corresponding to three transverse rolls and the fourth primary branch \(B_4\) corresponding to a \((1,1)\) structure (which are, respectively, two-time and three-time unstable at their onset) exchange stability through a short secondary branch which connects them. This branch (which can be denoted as \(B_{31}\) or \(B_{41}\)) bifurcates supercritically from \(B_3\) at \(Ra_c = 3609.24\), turns at a saddle-node point \((Ra_c = 3615.53)\), and connects with \(B_4\) at \(Ra_c = 3612.51\). The eigenvector at the secondary bifurcation point on \(B_3\) \((B_4)\) is similar to the flow solution on \(B_4\) \((B_3)\). The structure of the flow on the secondary branch is shown as inset in Fig. 5.5(a) at the saddle-node point. We see that this structure still includes oblique rolls, but with a \(\pi\)-rotation symmetry with respect to the \(y\) axis. Note that this secondary branch was calculated two times during the job, as it emerges from the secondary bifurcation points on both \(B_3\) and \(B_4\). In Fig. 5.5(a), the insets show the flow on the branches \(B_1, B_2, B_{21}, B_3\), and \(B_4\) at \(Ra = 4000\) and on the branch \(B_{31}\) at the saddle-node point \((Ra_c = 3615.53)\).

Finally, the whole bifurcation diagram in the range \(Ra \leq 10000\) is presented in Fig. 5.5(b) for the branches initiated from the first six primary bifurcations (\(P_1\) to \(P_6\)). The branches initiated from the next four primary bifurcations (\(P_7\) to \(P_{10}\)) are shown in Fig. 5.6. The separation of the bifurcation diagram into two plots (Figs. 5.5(b) and 5.6) was necessary in order to avoid confusion between neighbouring branches. For the same reason, we changed the value plotted in Fig. 5.6 from \(|u|_{\text{max}}\) to \(|w|_{\text{max}}\).

For all these diagrams, we only calculated one branch emerging from each bifurcation point. This is not a restriction in the horizontal case as we will see that all the bifurcations (as the primary bifurcations) are pitchfork bifurcations, for which the two emerging branches give equivalent solutions and can be plotted as a single curve in our diagrams featuring \(|u|_{\text{max}}\) or \(|w|_{\text{max}}\). Notice also that in Chapter IV we plotted the bifurcation diagrams in terms of \(Nu\) as a function of \(Ra\), while here we use \(|u|_{\text{max}}\) or \(|w|_{\text{max}}\) instead of \(Nu\). The choice of parameter in the ordinate is arbitrary when describing the stability of the system, as long as the parameter in the abscissa is the Rayleigh number \(Ra\). Neverthe-
V Bifurcation analysis of steady natural convection in tilted rectangular enclosures

Figure 5.6: Bifurcation diagram in the case of a horizontal $1 \times 1 \times 2$ cavity heated from below ($Pr = 1$). The ordinate indicates the maximum absolute value of the horizontal velocity in the direction of the duct axis. The solution branches obtained in the range $6000 \leq Ra \leq 10000$ and initiated from the first four primary bifurcations in this range (P7 to P10) are plotted.

less, for heat transfer applications, it is preferred to employ the average Nusselt number $Nu$ in the ordinate, while the maximum velocity within the cavity $V_{max}$ would be more convenient for fluid mechanic applications.

**Discussion about the flow stability in a horizontal truncated duct**

We see on these diagrams that the code was able to detect all the successive transitions on the different branches. The branches obtained previously in the range $Ra \leq 4000$ are not much modified when the $Ra$ range is extended to $Ra \leq 10000$. The branches $B_1$ and $B_2$ remain stable, and $B_4$ remains two-time unstable. $B_{21}$ is destabilized once, while $B_3$ is stabilized once, with the emergence of secondary $B_{32}$ and tertiary $B_{321}$ branches. The fifth primary branch $B_5$ remains four-time unstable except in the range $7349.63 \leq Ra \leq 9385.13$, where it is stabilized once by a secondary branch $B_{51}$ (which can be also denoted as $B_{52}$) with a saddle node at $Ra_c = 9389.13$. The solution at this saddle-node point is
Figure 5.7: Sketch of the bifurcation diagram (shown in Figs. 5.5 and 5.6) in the case of a horizontal $1 \times 1 \times 2$ cavity heated from below ($Pr = 1$). The sketch maps all the solutions that arise from the no-flow solution (NFS) and the ten primary bifurcations on the different branches in the range $Ra \leq 10000$. The solutions that are stable over certain ranges of Rayleigh numbers are encircled, and the solutions that have at least one unstable complex conjugate eigenvalue are printed in boldface. The connections between the different branches of solutions are shown. The solid linking lines indicate pitchfork bifurcations. The dashed arrows indicate a saddle-node bifurcation connecting two branches with similar solutions forming a closed loop.

shown as inset in Fig. 5.5(b): it has lost the symmetry with respect to the $y$ axis. The sixth primary branch (five-time unstable at its onset) is stabilized twice and destabilized once. Different secondary and even tertiary branches emerge from this primary branch. Some of the unstable eigenvalues become oscillatory by collision on the real axis of two steady eigenvalues, but no Hopf bifurcation was found in the calculated $Ra$ range. Concerning the next four primary branches ($B_7$ to $B_{(10)}$) shown in Fig. 5.6, they are highly unstable at their onset, but stabilized at different secondary bifurcation points, they still remain unstable until $Ra = 10000$. As already mentioned for the first sixth branch, some of the unstable eigenvalues become oscillatory for the following four branches (see Fig. 5.6).
Table 5.3: Critical Rayleigh number \( Ra_c \) for the secondary bifurcation points found in the range \( Ra \leq 10000 \) for a horizontal \( 1 \times 1 \times 2 \) cavity heated from below (\( Pr = 1 \)). \( S_iB_j \) denotes the \( i \)th secondary bifurcation point on the \( j \)th branch. All these secondary bifurcation points are pitchforks, except for \( S_1B_{31} \) and \( S_1B_{51} \) which are saddle-node points connecting \( B_{31} \) to \( B_{41} \) and \( B_{51} \) to \( B_{52} \), respectively.

<table>
<thead>
<tr>
<th>( S_1B_2 )</th>
<th>( S_1B_{31} )</th>
<th>( S_1B_3 )</th>
<th>( S_1B_{31} )</th>
<th>( S_2B_3 )</th>
<th>( S_1B_{32} )</th>
<th>( S_1B_4 )</th>
<th>( S_1B_5 )</th>
<th>( S_1B_{51} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3213.62</td>
<td>9606.06</td>
<td>3609.24</td>
<td>3615.53</td>
<td>7401.67</td>
<td>8000.68</td>
<td>3612.51</td>
<td>7349.63</td>
<td>9389.13</td>
</tr>
<tr>
<td>( S_2B_5 )</td>
<td>( S_1B_6 )</td>
<td>( S_1B_{61} )</td>
<td>( S_2B_6 )</td>
<td>( S_1B_6 )</td>
<td>( S_1B_7 )</td>
<td>( S_1B_8 )</td>
<td>( S_2B_8 )</td>
<td>( S_1B_9 )</td>
</tr>
<tr>
<td>9385.13</td>
<td>4885.29</td>
<td>7553.79</td>
<td>7223.76</td>
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<td>8901.59</td>
<td>9128.86</td>
<td>9395.13</td>
<td>8569.58</td>
</tr>
</tbody>
</table>

As the bifurcation diagram for the horizontal \( 1 \times 1 \times 2 \) cavity heated from below (shown in Figs. 5.5 and 5.6) is quite complex, a sketch mapping all the solutions that arise from the no-flow solution and the ten primary bifurcation points on the different branches in the range \( Ra \leq 10000 \) is presented in Fig. 5.7. This sketch also gives the connection between these different branches of solutions. In this mapping, the solutions that are stable over certain ranges of Rayleigh numbers are encircled and printed in blue colour, and the solutions that have at least one unstable complex conjugate eigenvalue are printed in boldface. The solid linking lines indicate pitchfork bifurcations. The dashed arrows indicate a saddle-node bifurcation connecting two branches with similar solutions forming a closed loop. A summary of the characteristics of this bifurcation diagram is finally given in Table 5.3 and Fig. 5.8.

In Table 5.3, we give the values of the critical Rayleigh number for all the secondary or tertiary bifurcations involved in the diagram. Here, 18 such bifurcations have been found, among which 13 are secondary pitchforks, 3 are tertiary pitchforks, and 2 are saddle nodes. All these bifurcation points were directly calculated as the solution of the system in Eq. (4.12), which allows to obtain results with a very good precision.

In Fig. 5.8, the 22 solutions obtained at \( Ra = 10000 \) on the different branches issued from the ten first primary bifurcation points are depicted. Note however that, as all the branches are initiated at pitchfork bifurcation points, equivalent solutions exist for each of these solutions, which are their symmetric with respect to the symmetries broken at the
corresponding previous pitchfork points. The solutions on the ten primary branches ($B_1$ to $B_{(10)}$) are similar to the eigenvectors that initiate them (at points $P_1$ to $P_{(10)}$, respectively) and have the same symmetries. The convective flows are, however, more intense, so that thinner boundary layers are observed. For the solutions on the secondary branches, one of the symmetries of the corresponding primary solutions has been broken, and a second symmetry breaking is observed in case of tertiary branches. More precisely, the $S_{A_z}$ symmetry of $B_2$ is broken on $B_{21}$, and the remaining $S_{P_z}$ symmetry is then broken on $B_{211}$. The $S_{A_y}$ symmetry of $B_3$ is broken on $B_{32}$, and the remaining $S_{P_y}$ symmetry is then broken on $B_{321}$. The $S_{P_z}$ and $S_{A_z}$ symmetries of $B_6$ are broken on $B_{61}$ which keeps the central $S_C$ symmetry, and this central symmetry is then broken on $B_{611}$. The $S_{P_z}$ symmetry

Figure 5.8: Vertical velocity contours in the horizontal midplane ($x = 0$) for the solutions at $Ra = 10000$ on the different branches issued from the ten first primary bifurcation points for a horizontal $1 \times 1 \times 2$ cavity heated from below ($Pr = 1$). Among these 22 solutions, only the solutions on the $B_1$ and $B_2$ branches are stable.
of $B_6$ is broken on $B_{62}$ which keeps the $S_{A_z}$ symmetry, while the $S_{A_y}$ symmetry of $B_6$ is broken on $B_{63}$ which keeps the $S_{P_z}$ symmetry. The $S_{P_z}$ symmetry of $B_7$ is broken on $B_{71}$ which keeps the $S_{P_y}$ symmetry. The $S_{A_x}$ symmetry of $B_8$ is broken on $B_{81}$ which keeps the $S_{A_y}$ symmetry, while the $S_{A_y}$ symmetry of $B_8$ is broken on $B_{82}$ which keeps the $S_{A_z}$ symmetry. Finally, the $S_{P_x}$ and $S_{P_y}$ symmetries of $B_9$ are broken on $B_{91}$ which keeps the $S_{A_x}$ symmetry. We have to recall that, among these solutions, only the first two solutions on $B_1$ and $B_2$ are stable. The solution on the $B_1$ branch corresponds to a transverse two-roll structure (denoted as a $T$ solution) and is stable at its onset at $P_1$ ($Ra_c = 2726.53$).

The solution on the $B_2$ branch corresponds to a longitudinal one-roll structure (denoted as a $L$ solution) and is stable beyond the secondary bifurcation $S_1B_2$ ($Ra_c = 3213.62$).

Additional computations for larger $Ra$ values were performed for these two branches. The branches appear to be stable in a large $Ra$ range, at least up to $Ra = 80000$. Their stability limits correspond to Hopf bifurcation points, which have been localized at $Ra_c = 87025$ and $81156$ for the $B_1$ and $B_2$ branches, respectively. The associated angular frequencies are $\omega = 154.43$ and $8.72$.

Note finally that the degeneracy of the solutions at the first bifurcation point in a cubical cavity (due to the $D_4$ symmetry, see §3.3) is suppressed when $A_z \neq A_y$ (change to a $D_2$ symmetry). In our cavity with $A_z = 2$ and $A_y = 1$, the $T$, $L$ and oblique solutions, which were triggered at the same bifurcation point in the cubical cavity, are now separated. More precisely, the $T$ and $L$ solutions still belong to primary branches (as they have the $D_2$ symmetries), the $T$ solution being the first to appear, whereas oblique solutions can be found on a secondary branch initiated from the $L$ branch. This sequence of primary bifurcations ($T$ solutions triggered before $L$ solutions) is similar as that found in longer or infinite square ducts [1, 148]. This is an argument for calling our parallelepiped cavity a truncated or finite length square duct and we can expect that the comparisons between our results and those in longer square ducts will make sense.
In this subsection, the influence on the stability of the system of an imposed tilt to the cavity is investigated. The truncated square duct is tilted by an angle \( \theta \) around the horizontal \(-z\) axis, as shown in Fig. 5.1. Here, the focus is put on the two branches which are stable (at least in part) in the horizontal situation, i.e. the \( B_1 \) and \( B_2 \) branches shown in Fig. 5.5(a). The symmetries of the problem are changed when a tilt is imposed to the cavity and, hence, the bifurcations found in the horizontal situation will change as well.
### Effect of a slight tilt on the stability of the system

To better analyse the influence of the tilt, we will compare the bifurcation diagram obtained in the horizontal situation ($\theta = 0^\circ$) with that obtained for a very small inclination angle, $\theta = 0.01^\circ$. The two calculated diagrams are plotted in Fig. 5.9 in the same $Ra$ range ($2600 \leq Ra \leq 3400$). In order to distinguish between roll structures with opposite sense of rotation, we now plot the velocity $u_1$ (along $x$) at a representative point ($x_1 = y_1 = 0.17419$, $z_1 = 0.2307$) as a function of $Ra$. In these diagrams, the stable solutions are given as solid lines whereas the unstable solutions are given as dashed lines.

When the cavity is tilted, there is no motionless diffusive solution and the convection sets in as soon as $Ra$ is different from zero. Due to the inclination $\theta$ chosen (around the $-z$ axis), this convection at small $Ra$ corresponds to a weak single longitudinal roll with the same sense of rotation as the inclination angle ($L-$ solution), a solution which has
Table 5.4: Critical Rayleigh number $Ra_c$ for the main bifurcation points found in the case of the horizontal cavity ($\theta = 0^\circ$) and the slightly inclined cavity ($\theta = 0.01^\circ$).

<table>
<thead>
<tr>
<th>$\theta$</th>
<th>$P_1 \rightarrow S_0$</th>
<th>$P_2 \rightarrow N_d$</th>
<th>$S_1 B_2 -$</th>
<th>$\rightarrow S$</th>
<th>$S_1 B_2 + \rightarrow S_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0^\circ$</td>
<td>2726.53</td>
<td>2818.78</td>
<td>3213.62</td>
<td></td>
<td>3213.62</td>
</tr>
<tr>
<td>0.01°</td>
<td>2726.60</td>
<td>2834.76</td>
<td>3205.33</td>
<td></td>
<td>3221.85</td>
</tr>
</tbody>
</table>

The $S_{Pz}$ and $S_{Az}$ symmetries. The primary bifurcation point $P_1$ is replaced by a secondary bifurcation point denoted as $S_0$. $S_0$ is still a pitchfork, as the eigenvector (which is close to a transverse two-roll flow) breaks the $S_{Az}$ symmetry of the longitudinal roll. The solutions on the branches emerging from $S_0$ have only the $S_{Pz}$ symmetry and cannot then be exact $T$ solutions, but, for $\theta = 0.01^\circ$, they still look similar to the transverse two-roll solutions obtained in the horizontal case, and they are stable. The bifurcation $P_2$, which leads from no-flow to longitudinal roll solutions for $\theta = 0^\circ$, is suppressed by the inclination (the solution at small $Ra$ is already of this type) and is replaced by an imperfect bifurcation. We have a leading branch which is the continuity of the branch obtained at small $Ra$ and corresponds to $L-$ solutions, and a disconnected branch which corresponds to $L+$ solutions (longitudinal roll with a sense of rotation opposite to the inclination angle) and exists beyond a saddle-node point $N_d$. Some solutions on the leading branch and on the disconnected branch are shown in Fig. 5.10. For the $L-$ solutions on the leading branch, the flow is still very weak at $S_0$ and associated with almost undeformed isotherms and a Nusselt number $Nu$ very close to 1. The flow increases for larger $Ra$ values, and at $S$ the longitudinal roll is already quite intense and associated with clearly deformed isotherms in the $xy$-plane and Nusselt numbers larger than 1. For the $L+$ solutions on the disconnected branch, the flow is very weak on the part of the branch which is close to the diffusive solution found in the horizontal case ($Nu \approx 1$). It is still weak, but increases, at the level of $N_d$ and becomes quite intense on the second part of the branch. As the flow for the $L+$ solutions is opposite to the flow for the $L-$ solutions, the deformation of the isotherms is also inverted and opposite to the inclination. The secondary bifurcations
Figure 5.11: Path of the different bifurcation points (secondary bifurcation points $S$, $S_0$, and $S_d$, saddle-node points $N_d$ and $N \pm$) as a function of $\theta$ ($0^\circ \leq \theta \leq 1^\circ$) for the tilted $1 \times 1 \times 2$ cavity. The abscissa is the inclination angle $\theta$ in degrees, and the ordinate is the critical Rayleigh number $Ra_c$. Solid circles indicate specific bifurcation points: those at $\theta = 0^\circ$, the connection point between $N \pm$ and $S_0$, and the collision point between $S_0$ and $S$. A zoom of the connection between $N \pm$ and $S_0$ is given in inset. The appearance of the two saddle-node points $N \pm$ from $S_0$ occurs at $\theta_s \approx 0.263^\circ$ before the collision between $S_0$ and $S$ at $\theta_c \approx 0.2714^\circ$.

$S_1B_2^+$ and $S_1B_2^-$, which were found in the horizontal case, are still present for $\theta = 0.01^\circ$, but they do not occur at the same critical value of $Ra$ and they will evolve differently when increasing $\theta$. In the inclined case, these secondary bifurcations are denoted as $S$ for the leading branch and $S_d$ for the disconnected branch. They are still pitchfork as they break the $S_A$ symmetry of the $L^+$ and $L^-$ solutions. The leading branch, which was destabilized at $S_0$, is restabilised at $S$, whereas the disconnected branch is stabilized beyond $S_d$. The solutions obtained on the branches bifurcating at $S$ and $S_d$ correspond, as for $\theta = 0^\circ$, to a kind of two-oblique-roll structure with the $S_P$ symmetry. These solutions are all one time unstable. The critical values for the different bifurcation points just mentioned for $\theta = 0^\circ$ and $0.01^\circ$ are given in Table 5.4.

The bifurcation diagram obtained for $\theta = 0.01^\circ$ has clearly shown the four bifurcation
points that are important in our inclined cavity situation, i.e. $S_0$, $N_d$, $S$, and $S_d$. It is then interesting to follow these points (expressed through their critical Rayleigh number) as a function of the inclination angle $\theta$ in order to provide a more complete description of the influence of the tilt on the stability of the system. The paths of these points for $0^\circ \leq \theta \leq 1^\circ$ are shown in Fig. 5.11. The bifurcation points $S_0$ and $S$, which belong to the same leading branch of $L-$ solutions, evolve differently with $\theta$: $Ra_{S_0}$ increases whereas $Ra_S$ decreases. The two points quickly collide and disappear at a critical angle $\theta_c \approx 0.2714^\circ$. Beyond this value of $\theta$, due to the disappearance of its unstable portion between $S_0$ and $S$, the leading branch of $L-$ solutions becomes continuously stable. This change can be observed in Fig. 5.12 where bifurcation diagrams, focused on the leading branch dynamics, are given for $\theta = 0.27^\circ$ and $0.28^\circ$, values below and above the critical angle $\theta_c$. This figure also
shows that, in the same process at $\theta_c \approx 0.2714^\circ$, the two secondary branches originally initiated at $S_0$ and $S$ connect between them, giving origin to two disconnected branches. These disconnected branches, which have the same dynamics, are initiated at saddle-node points denoted as $N+$ and $N−$. The two parts of these branches corresponding to solutions closer to a transverse two-roll structure are stable whereas the two other parts are one time unstable. The saddle-node points $N+$ and $N−$ are in fact not created at $\theta_c$ but a little before, more precisely at $\theta_s \approx 0.263^\circ$ when the bifurcation at $S_0$ becomes slightly subcritical. The subcritical character of the bifurcation at $S_0$ can be seen in Fig. 5.12(a) for $\theta = 0.27^\circ$. The saddle-node points $N+$ and $N−$ correspond to the same critical Rayleigh number and are globally denoted as $N\pm$. Their evolution with $\theta$ is depicted in Fig. 5.11: we see that their critical Rayleigh number $Ra_{N\pm}$ strongly increases with $\theta$. The appearance of these saddle-node points at $\theta_s \approx 0.263^\circ$, just before $\theta_c$, is also shown in the inset of the same figure. We now consider the variation with $\theta$ of the two bifurcation points $N_d$ and $S_d$ belonging to the disconnected branch of $L+$ solutions (Fig. 5.11). Their critical Rayleigh numbers $Ra_{N_d}$ and $Ra_{S_d}$ both increase with $\theta$, but a little more slowly for $Ra_{N_d}$ so that these points will not collide. The variation of $Ra_{S_d}$ is particularly important as it gives the critical value of the Rayleigh number above which the $L+$ solutions are stable and can thus be physically observed. Note finally that the secondary bifurcation points $S$ and $S_d$, which correspond to the same critical Rayleigh number for $\theta = 0^\circ$, have very different evolutions when $\theta$ is increased.

**Effect of a large tilt on the stability of the system**

The variation with $\theta$ of the main bifurcation points, in a larger range of $\theta$ values ($0^\circ \leq \theta \leq 20^\circ$), is depicted in Fig. 5.13. The critical Rayleigh number for the different points $N\pm$, $S_d$, and $N_d$ increases with $\theta$. The strongest increase is found for $N\pm$, a smaller increase is observed for $S_d$, and the weakest increase is found for $N_d$. Again, the evolutions of $N\pm$ and $S_d$ are of particular importance because these points indicate the values of $Ra$ and $\theta$ at which solutions are stabilized. For these different curves, there are limiting values of $\theta$.
corresponding to a very strong increase of the critical Rayleigh number. These values are \( \theta \approx 9.235^\circ, 9.445^\circ, \) and \( 19.56^\circ \) for \( N \pm, S_d, \) and \( N_d, \) respectively. Beyond these limiting angles, it can be expected that the corresponding bifurcation point will disappear. For \( N \pm, \) the limiting value of \( \theta \) is not shown in Fig. 5.13 because the critical Rayleigh numbers reached at this limiting value are about \( Ra_c \approx 540000, \) i.e. far above the \( Ra \) values plotted in the graph. The solutions which are stabilized at \( S_d \) and \( N \pm \) are given as insets in Fig. 5.13. The solution obtained at \( S_d, \) which corresponds to the longitudinal roll \( L^+ \) solution, is shown for \( \theta = 7^\circ. \) At \( N \pm, \) we have two equivalent solutions which are stabilized and look like two-oblique-roll structures. One of them is shown for \( \theta = 4^\circ \) in Fig. 5.13. The other solution can be deduced by applying the \( S_{Az} \) symmetry. They will be denoted as \( O \pm \).
solutions in the following.

**Stable solution diagram for a tilted square duct**

We finally present the domains of existence of the three different stable solutions $L^-$, $L^+$, and $O\pm$ in the $Ra - \theta$ parameter space in Fig. 5.14. Two plots are given, showing different ranges of $\theta$ and $Ra$ values: for $\theta \leq 1^\circ$ where interesting dynamics between the solutions are observable, and for $0^\circ \leq \theta \leq 20^\circ$ where a description for a broader inclination range is shown, from which the results in the whole $\theta$ range ($0^\circ \leq \theta \leq 90^\circ$) can be deduced. From the different domains of existence determined for the $L^-$, $L^+$, and $O\pm$ stable solutions, we can also define zones in the $Ra-\theta$ parameter space where one or several stable solutions are expected to exist. Five different zones can thus be found, which are shown in Fig. 5.14 and labelled with an encircled number.

We first comment on the domains of existence for each stable solution. The leading longitudinal roll $L^-$ solution (domain with grey background, zones 1, 3, 4, 5) exists in the whole $Ra - \theta$ range studied, except in the small area with a white background below $\theta_c \approx 0.2714^\circ$, and for $\theta = 0^\circ$ below $Ra_{S_1B_2} = 3213.62$. This $L^-$ solution indeed also exists for larger values of $\theta$ (up to $\theta = 90^\circ$), and it is in this domain the only existent solution (see the solutions obtained for $Ra = 10000$ and increasing $\theta$ in Figs. 5.15 and 5.16). The opposite longitudinal roll $L^+$ solution (domain with up-left directed oblique lines, zones 4, 5) exists above the line corresponding to the path of the $S_d$ bifurcation point (secondary bifurcation point on the disconnected branch). This line begins at $Ra_{S_1B_2} = 3213.62$ for $\theta = 0^\circ$, increases almost linearly with $\theta$, before a very steep increase for $\theta \approx 9.445^\circ$. This value of $\theta$ seems to be the limit to get such a $L^+$ solution. Finally, the two-oblique-roll $O\pm$ solutions (domain with up-right directed oblique lines, zones 2, 3, 5) exist above the line corresponding to the successive paths of the $S_0$ and $N\pm$ bifurcation points (the first bifurcation point on the leading branch and the saddle-node points which are further generated, respectively). This line begins at $Ra_{P_1} = 2726.53$, follows the curve of $S_0$, and then increases strongly along the path of $N\pm$, so that it intersects the $S_d$ path.
velocity (along $x$) indeed exists up to $\theta = 90^\circ$. A sketch of the different solutions, showing the sign of the $u$ velocity (along $x$) in the mid-$yz$-plane ($x = 0$), is finally given.

Figure 5.14: Domains of existence of the different stable solutions in the $Ra-\theta$ parameter space: the leading longitudinal roll $L_-$ solution (domain with grey background), the opposite longitudinal roll $L_+$ solution (domain with up-left directed oblique lines), the two two-oblique-roll $O\pm$ solutions (domain with up-right directed oblique lines). We can thus define five zones in the $Ra-\theta$ parameter space (labeled with an encircled number) where one or several stable solutions exist. We have one type of solutions in zones 1 and 2, two types in zones 3 and 4 and three types in zone 5. The first plot is a zoom of the second plot for small values of $\theta$. Note that the leading longitudinal roll $L_-$ solution (domain with grey background and zone 1) indeed exists up to $\theta = 90^\circ$. A sketch of the different solutions, showing the sign of the $u$ velocity (along $x$) in the mid-$yz$-plane ($x = 0$), is finally given.
The increase is almost linear for small values of $\theta$, but becomes then steeper. The value $\theta \approx 5^\circ$ reached for $Ra_c = 25000$ (limit of the graph) is not the limit value for the $N \pm$ path. As indicated before, the limit value was obtained at $\theta \approx 9.235^\circ$ and corresponded to $Ra_c \approx 540000$. We do not know if stable $O \pm$ solutions can be obtained up to so large values of $Ra_c$. In any case, as the destabilization of the stable $B_1$ and $B_2$ branches (from which the different $L$, $L+$, and $O$ stable solutions are obtained when $\theta \neq 0^\circ$) only occurs beyond $Ra = 80000$ (see at the end of §2.3), we can expect that the domains of existence of the different solutions will extend far above the limit value $Ra = 25000$ of our plots. We finally describe the five zones in the $Ra-\theta$ parameter space where one or several stable solutions exist. In zones 1 and 2, we only have one type of stable solutions: the $L$ solution in zone 1 (remember that this zone 1 extends up to $\theta = 90^\circ$) and the $O \pm$ solutions in zone 2. In zones 3 and 4, we have two types of stable solutions: the $L$ solution together with the $O \pm$ solutions in zone 3, and the $L$ solution together with the $L+$ solution in zone 4. Finally in zone 5, the three types of stable solutions can be obtained. We see that zones 2 and 3 are very small, whereas the other zones have a far larger extent, particularly zone 1.

All these stable solutions, however, cannot be reached so easily. It is then interesting to give some comments on the possibility or difficulty to reach them. In the horizontal situation, the transverse roll $T$ solution, which is triggered at the first primary bifurcation $P_1$, is naturally obtained from the no-flow solution by increasing $Ra$. This $T$ solution will also be eventually reached by increasing $Ra$ when $\theta$ is non-zero but smaller than $\theta_s \approx 0.2714^\circ$. In contrast, if $\theta$ is larger than $\theta_s$, only the longitudinal roll $L$ solution will be obtained if gradually increasing $Ra$ from $Ra = 0$. This indicates that a good horizontality of the cavity ($\theta < \theta_s$) is required to obtain the expected $T$ solution in the Rayleigh-Bénard situation. If we now proceed by increasing $\theta$ at constant $Ra$, we can first state that for $Ra \leq Ra_{P_1}$ ($Ra \leq 2726.53$), the $L$ solution will be continuously obtained up to $\theta = 90^\circ$. Beyond $Ra_{P_1}$, the transverse roll $T$ solution obtained at $\theta = 0^\circ$ will be maintained, although transformed into an oblique roll $O \pm$ solution, up to the limit $\theta$.
values corresponding to the \(S_0\) and \(N\pm\) curves shown in Figs. 5.11 and 5.13. Beyond these limit \(\theta\) values (which are in the range \(0^\circ \leq \theta \leq 9.235^\circ\)), we can expect that the \(L_–\) solution will still be obtained. In contrast, for decreasing \(\theta\) (from, for example, \(\theta = 90^\circ\)) at constant \(Ra\), the \(L_–\) solution will be always obtained, except for \(2726.53 \leq Ra \leq 3213.62\), in the small domain close to \(\theta = 0^\circ\) corresponding to the zone 2 in Fig. 5.14, where an \(O\pm\) solution can be expected. Finally, the \(L_+\) solution, though it is stable in a certain parameter range, seems difficult to obtain as it is on a disconnected branch. One possibility would be to get an \(L_–\) solution at small \(\theta\) in this stable parameter range and to invert the tilt of the cavity (opposite value of \(\theta\)). We can expect that this solution, which will be an \(L_+\) solution due to the tilt inversion, will proceed and can be maintained for increased \(\theta\) values up to the limit \(\theta\) values corresponding to the \(S_d\) curve shown in Figs. 5.11 and 5.13.

2.5 Discussion and Comparison with the Literature

It is interesting to compare our results to those obtained in some papers dealing with the influence of a tilt on Rayleigh-Bénard convection. This is useful to highlight the new results produced by this work, as well as the advantages of our method. Here, the papers of Cliffe and Winters [47], Adachi [1] and Ozoe et al. [148] are considered.

Comparison with the Work of Cliffe and Winters (1984)

Cliffe and Winters [47] consider the Rayleigh-Bénard convection in a two-dimensional square cavity tilted by an angle \(\theta\) with the horizontal. This two-dimensional cavity can also be seen as a square duct with an infinite extension, to be compared with our three-dimensional finite length square duct. The sidewalls are insulated as in our case. The authors show that the pitchfork bifurcation at which the one-roll solutions are triggered for \(\theta = 0^\circ\) is changed by a cusp catastrophe when \(\theta\) is not zero: the flow then develops smoothly from zero Rayleigh number on a leading branch, and two other solutions appear on a disconnected branch terminating at a saddle-node point, one of these solutions
being stable. The stable solution on the disconnected branch is called anomalous and it corresponds to a one-roll flow with opposite sense of rotation with regard to the stable leading solution. It is exactly what we obtain in our three-dimensional situation at the primary bifurcation point $P_2$ where a longitudinal one-roll solution is triggered at $\theta = 0^\circ$: we see the disappearance of $P_2$ when a tilt is imposed and the presence of a leading branch and a disconnected branch. The difference with the two-dimensional case is that in the three-dimensional situation $P_2$ is not the first primary bifurcation point to appear, so that the branches initiated at $P_2$ for $\theta = 0^\circ$ and those obtained from them when $\theta$ is not zero are all unstable (at least for small $\theta$ and close to $P_2$). Cliffe and Winters [47] also give the path of the saddle-node point in the $Ra_c-\theta$ parameter space and mention the cusp shape close to $\theta = 0^\circ$ and the limiting value for this path at $\theta = 22^\circ$. The cusp shape can be seen in our case in Fig. 5.11 ($N_d$ curve close to $P_2$) and the limiting value is shown in Fig. 5.13 and corresponds to $\theta \approx 19.56^\circ$. The limiting value is about $2^\circ$ smaller in our three-dimensional situation than in the two-dimensional cavity, but both values are roughly about $20^\circ$. The three-dimensional confinement may be responsible for the difference in the limiting angle.

**Comparison with the Work of Adachi (2006)**

Adachi [1] considers the stability of natural convection in an inclined square duct with perfectly conducting sidewalls. His stability analysis considers two-dimensional basic flows in the square cross-section, which could be a conducting solution or a one-roll solution, and the perturbations are three-dimensional. Without inclination, in this square duct with infinite extension, the first transition from the no-flow conducting solution is to a transverse multi-roll solution denoted as $T$-roll solution and occurs at $Ra_c = 2936.4$. The transition to a longitudinal one-roll solution, denoted as $L$-roll solution, occurs later at $Ra_c = 5011.7$. These thresholds can be compared to our thresholds $Ra_{P_1} = 2726.53$ and $Ra_{P_2} = 2818.78$ leading to $T$ and $L$ solutions, respectively. In both cases, the thresholds for the $T$ solutions occur before those for the $L$ solutions. Our values are however smaller.
Two effects influence the thresholds: the three-dimensional confinement must increase the thresholds, but the adiabatic boundaries must decrease them. The second effect seems to overcome the first effect in the situation we have chosen. At $\theta = 0^\circ$, the $L$-roll solution is found by Adachi [1] to be unstable, which is expected because of the previous transition to $T$-rolls, but the further stabilization of this $L$-roll solution is not mentioned. Concerning the $T$-rolls (which are three-dimensional structures), his method is not able to calculate them. Adachi [1] further considers a small inclination, $\theta = 0.01^\circ$. For the $L$-roll solution, he is able to calculate the leading branch, and the disconnected branch, which is initiated at a saddle-node point at $Ra_c = 5042$. The stability analysis of these branches shows that the leading branch is stable up to $Ra_c = 2941.6$, which is the new threshold associated to $T$-roll perturbations for $\theta = 0.01^\circ$, whereas the disconnected branch is unstable. The same type of behavior has been found in our case. He also indicates that the transition at $Ra_c = 2941.6$ must lead to a superposed flow between $L$-roll and $T$-rolls, which corresponds to our oblique roll $O\pm$ solutions. Our three-dimensional calculations in a truncated square duct of dimensionless length 2 have then confirmed the findings of Adachi [1], but for adiabatic sidewalls. Furthermore, our calculations have also extended the results to all the three-dimensional solutions, which were followed by continuation, and in a large range of $\theta$ values. Our results have also put into light new behaviours as the further stabilization of the $L$-roll branch, which lead to very interesting dynamics when the cavity is tilted. The dynamics are particularly rich for small angles of inclination (e.g., $\theta \leq 1^\circ$ at $Pr = 1$). Such slight inclination angles could be of great relevance in real physical situations where the parallelepiped cavity is intended to be horizontal but no specific precautions are taken to increase the accuracy of its horizontality.

**Comparison with the work of Ozoe et al. (1974)**

Ozoe et al. [148] study the heat transfer properties of natural convection in an inclined square channel with insulated sidewalls. They perform two-dimensional simulations in the inclined square cross-section for a channel considered as infinite and obtain one-roll
solutions featuring the longitudinal roll solutions obtained in the three-dimensional channels. They also perform experiments with glycerol in a three-dimensional convection channel with dimensions $15 \text{ mm} \times 15 \text{ mm} \times 270 \text{ mm}$, i.e. with an aspect ratio $A_e = 18$. In these experiments, the inclination $\theta$ is progressively decreased from $90^\circ$ to $0^\circ$. For fixed values of the Rayleigh number, they numerically and experimentally obtain the Nusselt number as a function of the inclination angle $\theta$. The numerical and experimental curves agree quite well for $\theta > 10^\circ$ and indicate a maximum heat transfer for $\theta \approx 50^\circ$. The flow in this $\theta$ range corresponds to a longitudinal roll. For smaller inclinations, transverse rolls or more complex flow structures (which are not precisely described) are obtained experimentally (whereas only longitudinal rolls can be obtained numerically), inducing the presence of a minimum heat transfer at an inclination of about $10^\circ$. It is also indicated that the transverse roll solution is the solution obtained when the cavity is kept almost horizontal, with say less than one degree of inclination. Interesting comparisons with our results can be obtained. The longitudinal roll mentioned by Ozoe et al. [148] for $\theta > 10^\circ$ must be the longitudinal roll $L_-$ solution obtained in our study. From Fig. 5.14, this $L_-$ solution is also in our case the only solution for $\theta > 10^\circ$. The more complex solutions obtained for $\theta < 10^\circ$ could be our $O \pm$ solutions. For small inclination angles, these $O \pm$ solutions look like transverse roll solutions when $Ra$ is sufficiently high (see the flow structures in Fig. 5.12(b) for $\theta = 0.28^\circ$ and $Ra = 3400$) and, for $\theta \leq \theta_c \approx 0.2714^\circ$, these solutions can be reached easily by simply increasing $Ra$ (in contrast, for larger inclinations, they belong to disconnected branches). This observation is in accordance with the fact that Ozoe et al. [148] mention the existence of transverse roll solutions only for $\theta \lesssim 1^\circ$. Concerning the $L_+$ solutions, which, as the $L_-$ solutions, are quite easily recognizable, we can think that Ozoe et al. [148] did not obtain them due to the fact that these solutions are on a disconnected branch and the authors gradually decreased the inclination of the cavity from $\theta = 90^\circ$ step-by-step while fixing $Ra$. Ozoe et al. [148] also did not mention these $L_+$ solutions in their two-dimensional numerical study. In any case, the comparisons cannot be expected to be perfect due to the differences between our approaches.
First our simulations concern a finite-length square duct with \( A_z = 2 \) compared to \( A_z = 18 \) and \( A_z \to \infty \) in the experiment and calculations of Ozoe et al. [148], respectively. Then, our calculations are performed for a Prandtl number \( Pr = 1 \) whereas Ozoe et al. [148] use \( Pr = 10 \) in their two-dimensional calculations and give values of \( Pr \) between 2690 and 2580 for their experiments. Finally, our simulations can determine all the possible stable solutions by continuation whereas Ozoe et al. [148] realize temporal evolutions (either numerically or experimentally) from different initial conditions and the stable solutions obtained are those which exert the strongest attraction in the corresponding phase space.

Nevertheless, in order to complement our comparisons with the work of Ozoe et al. [148], we have calculated the Nusselt number as a function of the inclination angle for the stable \( L^- \), \( L^+ \), and \( O^\pm \) solutions obtained for \( Ra = 10000 \). The results are shown in Fig.
5.15(a) for $0^\circ \leq \theta \leq 90^\circ$. The values of the flow rate $Q$ for the $L-$ and $L+$ solutions are given in Fig. 5.15(b). This dimensionless flow rate has been obtained by integration of the $u$ velocity (along $x$) on one half of the $yz$-plane ($y \leq 0$ or $y \geq 0$). For $Ra = 10000$, the $L-$ solution is stable in the whole range of studied $\theta$ values. The curve obtained in the $Nu$-$\theta$ parameter space for this $L-$ solution is similar to the curves obtained by Ozoe et al. [148]. The Nusselt number is found to be maximum for $\theta \approx 49.55^\circ$, in close agreement with the value $\theta \approx 50^\circ$ given by Ozoe et al. [148]. The Nusselt number values obtained with this $L-$ solution at $Ra = 10000$ are within the range $2.05 \leq Nu \leq 2.4$. Despite the very different Prandtl number, these values are a little smaller but not far from the values obtained by Ozoe et al. [148] (e.g. $2 \leq Nu \leq 2.4$ for $Ra = 8000$ and $2.2 \leq Nu \leq 2.65$ for $Ra = 11000$). For $Ra = 10000$, the $O\pm$ solutions exist and are stable in a small range of $\theta$ values, from $0^\circ$ up to the saddle-node point $N\pm$ at $\theta = 2.5418^\circ$. The Nusselt number for these $O\pm$ solutions increases with $\theta$, and at fixed $\theta$, the values obtained are larger than those for the $L-$ solution. Concerning the $L+$ solution, it exists up to the saddle-node point $N_d$ at $\theta = 16.4577^\circ$, but is stable only up to the secondary bifurcation point $S_d$ at $\theta = 6.697^\circ$ (the unstable solutions are given as dashed lines in Fig. 5.15). The Nusselt number for this $L+$ solution strongly decreases when $\theta$ is increased, and this decrease becomes very steep, almost vertical, at the existence limit of the solution at the saddle-node point $N_d$. For these $L+$ solutions, the decrease of $Nu$ is justified by the fact that the intensity of the roll, which rotates in a sense opposite to the inclination, is decreased when the inclination is increased (see Fig. 5.15(b)). Notice that, as expected, the $L-$ and $L+$ solutions have the same Nusselt number at $\theta = 0^\circ$. We can finally mention that, in our case, we do not obtain a minimum Nusselt number as the one found experimentally by Ozoe et al. [148] for $\theta \approx 10^\circ$. Concerning the flow rate $Q$ shown in Fig. 5.15(b), we see that its variation with $\theta$ for the $L-$ solution has a similar bell shape as the $Nu$ curve, but with a maximum which occurs at a far smaller inclination, at $\theta \approx 29.1^\circ$. The differences which can be observed between the $Nu$ and $Q$ curves indicate that, when $\theta$ is increased, the heat transfer is not directly correlated with the intensity of the flow for
Figure 11: Velocity vector field and isovalues of the temperature in the square cross-section at \( z = 0 \) (mid-xy-plane) for the stable \( L^- \) solutions at \( Ra = 10000 \) and for different values of the inclination \( \theta \). The isotherms are rather horizontal near the boundaries and vertical in the core for \( \theta = 0^\circ \) and rather vertical near the boundaries and horizontal in the core for \( \theta = 90^\circ \). Correspondingly, the flow evolves from a circular roll at \( \theta = 0^\circ \) to a more square-shaped roll at \( \theta = 90^\circ \).

In order to clarify these observations, the flow structures for these stable \( L^- \) solutions at \( Ra = 10000 \) and for different values of the inclination \( \theta \) from \( \theta = 0^\circ \) to \( \theta = 90^\circ \) are depicted in Fig. 5.16. In each case, the velocity vector field and the isovalues of the temperature are plotted in the square cross-section at \( z = 0 \) (mid-xy-plane), which is the main flow plane for these \( L^- \) solutions. As expected, a one-roll flow is found for all these \( L^- \) solutions.

To better analyse these results, we have to remember that the isotherms create a buoyancy effect only when they are not horizontal, the strongest effect being connected to vertical isotherms. We can observe that for \( \theta = 0^\circ \), a situation where the diffusive state corresponds to horizontal isotherms, the isotherms remain almost horizontal along the boundaries (in connection with the no-slip and adiabatic conditions at these boundaries) and are only deformed by the flow in the core of the cavity. The buoyancy effect is then
mainly effective in the core of the cavity and the flow then rather appears as a circular roll. In this situation, the flow can be strong, without too strongly affecting the thermal boundary layers, i.e. the Nusselt number can be moderately affected by the intensity of the flow. In contrast, for $\theta = 90^\circ$, a situation where the diffusive state would correspond to vertical isotherms, the isotherms remain rather vertical along the boundaries and become almost horizontal in the core. The buoyancy effect is then mainly effective along the boundaries and the flow appears as a more square-shaped roll with a quiescent core. In that case, the flow can be reduced by the absence of buoyancy effect in the core, but can nevertheless affect the thermal boundary layers and maintain a relatively strong Nusselt number. This can explain that the Nusselt number remains strong for $\theta = 90^\circ$ while the intensity of the flow rate is reduced, whereas a smaller value of $Nu$ is obtained for $\theta = 0^\circ$ with a much stronger flow rate.

We can finally analyse the changes which occur when $\theta$ is increased from $\theta = 0^\circ$. With the inclination of the cavity ($\theta \neq 0$), the buoyancy effect becomes effective closer to the boundaries (inclination of the isotherms close to the boundaries), which induces an increase of the flow, but this buoyancy effect will be progressively reduced in the core where the isotherms evolve from vertical to horizontal, which will reduce the increase of the flow. According to Fig. 5.15, the increase of the flow rate is effective up to $\theta \approx 29.1^\circ$, and it induces an increase of $Nu$. For larger values of $\theta$, as shown for $\theta \geq 45^\circ$ in Fig. 5.16, the isotherms become horizontal in the core (no buoyancy effect). The flow rate will decrease, but the Nusselt number will continue to increase due to the sustained flow along the boundaries. According to Fig. 5.15, $Nu$ will eventually decrease only beyond $\theta \approx 49.55^\circ$, but this decrease will be less steep than the decrease of the flow rate.
3  
STEADY CONVECTION IN A TILTED CUBICAL CAVITY  
WITH A HORIZONTAL EDGE  

In this section, we first focus on a cubical cavity filled with water. Most of the numerical studies dealing with water assume $Pr = 7.0$, which corresponds to $T_m^* \approx 20^\circ C$. The Prandtl number of water is, however, strongly dependent on temperature, particularly at lower temperature values. We assume $Pr = 5.9$ for water at $T^* \approx 27^\circ C$. This choice is based on the experimental work of Chapter VI. Detailed bifurcation diagrams for water are first calculated for the horizontal case, $\theta = 0^\circ$. The bifurcation diagrams are then calculated for the slightly inclined case, $\theta = 0.1^\circ$. The two sets of bifurcation diagrams (at $\theta = 0^\circ$ and $\theta = 0.1^\circ$) are compared to discuss the influence of a slight tilt on the stability of the flow. Stability diagrams are then calculated to describe the system at larger $\theta$. Finally, the influence of the Prandtl number on the different critical angles $\theta_c$ that limits the existence range of stable solutions is discussed.

3.1 GEOMETRY AND SYMMETRY GROUPS

The geometry consists of an inclined cubical cavity, which has dimensions $l^* \times l^* \times l^*$, four adiabatic sidewalls, and lower and upper (defined with respect to the horizontal case) isothermal walls at $T_{H}^*$ and $T_{C}^*$ ($T_C^* < T_H^*$), respectively. The cavity is inclined about a lower horizontal edge, as shown in Fig. 5.17. Its isothermal walls form an angle $\theta$ with the horizontal plane. The inclination vector is $\Theta = -\theta e_z$, where $e_z$ is the unit vector in the $z$ direction; here, $\theta$ is chosen in the range $0^\circ \leq \theta \leq 90^\circ$. The origin of the coordinate system is placed at the lower vertex of the cavity, with the Cartesian coordinate axes along its edges. Notice that for the cubical enclosure the origin of the coordinate system is different to that chosen in §2 for the truncated square duct (see Fig. 5.1). The $x^*$ axis is perpendicular to the heated walls and the coordinates $(x^*, y^*, z^*)$ are normalized by $l^*$ in order to obtain $(x, y, z)$, as shown in Fig. 5.17(b). This figure also shows the mesh chosen
for these calculations, i.e. $31 \times 31 \times 31$. The accuracy assessment performed for this mesh is presented in Chapter IV §3.2.

There are few symmetries in the case of an inclined cubical enclosure, whereas numerous symmetries are involved when the cubical enclosure is horizontal. The symmetry properties of the solutions for a horizontal cubical enclosure can be found in [170]. In this section, we briefly recall the symmetry properties in both horizontal and inclined situations in order to be able to understand the symmetry breakings that will occur after increasing $Ra$ or $\theta$.

The basic no-flow solution in the horizontal situation, under the approximation of the model, presents different symmetries which belong to the symmetry group $D_{4h} = Z_2 \times D_4$, where $Z_2$ is generated by the reflection about the horizontal yz-mid-plane, $S_P$, and $D_4$ is the dihedral group, which is the symmetry group of a square [23]. The $D_4$ group contains eight elements: the four rotations $R^k$, $k = 0, 1, 2, 3$, where $R$ is a $\pi/2$-rotation around the $x$-axis and $R^0$ is the identity $I$, and the four reflections with respect to vertical planes, the

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Figure 5.17: Geometry of the inclined heated cubical cavity. (a) Dimensional cavity with its edges along the $y^*$ axis tilted with respect to the horizontal plane by an angle $\theta$. The inclination vector is $\Theta = -\theta e_z$. (b) The normalized and spatially discretised cavity. The $yz$-planes at $x = 0$ and $x = 1$ are set at constant dimensionless temperatures $T_H$ and $T_C$, respectively. The remaining sidewalls are set adiabatic.
two \(xz\)- and \(xy\)-mid-planes and the two diagonal planes \(P_{d^+}\) \((z = y)\) and \(P_{d^-}\) \((z = 1 - y)\), which are denoted as \(S_{P_z}\), \(S_{P_x}\), \(S_{P_{d^+}}\) and \(S_{P_{d^-}}\), respectively. (Note that only two reflection symmetries that do not commute, as \(S_{P_z}\) and \(S_{P_{d^+}}\), are enough to generate \(D_4\).) The \(Z_2\) group has two elements, \(S_{P_x}\) and the identity \(I\), which induces that the \(D_4h\) group contains sixteen elements, the symmetries of \(D_4\) and the products of these symmetries with \(S_{P_z}\). As an example, we give the action of the reflection symmetries \(S_{P_z}\) and \(S_{P_{d^+}}\) on the solutions of Eqs. (4.1), from which the other reflection symmetries can be deduced:

\[
\begin{align*}
S_{P_z}: \ (x, y, z) &\rightarrow (x, y, 1 - z), \quad (u, v, w, T) \rightarrow (u, v, -w, T), \\
S_{P_{d^+}}: \ (x, y, z) &\rightarrow (x, z, y), \quad (u, v, w, T) \rightarrow (u, w, v, T).
\end{align*}
\] (5.3)

Among the symmetries obtained by the products of the \(D_4\) symmetries with \(S_{P_z}\), there exist the central symmetry \(S_C\) and the \(\pi\)-rotational symmetries about horizontal axes, namely \(S_{A_y}, S_{A_z}, S_{A_{d^+}}\) and \(S_{A_{d^-}}\) associated with the two middle axes \(A_y\) and \(A_z\) and the two middle diagonal axes \(A_{d^+}\) (perpendicular to \(P_{d^+}\)) and \(A_{d^-}\) (perpendicular to \(P_{d^-}\)), respectively. The type of actions that these axial symmetries have on the solutions are given by:

\[
\begin{align*}
S_{A_y}: \ (x, y, z) &\rightarrow (1 - x, 1 - y, z), \quad (u, v, w, T) \rightarrow (-u, -v, w, -T), \\
S_{A_{d^+}}: \ (x, y, z) &\rightarrow (1 - x, 1 - z, 1 - y), \quad (u, v, w, T) \rightarrow (-u, -w, -v, -T).
\end{align*}
\] (5.4)

Note that there also exists the \(S_{A_x}\) symmetry, which is an element of \(D_4\) \((S_{A_x} = R^2)\).

When the cubical cavity is tilted by \(\Theta\), we can expect the no-flow solution to disappear for \(Ra \neq 0\) [47]. The convection is first introduced by a single transverse roll whose axis of rotation is in the same direction as \(\Theta\). The symmetries that account for this inclined case are the \(S_{P_z}\), \(S_{A_y}\), and \(S_C\) symmetries. These symmetries belong to a \(Z_2 \times Z_2 = D_2\) group, which contains four elements (including the identity \(I\)).

Remember that for any steady solution \(B = (u, T)\) of Eqs. (4.1), its transformation \(SB\) by a symmetry \(S\) of the problem is also a steady solution. The set of all solutions obtained from \(B\) by applying all the symmetries of the problem (symmetry group denoted
V Bifurcation analysis of steady natural convection in tilted rectangular enclosures

as $\Sigma_P$) is called the orbit of the solution $B$. If $SB = B$, it means that $S$ is a symmetry of the solution $B$, otherwise if $SB \neq B$, a new steady solution is generated. If $\Sigma_B$ is the subgroup of $\Sigma_P$ containing the symmetries of the solution $B$ (isotropy subgroup of $B$), the number of different solutions in the orbit of $B$ is given by $|\Sigma_P|/|\Sigma_B|$. 

In this study, the ensemble of all the solutions belonging to the same orbit are said to be equivalent (they behave with the same dynamics and are destabilized at the same critical parameters) and to build what we call a flow pattern. In the horizontal case, up to 16 distinct solutions can exist in a flow pattern, whereas this number is limited to 4 in the inclined case. These maximum numbers occur when the flow patterns have no more symmetries.

In both the horizontal and tilted situations, the basic flow (no-flow diffusive solution and leading transverse roll solution, respectively) has all the symmetries of the problem. When increasing $Ra$, new states with less symmetries will appear, generally at bifurcation points.

3.2 BIFURCATION DIAGRAM FOR A HORIZONTAL CUBICAL CAVITY: $\theta = 0^\circ$

In Chapter IV §3.3 we focused on a single solution belonging to each flow pattern. We then described the solutions of the system by using the average Nusselt number, $Nu$, as a representative amplitude in the ordinate of the bifurcation diagram, because the solutions with the same flow pattern have the same profile $Nu(Ra)$. In contrast, in tilted enclosures, the equivalent branches representing a flow pattern are expected to split. Therefore, a representative amplitude that is capable of distinguishing the different solution branches must be used to represent all the solutions of the system with a single bifurcation diagram. This amplitude can be either the temperature or a component of the velocity vector at a representative grid point within the cavity. The representative point should not be taken on a symmetry plane or axis in order to avoid the overlapping of the solution branches.
Figure 5.18: Bifurcation diagram for water \((Pr = 5.9)\) inside a horizontal cubical cavity in the range \(Ra \leq 8000\). The abscissa indicates \(Ra\) and the ordinate indicates the vertical velocity \(u_1\) at the representative grid point \((x_1, y_1, z_1) \approx (0.9, 0.79, 0.9)\). Four stable solutions \((B_{\pm x} \text{ and } B_{\pm y})\) and four unstable solutions \((B_{\pm (y+z)} \text{ and } B_{\pm (y-z)})\) emerge from \(P_1\). Two unstable solutions \((B_{R4 \pm})\) emerge from \(P_2\). The branches that emerge from \(P_3\) are omitted. The flow at \(Ra = 8000\) is shown in the insets for all the branches. Here and in all subsequent velocity contour insets, positive and negative values of \(u\) on the \(yz\)-midplane \(x = 1/2\) (horizontal plane for \(\theta = 0^\circ\)) are depicted by solid and dashed lines, respectively.

**Transverse solutions near the first instability threshold**

Figure 5.18 shows the bifurcation diagram of a horizontal cubical cavity filled with water in the range \(Ra \leq 8000\). Here, the vertical axis represents the vertical velocity \(u_1\) at the grid point \((x_1, y_1, z_1) \approx (0.9, 0.79, 0.9)\). The insets in this figure, as in §2, indicate the vertical velocity contours in the \(yz\)-midplane at \(x = 1/2\) (horizontal plane for \(\theta = 0^\circ\)), where solid and dashed lines represent positive and negative values of \(u\), respectively. These insets give a clear depiction of the flow structure on each solution branch and, hence, they are very useful to explain the bifurcation diagram.
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Figure 5.19: Convective heat transfer of a fluid ($Pr = 5.9$) within a horizontal cubic cavity for the four stable transverse rolls at $Ra = 8000$. The temperature is contoured over the iso-velocity surface at $V = 13$. Heat is carried by convection from the lower plate to the upper plate according to the direction of each roll; the average Nusselt number is $Nu = 1.8$.

The bifurcation diagram shown in Fig. 5.18 clearly describes all the solutions that arise after the first and second instability thresholds, i.e. $P_1$ and $P_2$, respectively. All the bifurcations that emerge from the no-flow solution (primary bifurcations) are pitchfork bifurcations due to the breaking of the up-down symmetry. There are two types of flow patterns evolving from $P_1$, one stable and another unstable (see branches $B_1$ and $B_2$ in Chapter IV §3.3). Each of these flow patterns contains four equivalent solutions: four stable transverse rolls and four unstable diagonal rolls. Figure 5.19 shows the iso-velocity surfaces $V = 13$ for the stable transverse rolls with the temperature contoured over this surface. These figures indicate how the heat is carried from the lower hot surface to the upper cold surface. Moreover, there are two equivalent four-roll solutions emerging from $P_2$. The solution branches emerging from $P_3$ are omitted because they are not directly related to stable solutions even for larger $Ra$.

As explained before, for the solutions corresponding to a single roll, the branches are denoted by the rotation vector corresponding to this roll. Thus, for the group of stable solutions $B_1$ (see Chapter IV §3.3), we have the branches $B_y$, $B_z$, $B_{−y}$, and $B_{−z}$, representing transverse stable rolls with their respective rotation vector in the same direction as the unit vectors $e_y$, $e_z$, $−e_y$, and $−e_z$. The branches $B_y$ and $B_{−y}$ (also written as $B_{±y}$) have the $S_{P_y}$ and $S_{A_y}$ symmetries, while the branches $B_{±z}$ have the $S_{P_z}$ and $S_{A_z}$ symmetries. For the
group of unstable solutions $B_2$, we have the branches $B_{y+z}$, $B_{y-z}$, $B_{-y+z}$, and $B_{-y-z}$, representing diagonal unstable rolls with the rotation vector in the same direction as $(e_y + e_z)$, $(e_y - e_z)$, $(-e_y + e_z)$, and $(-e_y - e_z)$, respectively; $B_{\pm(y+z)}$ account for the diagonal symmetries $S_{pd}$ and $S_{Ad}$, while $B_{\pm(y-z)}$ account for $S_{pd}$ and $S_{Ad}$. For all these one-roll solutions, the $S_C$ and trivial $I$ symmetries are also valid. In contrast, the two four-roll solutions are named $B_{R4+}$ and $B_{R4-}$; in the subscript, R4 stands for four-roll and the sign accounts for the direction of the vertical velocity $u$ in the midplane $x=1/2$ for $y>1/2$ and $z>1/2$. Each $B_{R4\pm}$ has eight symmetries, in particular both diagonal plane symmetries $S_{pd}$ and both $\pi$-rotational symmetries about horizontal axes, $S_{Ay}$ and $S_{Az}$. Note that the branches that emerge from primary bifurcations are prompted by eigenvectors with the same topological structure.

**FOUR-ROLL SOLUTIONS**

Figure 5.20 focuses on the four-roll solution branch $B_{R4-}$ and its derivative branches emerging from the stabilizing steady bifurcation point $S_1B_{R4-}$. The branch $B_{R4+}$ is omitted since it has a similar evolution with $Ra$. The unstable solutions are calculated because they might have a determining role in the stability of the system after imposing a tilt. This result shows that the stability threshold at $S_1B_{R4-}$ is larger for water [$Ra_c(Pr = 5.9) \approx 9521.3$] than for air [$Ra_c(Pr = 0.71) \approx 8270.4$]. Moreover, in Fig. 5.20, instead of $u_1$ we opted to take the horizontal velocity $w_1$ as amplitude in order to clearly depict these branches (reduce the overlapping). Again, any representative amplitude can be chosen, as long as $Ra$ is taken as abscissa and the various branches and bifurcation points are properly labelled. Note that $B_{R4-}$ is the upper branch in Fig. 5.20, whereas it corresponds to the lower branch in Fig. 5.18.

Eight unstable solutions evolving from the bifurcation point $S_1B_{R4-}$ are shown in Fig. 5.20: four are once unstable (dashed lines) and four are twice unstable (dotted lines). The flows are shown in the insets at the bifurcation point $S_1B_{R4-}$ and at $Ra = 15000$, the limit value of $Ra$ in the bifurcation diagram. The once unstable branches are denoted
as \( \mathbf{V}_y, \mathbf{V}_z, \mathbf{V}_{-y}, \) and \( \mathbf{V}_{-z}, \) corresponding to the transverse roll eigenvectors at \( S_1B_{R4-} \) which have the directions \( e_y, e_z, -e_y, \) and \( -e_z, \) respectively. We can see in the insets that the flow structure on these branches is the four-roll structure obtained at \( S_1B_{R4-} \) modified by the eigenvector, e.g. there is a larger area of positive vertical velocity on the branch \( \mathbf{V}_{-y} \) for \( z < 1/2 \) accounting for the eigenvector in the \(-e_y\) direction. Moreover, the twice unstable branches are denoted as \( \mathbf{V}_{y+z}, \mathbf{V}_{y-z}, \mathbf{V}_{-y+z}, \) and \( \mathbf{V}_{-y-z}, \) accounting for the diagonal eigenvectors that produce the instability at \( S_1B_{R4-} \) and have the directions \( (e_y + e_z), (e_y - e_z), (-e_y + e_z), \) and \( (-e_y - e_z), \) respectively. These unstable solutions only have one symmetry left (apart the identity \( I \)), the \( \pi \)-rotational symmetry with respect to a transverse axis for the once unstable solutions and the symmetry with respect to a vertical diagonal plane for the twice unstable solutions.
Figure 5.21: Bifurcation diagram in a horizontal cubical cavity (Pr = 5.9) for the branches related to stable solutions in the range Ra ≤ 150000. The abscissa and ordinate axes indicate Ra and Nu, respectively. The flow is depicted within the white background insets at various Ra and at Ra = 150000. See Fig. 5.18 for the line type notation within these insets. The eigenfunction at the bifurcations S1B1, S1B11, S1B2, and S1B3 is shown in the gray background insets.

**STABLE SOLUTIONS AT MODERATE Rayleigh numbers: Ra ≤ 150000**

Figure 5.21 shows the bifurcation diagram in a horizontal cubical cavity for Pr = 5.9 at moderate Rayleigh numbers (Ra ≤ 150000). Instead of showing multiple stable and unstable branches in this range, as in Fig. 5.5, only the branches that have a stable part are plotted. In addition to the stable solutions shown in Figs. 5.18 and 5.20, i.e. the transverse-roll B1 and four-roll solutions B3, the diagonal-roll solutions B2 are included. A detailed branching is not necessary for B2 in terms of u1 as a function of Ra because this solution is stabilized once at S1B2 changing from one positive eigenvalue to zero positive eigenvalues and, therefore, a simple pitchfork bifurcation with two symmetry related unstable branches is obtained. In the case of B3, on the other hand, the solution is
Table 5.5: Summary for the range of existence, the stability character, and the symmetry properties of the branches depicted in Fig. 5.21 \((Pr = 5.9)\). \(B_3\) continues to be stable beyond \(Ra = 10^6\).

<table>
<thead>
<tr>
<th>Branch</th>
<th>Range of existence</th>
<th>Range of stability</th>
<th>Number of symmetries, (\Sigma_b)</th>
<th>Generated by</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B_1)</td>
<td>3388.5 –</td>
<td>3388.5 – 54 961.2</td>
<td>4</td>
<td>(S_P + S_A) or (S_P + S_A)</td>
</tr>
<tr>
<td>(B_{11})</td>
<td>54 961.2 –</td>
<td>54 961.2 – 71 445.2</td>
<td>2</td>
<td>(S_P) or (S_P)</td>
</tr>
<tr>
<td>(B_{111})</td>
<td>71 445.2 –</td>
<td>71 445.2 – 99 333.6, 102 968.9 – 312 796</td>
<td>1</td>
<td>(I) (non-symmetric)</td>
</tr>
<tr>
<td>(B_2)</td>
<td>3388.5 –</td>
<td>73 587.7 – 213 233.9</td>
<td>4</td>
<td>(S_{P+} + S_{A+}) or (S_{P-} + S_{A-})</td>
</tr>
<tr>
<td>(B_3)</td>
<td>5900.4 –</td>
<td>9521.3 – ((10^6)) –</td>
<td>8</td>
<td>(S_{P+} + S_{A+})</td>
</tr>
</tbody>
</table>

stabilized twice at \(S_1B_3\), resulting in eight unstable solution branches emerging from this point, as shown in Fig. 5.20. The branches in Fig. 5.21 are then plotted in terms of \(Nu\) as a function of \(Ra\) in order to show in a single diagram the secondary and Hopf bifurcations on the branches that were found to have a stable part in the range \(Ra \leq 150 000\).

The results indicate that the stable transverse solutions (corresponding to four equivalent solutions), which emerge at \(P_1\), are destabilized once at the steady bifurcation points \(S_1B_1\) and the stable emerging branches \(B_{11}\) (corresponding to eight equivalent solutions) are destabilized once at \(S_1B_{11}\). Finally, the resulting stable branches \(B_{111}\) (there are sixteen overlapping branches of this type) become unstable at the Hopf bifurcation \(H_1B_{111}\), but are further stabilized at \(H_2B_{111}\) for a slightly higher \(Ra\). In contrast, the diagonal-roll solutions \(B_2\) (corresponding to four equivalent solutions) and the four-roll solutions \(B_3\) (corresponding to two equivalent solutions), which emerge from \(P_1\) and \(P_2\), respectively, are initially unstable but are later stabilized at \(S_1B_2\) and \(S_1B_3\). The flow structure for each branch is depicted by vertical velocity contours at the horizontal midplane within the white background insets at the four secondary bifurcations and at \(Ra = 150 000\). The gray background insets similarly show the eigenfunction at the secondary bifurcations. The range of existence, the range of stability, and the symmetry properties for these branches are listed in Table 5.5. The stability of \(B_3\) was confirmed until \(Ra = 10^6\).
The effect of the Prandtl number on the stability of the system is evident when comparing the bifurcation diagrams in Figs. 4.10 and 5.21, for $Pr = 0.71$ and $Pr = 5.9$, respectively. In both cases the stable solutions $B_1, B_{11}$, and $B_3$ are present. However, for $Pr = 0.71$ the bifurcation point $S_1B_{11}$ does not exist; the stable branches $B_{11}$ and $B_3$ are destabilized at higher $Ra_c$ without prompting any stable steady solutions; and the diagonal solutions $B_2$ are always unstable. In contrast, for $Pr = 5.9$ the stable solutions $B_{11}$ are destabilized once at $S_1B_{11}$, prompting the stable branch $B_{111}$ that is unstable for a small range of $Ra$ between the Hopf bifurcations $H_1B_{111}$ and $H_2B_{111}$ and for $Ra_c > 312796$; and the diagonal solutions $B_2$ are stable for the range specified in Table 5.5.

3.3 BIFURCATION DIAGRAM FOR A SLIGHTLY TILTED CUBICAL CAVITY: EFFECTS OF THE INCLINATION ANGLE $\theta$

The effects of the inclination vector $\Theta$ on the bifurcations shown in Fig. 5.21 are of particular interest since these bifurcations determine the range of existence of the stable solutions. Special attention is given to the effect of the tilt around the first instability threshold, $P_1$, and on the Hopf bifurcations $H_1B_{111}$ and $H_2B_{111}$ at higher values of $Ra$. In §3.2, we showed in detail the different flow patterns that emerge from $P_1$ and $S_1B_3$. In this section, we calculate the bifurcation diagrams for the slightly inclined cavity at $\theta = 0.1^\circ$, following the three bifurcation diagrams shown in Figs. 5.18, 5.20, and 5.21. In order to distinguish the branches with originally the same flow pattern, the bifurcation diagrams are again presented using a velocity component at a reference point as amplitude.

NEAR THE FIRST INSTABILITY THRESHOLD

Figure 5.22 shows the bifurcation diagram for water ($Pr = 5.9$) inside a cubical cavity slightly tilted by $\theta = 0.1^\circ$ in the range $Ra \leq 8000$. The velocity $u_1$ at the representative grid point $(x_1, y_1, z_1) \approx (0.9, 0.79, 0.9)$ is plotted as a function of $Ra$. The insets depict the velocity contour $u$ on the $yz$-midplane ($x = 1/2$) at the bifurcations (pitchforks and saddle
Figure 5.22: Bifurcation diagram \((Pr = 5.9)\) inside a cubical cavity tilted by \(\theta = 0.1^\circ\) in the range \(Ra \leq 8000\). The vertical velocity \(u_1\) at a representative grid point is plotted as a function of \(Ra\). The number of positive eigenvalues is encircled for each dotted branch. The branches that emerge from \(S_2\) and \(S_3\) are omitted. The contours at the saddle-node bifurcation points \(C_{\pm y-z}\), the bifurcation point \(S_z\), and solutions at \(Ra = 8000\) are shown in the white background insets. The gray background insets indicate the eigenfunction at the bifurcation. The light gray curves are the solutions in the horizontal case shown in Fig. 5.18.

Nodes) and for the branches at \(Ra = 8000\). The flow transition that occurs between the horizontal case and the slightly inclined case around the primary bifurcation \(P_1\) is clarified from this figure. Connections now appear between the unstable diagonal rolls and stable transverse rolls previously obtained in the horizontal case (see Fig. 5.18). The effect of the slight inclination on each group of solutions is described in the following.

(i) **Formation of a leading branch \(B_{-z}\) consisting of a stable transverse roll in the direction of the inclination vector \(\Theta\).** When the cavity is tilted, the trivial solution found in the horizontal case before the first instability threshold \(P_1\) ceases to exist, becoming a weak convective solution of \(B_{-z}\) type which exists as soon as \(Ra \neq 0\). This weak \(B_{-z}\)
solution evolves continuously toward the $B_{-z}$ branch previously obtained for $\theta = 0^\circ$, without the presence of any bifurcation point, i.e. the bifurcation point $P_1$ (obtained for $\theta = 0^\circ$) has disappeared on this branch. Figure 5.23 shows the upper and lateral views of the flow along this branch on the midplanes $x = 1/2$ and $z = 1/2$, respectively. For $Ra < Ra_c(P_1)$ ($Ra_c(P_1)$ is the $Ra_c$ value for the bifurcation point $P_1$ obtained for $\theta = 0^\circ$), the heat transfer due to conduction is dominant, as indicated by the values of $Nu$ close to 1 and the quasi-flat isotherms in this range. In contrast, the amplitude of the rolls becomes stronger for $Ra > Ra_c(P_1)$, resulting in a larger $Nu$. It is important to acknowledge that the rolls in the direction of the inclination, here after called $\theta$–rolls, are obtained when $Ra$ is gradually increased from $Ra \to 0$ while maintaining a constant tilt $\theta \neq 0$. Therefore, this solution is the most likely to be encountered in a real physical situation and, hence, it is of main interest. This result agrees qualitatively with that reported by [47] for convection in a two-dimensional tilted square.

(ii) **Formation of a disconnected branch $B_z$ consisting of stable and unstable rolls in the direction opposite to the inclination vector $\Theta$.** This set of solutions is detached from
(a) $B_z$

<table>
<thead>
<tr>
<th>$Ra$</th>
<th>5000 (sta.)</th>
<th>3742.10 ($S_z$)</th>
<th>3475.93 ($C_z$)</th>
<th>5900.54 ($S_z$)</th>
<th>7456.22 ($S_z$)</th>
<th>8000 (uns.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{</td>
<td>u</td>
<td>}{mx}$</td>
<td>11.0355</td>
<td>5.1068</td>
<td>0.0712</td>
<td>0.0658</td>
</tr>
<tr>
<td>$Nu$</td>
<td>1.40290</td>
<td>1.01001</td>
<td>1.00002</td>
<td>1.00001</td>
<td>1.00001</td>
<td></td>
</tr>
</tbody>
</table>

(b) $B_{\pm y+z}$

$Ra$ | 3800 | 4000 | 5000 | 8000 |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{</td>
<td>u</td>
<td>}{mx}$</td>
<td>5.6513</td>
<td>7.1743</td>
</tr>
</tbody>
</table>

Figure 5.24: Solutions along the branches $B_z$ and $B_{\pm y+z}$ in Fig. 5.22 ($\theta = 0.1^\circ$) at different $Ra$. These solutions have in common the bifurcation point $S_z$. (a) The flow on $B_z$ has a structure that consists of rolls in the opposite direction of the inclination vector $\Theta$, as indicated by the vertical velocity contours at $x = 1/2$. The number of $u$ contours is doubled at $Ra = 8000$ in order to visualize the weak rolls at the corners that appear after $S_z$. The flow is weak in the unstable solutions near the trivial solution at $\theta = 0^\circ$. The lateral view of the flow in a vertical midplane $z = 1/2$ and the corresponding isothermal lines are also shown for the solution on $B_z$. (b) The evolution of the unstable solutions $B_{\pm y+z}$ that arise at $S_z$ is shown by the vertical velocity contours at different $Ra$. 

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the leading stable branch $B_{-z}$ and exists after the saddle-node point $C_z$, souvenir of the bifurcation point $P_1$ obtained for $\theta = 0^\circ$. The solutions around $C_z$ are unstable. The solutions encounter the bifurcation point $S_z$ on the branch with stronger amplitude. This bifurcation stabilizes the rolls opposite to the inclination, here after called $-\theta$–rolls, and generates two branches which are described in the next item. Furthermore, these results indicate that the unstable trivial solutions found in the horizontal case after $P_1$ become weak unstable $-\theta$–rolls. A detailed depiction of the flow is shown in Fig. 5.24(a). Here, the flow is depicted starting from the stable part of the branch at $Ra = 5000$, decreasing $Ra$ to pass through the bifurcation point $S_z$, reaching the saddle-node bifurcation $C_z$, and then increasing $Ra$ passing through the secondary bifurcations $S_2$ and $S_3$ until $Ra = 8000$. Note that the primary bifurcations $P_2$ and $P_3$ have become $S_2$ and $S_3$, respectively. This result agrees qualitatively with those reported by [47] for a two-dimensional square. The non-linear three-dimensional approach produced additional information such as the secondary bifurcation points $S_z$, $S_2$, and $S_3$.

(iii) **Formation of the branches $B_{\pm y+z}$ consisting of semi-diagonal rolls with a component opposite to the inclination vector $\Theta$.** As shown in Fig. 5.22, these branches emerge at $S_z$ and are unstable, as were the original diagonal rolls solutions calculated in the horizontal case. For this group, the initiation point has evolved from $P_1$ ($Ra_c = 3388.52$) in the horizontal case to $S_z$ ($Ra_c = 3742.10$) in the slightly inclined case for $\theta = 0.1^\circ$ (more precisions on that in §3.4). Figure 5.24(b) depicts the flow evolution from the $-\theta$–rolls at $S_z$ to the semi-diagonal $B_{y+z}$ rolls (upper right contours) and the semi-diagonal $B_{-y+z}$ rolls (lower right pictures). The solutions corresponding to the branches $B_{y+z}$ and $B_{-y+z}$ are equivalent solutions related to each other by the $S_P$ symmetry. The transition from $-\theta$–rolls to semi-diagonal rolls with a component opposite to the inclination vector is clearly shown in this figure.

(iv) **Formation of two disconnected branches consisting of semi-diagonal and semi-transverse rolls whose axes of rotation have a component in the direction of the inclination vector $\Theta$.** Figure 5.22 shows these two disconnected branches that emerge at the
saddle-node points $C_{y-z}$. These solutions consist of semi-diagonal rolls ($B_{y-z}$ unstable solutions) and semi-transverse rolls ($B_{y}$ stable solutions) whose axis of rotation has a component in the direction of $\Theta$. These solutions, which emerged from the trivial solution at $P_1$ for $\theta = 0^\circ$, have now merged in pairs to form disconnected branches above $C_{y-z}$. Figure 5.25 depicts the evolution of the flow structure with increasing $Ra$ on these branches. The transition between $B_{y}$ and $B_{y-z}$ is clarified in this figure.

The points mentioned above describe the effects of a slight $\Theta$ on the stability of the system around $P_1$. Two-dimensional methods [1, 47, 48] cannot predict these results. Let us summarize these findings. Firstly, the trivial no-flow solution is replaced by a leading branch consisting of rolls favoured by $\Theta$ commencing at $Ra \to 0$. Secondly, the
branch that is unfavoured by $\Theta$ is disconnected and stabilized at a bifurcation where semi-diagonal unstable rolls emerge with their axes of rotation having a component opposite to $\Theta$. Thirdly, semi-transverse and semi-diagonal rolls, whose axes of rotation have a component in the direction of $\Theta$ and which are stable and unstable, respectively, exist after a saddle node.

**FOUR-ROLL AND DIAGONAL-ROLL SOLUTIONS**

In §3.2 we show that for $\theta = 0^\circ$ there are two types of flow patterns that are unstable just after emerging from a primary bifurcation but are stabilized at secondary bifurcations. These solutions are the two four-roll solutions and the four diagonal-roll solutions, the former being stabilized at $Ra_c \approx 9521$ and the latter at $Ra_c \approx 73588$.

Figure 5.26 shows the bifurcation diagram focused on the four-roll solutions related to the branch $B_{R_4}^-$ when the cavity is tilted by $\theta = 0.1^\circ$. The branches calculated for $\theta = 0^\circ$, which are shown and labelled in Fig. 5.20, are plotted in lightgray to ease the comparison. We can see in this figure that the stable branches in the horizontal and slightly tilted cases are very close together, except for the anomaly around the saddle node $C_{R_4}^{-z}$. The values of $Ra_c$ corresponding to $C_{R_4}^{-z}$ are listed in Table 5.6 for $\theta = 0.01^\circ$ and $0.1^\circ$.

The insets in Fig. 5.26 depict the $u$-velocity contours on the $yz$-midplane at the pitchfork bifurcation point $S_{R_4}^z$, the saddle-node bifurcation points $C_{R_4}^{-z}$, $C_{R_4}^{+y}$, and on the solution branches at $Ra = 15000$. As in previous figures, these insets bring into light the evolution of the solutions along the branches. Note that the minus sign ”$-$” in the subscript R4 $-$ is omitted for the sake of clarity. The reader should bear in mind that there is another four-roll solution (with the subscript R4+) with the same stability properties.

These results show that the stable four-roll solution branches, which in the horizontal case are stabilized at $S_1 B_{R_4}^{\pm}$, are now disconnected when the cavity is slightly tilted. The disconnected stable branch starts from the saddle-node bifurcation point $C_{R_4}^{-z}$. The unstable solutions $V_{-z}$, which are favoured by the inclination, are linked to the stable branch through $C_{R_4}^{-z}$. Special attention must be given to this saddle-node point, since it represents
the lower limit in $Ra$ for the stable four-roll solutions. Moreover, it is interesting to notice that the bifurcation points $S^z_{R4}$ are on what appears to be a "secondary" leading branch that starts from the secondary bifurcation point $S_2$. However, in contrast to the leading branch $B_{-z}$ shown in Fig. 5.22, this "secondary" leading branch is unfavoured by the inclination, as indicated by the flow structure at $S^z_{R4}$. This is because $S_2$ is now on the disconnected branch $B_{-z}$, which consists of weak rolls with the rotation vector in the opposite direction to $\Theta$.

Figure 5.26 also shows that the four-roll solutions $V_{-y}$ and $V_{-y-z}$ are linked by the saddle-node point $C^{-y}_{R4}$, while $V_y$ and $V_{y-z}$ are linked by $C^{y}_{R4}$. Notice that the saddle node

Figure 5.26: Bifurcation diagram of the four-roll solutions inside a cubical cavity ($Pr = 5.9$) inclined by the angle $\theta = 0.1^\circ$ for the range $Ra \leq 15000$. The horizontal velocity $w_1$ at a representative point is plotted as a function of $Ra$. The light gray curves are the solutions calculated in the horizontal case (see Fig. 5.20). The insets show the flow at the saddle-node bifurcation points $C^{-z}_{R4}$, $C^{z+}_{R4}$, the bifurcation point $S^z_{R4}$, and at $Ra = 15000$ for the plotted branches. The relation between the different solutions is indicated. This bifurcation diagram has been obtained for the $B_{R4-}$ branch, but a similar diagram can be plotted for the $B_{R4+}$ branch.
Figure 5.27: Bifurcation diagram for the diagonal-roll solutions \( B_{-y-z} \) around the stabilizing bifurcation \( S_1 B_2 \) when the cubical cavity is horizontal, \( \theta = 0^\circ \), and slightly inclined, \( \theta = 0.1^\circ \). The velocity \( u_1 \) at a representative point is plotted as a function of \( Ra \). The insets show the flow transition between the horizontal and slightly inclined cases.

\( C_{R4}^y \) does not belong to the branch \( B_{R4-} \), even though they appear to be very close on the plot.

Figure 5.27 shows the bifurcation diagram for the diagonal solutions \( B_{-y-z} \) around the bifurcation point \( S_1 B_2 \) for \( \theta = 0^\circ \) and \( 0.1^\circ \). The same as for the four-roll solutions shown in Fig. 5.26, the stabilizing steady bifurcation point is transformed from a pitchfork bifurcation in the horizontal case to a saddle node in the slightly inclined case and the stable solutions (which have now lost their main symmetries and only kept the central symmetry) are on one of the branches emerging at the saddle-node point. Again, the reader should bear in mind that there are four diagonal-roll solutions. Both \( B_{-y-z} \) and \( B_{y-z} \) have a component in the same direction as the inclination vector \( \Theta \) and, therefore, the resulting saddle node in the inclined case can be written as \( C_1 B_2^+ \) (the "+" in the superscript indicates that these diagonal rolls are favoured by the inclination). On the other hand, the diagonal-roll solutions \( B_{-y+z} \) and \( B_{y+z} \) have their rotation vector with a component opposite to \( \Theta \) and, therefore, the saddle-node point at which these stable
BRANCHES COMMENCE CAN BE WRITTEN AS $C_1B_2^-$ (THE "$-" IN THE SUPERSCRIPT INDICATES THAT THESE DIAGONAL ROLLS ARE UNFAVoured). THE VALUES OF $Ra_c$ CORRESPONDING TO $C_1B_2^+$ AND $C_1B_2^-$ ARE LISTED IN TABLE 5.6 FOR $\theta = 0.01^\circ$ AND $0.1^\circ$.

**SYMMETRY BREAKING OF THE TRANSVERSE FLOW PATTERNS FOR $Ra \leq 150000$**

In Fig. 5.22, we showed the effect of a slight inclination on the stability of the system around the first instability threshold $P_1$. However, as shown in Fig. 5.21, there are secondary ($S_1B_1$), tertiary ($S_1B_{11}$), and Hopf ($H_1B_{111}$) bifurcations at higher Rayleigh numbers. The stable solution ranges shown in Table 5.5 are of great importance and, thus,
they need to be calculated at $\theta \neq 0^\circ$.

The continuation procedure is extended to the range $Ra \leq 150000$ for the slightly inclined case. Figure 5.28 shows the calculation results, where the solutions depicted at $Ra = 8000$ in the insets of Fig. 5.22 are used as initial guess in the numerical procedure. Only the disconnected branch that evolves from the saddle-node point $C_1B_{y1}$ was calculated by using the stable solution at $\theta = 0^\circ$ and for large $Ra$ as initial guess. Notice that some branches in Fig. 5.28 are omitted: the semi-diagonal solutions $B_{\pm(y+z)}$ which remain unstable until $Ra = 150000$, the solutions $B_{-y}$ which have the same stability properties than $B_{y}$, and the stable four-roll and diagonal-roll solutions which remain stable for this range of $Ra$. The flow corresponding to each branch is depicted in the white background insets. The eigenfunction responsible for the instability of the resulting branch is shown in the gray background insets.

In Fig. 5.28, the leading branch $B_{-z}$, the disconnected branch $B_{z}$, and the semi-transverse disconnected branch $B_{y}$ are shown with their corresponding derived branches. Note first that the bifurcation at $S_1B_{y1}$ (which lead to asymmetric solutions for $\theta = 0^\circ$) has disappeared because, with the tilt, the stable solution emerging at $S_1B_{y}$ has already lost all symmetries. We then have a stable leading branch, which is the continuity of the branch emerged at $S_1B_{y}$ and a stable disconnected branch above a saddle-node point $C_1B_{y1}$, souvenir of $S_1B_{y1}$ obtained for $\theta = 0^\circ$. It is also interesting to notice that the secondary bifurcation points ($S_1B_{-z}$, $S_1B_{z}$, and $S_1B_{\pm y}$) and the tertiary bifurcation points ($S_1B_{-z1}$, $S_1B_{z1}$, and $C_1B_{\pm y1}$) that were originally at $S_1B_{1}$ and $S_1B_{11}$, respectively (see Fig. 5.21), have now shifted in the $Ra$ domain. The same occurs for the Hopf bifurcation points. In Table 5.6 the shift of the critical Rayleigh numbers $Ra_c$ corresponding to the bifurcations related to the stable solutions is listed. The shift is generally positive, but can also be negative, particularly for the bifurcation points related to the $B_{z}$ branch.

Notice that, in order to ease the comparison between Figs. 5.21 and 5.28, the notation of the bifurcation points for the tilted case (Fig. 5.28) is based on their position relevant to the horizontal case (Fig. 5.21). In fact, the Hopf bifurcation $H_1B_{\pm y1}$ for $\theta \neq 0$ is
Table 5.6: Shift of the critical Rayleigh number $Ra_c$ of the bifurcation points related to the stable solutions ($Pr = 5.9$) from the horizontal case ($\theta = 0^\circ$) to the slightly titled case ($\theta = 0.01^\circ$ and $0.1^\circ$). See Figs. 5.21 and 5.28 to identify the bifurcation points in the horizontal and tilted cases, respectively.

<table>
<thead>
<tr>
<th>From</th>
<th>Transition</th>
<th>$Ra_c$, $\theta = 0^\circ$</th>
<th>$0.01^\circ$</th>
<th>$0.1^\circ$</th>
</tr>
</thead>
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<tr>
<td></td>
<td>$P_1 \rightarrow S_z$</td>
<td>3388.53</td>
<td>3459.27</td>
<td>3742.10</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow C_{\pm y - z}$</td>
<td>3552.89</td>
<td>4309.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S_1B_1 \rightarrow S_1B_{-2}$</td>
<td>54961.2</td>
<td>55013.8</td>
<td>55490.7</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow S_1B_c$</td>
<td>54908.8</td>
<td>54441.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\rightarrow S_1B_{\pm y}$</td>
<td>54961.8</td>
<td>55020.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S_1B_2 \rightarrow C_1B_2^+$</td>
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<td>76408.7</td>
<td>88179.2</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow C_1B_2^-$</td>
<td>76454.8</td>
<td>88675.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S_1B_3 \rightarrow C_1B_{\pm y}$</td>
<td>9521.28</td>
<td>9594.98</td>
<td>9873.46</td>
</tr>
<tr>
<td></td>
<td>$S_1B_{11} \rightarrow S_1B_{-z1}$</td>
<td>71445.2</td>
<td>71609.7</td>
<td>73127.7</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow S_1B_{z1}$</td>
<td>71281.6</td>
<td>69844.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\rightarrow C_1B_{\pm y1}$</td>
<td>72974.7</td>
<td>78855.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$H_1B_{11} \rightarrow H_1B_{-z11}$</td>
<td>99333.6</td>
<td>99580.4</td>
<td>101794</td>
</tr>
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<td></td>
<td>$\rightarrow H_1B_{z11}$</td>
<td>99086.8</td>
<td>96866.6</td>
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<tr>
<td></td>
<td>$\rightarrow H_1B_{\pm y11}$</td>
<td>98898.2</td>
<td>96065.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$H_2B_{11} \rightarrow H_2B_{-z11}$</td>
<td>102969</td>
<td>103203</td>
<td>105441</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow H_2B_{z11}$</td>
<td>102738</td>
<td>100776</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\rightarrow H_2B_{\pm y11}$</td>
<td>103159</td>
<td>103864</td>
<td></td>
</tr>
</tbody>
</table>

no longer on a tertiary branch (but on a secondary branch) since the pitchfork bifurcation $S_1B_{11}$ is transformed into a saddle node $C_1B_{\pm y1}$ on a disconnected branch due to the slight inclination. Moreover, the effect of the slight tilt is more prominent at higher $Ra$. For example, the stable range after the stabilizing Hopf bifurcations $H_2B_{\pm y11}$ and $H_2B_{z11}$ (before $C_1B_{\pm y11}$ and $C_1B_{z11}$, respectively) has been largely reduced. Furthermore, the unstable part of the branches $B_{\pm y}$ after the pitchfork bifurcations $S_1B_{\pm y}$ is now quite deformed, with two turning points before its stabilization at the pitchfork bifurcation $S_2B_{\pm y}$.

At this point, even though the bifurcation diagrams at $\theta = 0^\circ$ and $0.1^\circ$ have been determined, the transition between these two states is still unclear. Moreover, we need to
calculate the critical Rayleigh number of these bifurcation points at steeper inclinations in order to clarify the different stable regimes for $\theta > 0^\circ$.

### 3.4 Evolution of the Stable Solution Ranges as a Function of $\theta$

In this section, we first discuss the trajectory of the bifurcation points (pitchfork, saddle-node, and Hopf) in the $Ra - \theta$ parameter space for slight and larger inclinations. Then, stability diagrams are presented in order to clearly describe the different stable regimes.

**For slight inclinations**

Figure 5.29 shows the effect of slight inclinations on the bifurcation diagram. The deformation of the leading branch $B_z$ and the disconnected branch $B_{-z}$ is shown in Fig. 5.29(a) as $\theta$ is increased. The results indicate that the stable solutions on the leading branch become predominant at steeper $\theta$, as stable strengthening flows can be obtained from $Ra = 0$. In Fig. 5.29(a), the saddle-node bifurcation $C_z$ and the stabilizing bifurcation $S_z$ are tracked for angle increments of $\Delta \theta = 0.5^\circ$, $0.1^\circ$, $0.01^\circ$, and $0.001^\circ$. It is clear that not only the saddle-node point $C_z$, but also the stabilizing bifurcation $S_z$, emerge from the primary bifurcation $P_1$ initially found at $\theta = 0^\circ$. Figure 5.29(b) shows the trajectory of the saddle-node bifurcations $C_z$, $C_{\pm y - z}$ and the pitchfork bifurcation $S_z$. $C_{\pm y - z}$ reach $Ra = 5000$ at $\theta \approx 0.19^\circ$, indicating that these bifurcations are strongly dependent on the tilt. $S_z$ and $C_z$ reach $Ra = 5000$ at $\theta \approx 0.64^\circ$ and $5.08^\circ$, respectively. Even though $C_z$ has a relatively weak dependence with $\theta$, this saddle-node bifurcation is surrounded only by unstable solutions and, therefore, is of less importance than $S_z$ and $C_{\pm y - z}$, which determine the limit of existence of the stable solutions.

The bifurcation diagrams prove to be very useful when describing the stability of the system at a fixed $\theta$, as can be seen in Fig. 5.28. When considering an inclination range, however, bifurcation diagrams are not so useful since the branches overlap resulting in
overcrowded figures. One possibility is to describe the stability of the system by tracking the bifurcation points as a function of $Ra$ and $\theta$, and then plot these trajectories in the $Ra-\theta$ parameter space. Figure 5.30(a) shows the locus of the three bifurcations that emerge from $P_1$ as a function of $Ra$ and $\theta$. This figure is the projection of the values shown in Fig. 5.29 onto the $Ra-\theta$ plane. The cusp over this narrow range of angles is evident for $C_z$, $S_z$, and $C_{\pm y-z}$. The result for $C_z$ has a qualitative agreement with that reported by [47]. However, the cusp for $S_z$ and $C_{\pm y-z}$ was not reported because these points were not obtained in their two-dimensional calculations.

Figure 5.30 shows the locus of the bifurcation points as a function of $Ra$ and $\theta$ in the range $\theta \leq 0.1^\circ$ around the (a) primary $P_1$, (b) secondary $S_1 B_1$, (c) tertiary $S_1 B_{11}$ and secondary $S_1 B_2$, and (d) Hopf $H_1 B_{111}$ and $H_2 B_{111}$ bifurcation points. The evolution of
Figure 5.30: Trajectory of the critical Rayleigh numbers $Ra_c$ in the range $\theta \leq 0.1^\circ$ for the stable branches emerging at $P_1$ for $\theta = 0^\circ$. $S$, $C$, and $H$ stand for secondary pitchfork, saddle-node, and Hopf bifurcations, respectively. The locus of these bifurcations is plotted as a function of $Ra_c$ and $\theta$ around (a) $P_1$, (b) $S_1B_1$, (c) $S_1B_{11}$, $S_1B_2$, and (d) $H_1B_{111}$, $H_2B_{111}$. The dotted, dashed, and solid lines represent the bifurcation points related to zero, one, and two stable flow patterns, respectively. The black lines are those bifurcations related to the $-\theta$-rolls (disconnected branch starting at the saddle-node $C_z$); the dark-gray lines are those bifurcations related to the $\theta$-rolls (leading branch); the light-gray lines are those bifurcations related to semi-transverse and semi-diagonal rolls whose axis of rotation have a component in the direction of $\Theta$. In (c), the bifurcations emerging from $S_1B_2$ are plotted with different gray scale to distinguish the similar but different trajectories of $C_1B_2^+$ and $C_1B_2^-$. 
these points in the range $0^\circ \leq \theta \leq 0.1^\circ$ is now clear (the limiting values are listed in Table 5.6). In addition to the cusp of $C_{\pm y-z}$, the subsequent bifurcations $S_1B_{\pm y}$ and $C_1B_{\pm y1}$ also exhibit a cusp, with $dRa/d\theta \to 0$ at $\theta \to 0^\circ$ for the former and $dRa/d\theta \to \infty$ at $\theta \to 0^\circ$ for the latter. In contrast the trajectory of the bifurcations related to the $\theta$-rolls and $-\theta$-rolls are smooth lines, except for the cusps at $P_1$.

Since there are four stable transverse solutions emerging from $P_1$ in the horizontal case (see Fig. 5.18), then four trajectories should evolve from each secondary bifurcation related to these branches when the cavity is slightly tilted. Nevertheless, one edge of the cavity is kept horizontal and, hence, the solutions related to $C_{\pm y-z}$ belong to the same flow pattern, i.e. their locus overlap in the $Ra-\theta$ domain. Three trajectories are then obtained evolving from each secondary bifurcation at $\theta = 0^\circ$, as shown in Fig. 5.30. Furthermore, as mentioned in §3.3, there are four unstable diagonal-roll solutions, which form two pairs that are similarly influenced by the inclination, i.e. $B_{\pm y-z}$ which are favoured by $\Theta$ and $B_{\pm y+z}$ which are opposed to $\Theta$. Therefore, two loci evolve from $S_1B_2$, as shown in Fig. 5.30(c). In the case of the four-roll solutions, two branches with the same flow pattern evolve from $P_2$ in the horizontal case. These solutions are similarly influenced by the inclination and, therefore, the loci of $C_{R_{\pm y0}^{-z}}$ overlap (see Fig. 5.31).

**FOR LARGER INCLINATIONS**

The locus of the bifurcation points determined in Fig. 5.28 is calculated as a function of $Ra$ and for increasing $\theta$ until the calculation stops when even a very small increase of $\theta$, $\Delta \theta$, cannot afford convergence (this generally occurs when $dRa/d\theta \to \infty$). Figure 5.31 shows the calculation results in the range $Ra \leq 110000$ and $\theta < 7^\circ$. These results are of great importance because they show the ranges for the different stable regimes. The loci are plotted using three line styles (solid, dashed, and dotted) with different gray scales (black, gray, and light-gray). The solid lines indicate the transition from one stable flow pattern to another through a pitchfork bifurcation $S$; the dashed lines indicate the transition between an unstable flow pattern and a stable flow pattern, or vice-versa, through
Figure 5.31: Stability diagram in the $Ra - \theta$ domain for the bifurcation points found in Fig. 5.28. The $Ra_c$ corresponding to the saddle-node $C$, secondary $S$, and Hopf $H$ bifurcations is plotted as a function of $\theta$ for $Pr = 5.9$ in the range $Ra \leq 110000$. The solid lines indicate the $S$ bifurcations connected to two stable flow patterns at a slightly higher and lower $Ra$. The dashed lines indicate the $S$, $C$, and $H$ bifurcations connected to one stable flow pattern. The dotted lines indicate the bifurcations that are not related to any stable solution. The open circles indicate the angles where a group of solutions ceases to exist, i.e. $\theta_{zcri} \approx 4.68^\circ$ and $\theta_{\pm ycri} \approx 2.27^\circ$. Refer to Fig. 5.30 for the notations corresponding to the gray scales of the lines.
pitchfork \( S \) or saddle node \( C \) bifurcations; the dotted lines indicate the transition between two unstable flow patterns. In Fig. 5.31, only the locus of \( C_z \) is unrelated to stable solutions. The dashed lines belonging to the Hopf bifurcations represent a transition between a stable steady state and a periodic solution. Furthermore, all saddle-node bifurcations in this plot are supercritical and, therefore, for an increasing \( Ra \) at constant \( \theta \) there is one stable solution above the locus of \( C \) in Fig. 5.31 (except for \( C_z \)). Concerning the gray scales in Figs. 5.30 and 5.31, the gray lines are related to the solutions consisting of \( \theta \)-rolls; black lines are related to the solutions consisting of \(-\theta\)-rolls; light-gray lines represent the locus of the bifurcations related to the stable solutions evolving from \( C_{\pm y-z} \). Light-gray lines are also used for \( C_{R4}^{\pm z} \) related to the four-roll solution.

**Solutions which are favoured by the inclination.** As the pure \( \theta \)-rolls are stable for \( 0 \leq Ra \leq Ra_c(S_1B_{-z}) \), the less-symmetric bifurcated \( \theta \)-rolls for \( Ra_c(S_1B_{-z}) \leq Ra \leq Ra_c(S_1B_{-z1}) \), and the non-symmetric \( \theta \)-rolls for \( Ra \geq Ra_c(S_1B_{-z1}) \) (except between the lines related to \( H_1B_{-z11} \) and \( H_2B_{-z11} \)), the increase of \( Ra_c \) with \( \theta \) for \( S_1B_{-z} \) and \( S_1B_{-z1} \) (solid lines, dark-gray trajectories) indicates that the leading branch of \( \theta \)-rolls is favoured by the inclination. This result is rather expected following the limiting case of a cavity heated from the sides (\( \theta = 90^\circ \)) where only one stable solution corresponding to \( \theta \)-rolls exists at a given \( Ra \) before the oscillatory state. For \( Pr = 5.9 \), the secondary bifurcation point \( S_1B_{-z} \) reaches \( dRa/d\theta \rightarrow \infty \) at \( \theta_{Bcri} \approx 24.461^\circ \) and \( Ra > 3 \times 10^6 \). Therefore, the transition between the more complex Rayleigh-Bénard convection and the simpler heated-from-the-sides configuration could be defined at this critical angle. The influence of \( Pr \) on \( \theta_{Bcri} \) is discussed in §3.5. Our main interest here is to describe the dynamics of the system before \( \theta_{Bcri} \), specially for the different disconnected branches.

**Solutions which are unfavoured by the inclination.** Concerning the solutions opposite to the inclination \((-\theta\)-rolls, black lines), the stable solution region between \( S_z \) and \( H_1B_{z11} \) decreases with increasing tilt until disappearing at a critical angle \( \theta_{zcri} \approx 4.68^\circ \) at \( Ra \approx 37698 \), as revealed by the stability diagram of Fig. 5.31. The stable solutions above
$H_2B_{c11}$ are expected to disappear at $\theta_c \approx 0.8^\circ$. This means that the stable $-\theta$–rolls are not only unfavoured by $\theta$, as shown in Fig. 5.31, but are also ultimately annihilated at this inclination threshold $\theta_{cri}$. It is interesting to find that the locus of the bifurcation points $S_z$, $S_1B_z$, $S_1B_z$, and $H_1B_{c11}$ simultaneously converge at the critical angle $\theta_{cri}$. The unstable $-\theta$–rolls, in contrast, disappear at a larger inclination, when the saddle-node bifurcation $C_z$ reaches $dRa_c/d\theta \to \infty$ at $\theta \approx 17.46^\circ$.

**Solutions originally perpendicular to the inclination.** Concerning the stable solutions that emerge from the solutions consisting of $\pm y$-rolls (shown in light-gray in Fig. 5.31), the locus of the saddle-node bifurcation point $C_{\pm y-\pm z}$, the pitchfork bifurcation $S_1B_{\pm y}$, and the Hopf bifurcation $H_1B_{\pm y11}$, have the steepest increase $dRa_c/d\theta$ at the critical angle $\theta_{\pm ycri} \approx 2.27^\circ$ around $Ra_c \approx 84300$. The collision of these trajectories suggest that there is no stable solution beyond this inclination. On the other hand, the saddle-node $C_1B_{\pm y1}$, which limits a disconnected branch, increases with $\theta$, disappearing at the critical angle $\theta_{cri} \approx 2.01^\circ$ for $Ra > 250504$ (outside the range of Fig. 5.31).

**Four-roll and diagonal-roll solutions.** Finally, concerning the four-roll and diagonal-roll solutions that emerge from $S_1B_3$ and $S_1B_2$, respectively, the loci of $C_{R4\pm}^{-z}$ and $C_{B2}^{z}$ are also plotted in Fig. 5.31. For the four-roll solutions, the trajectories of $C_{R4\pm}^{-z}$ and $C_{R4-}^{-z}$ coincide, becoming very steep ($dRa_c/d\theta \rightarrow \infty$) at $\theta_{R4cri} \approx 11.18^\circ$. For $C_{B2}^{z}$ and $C_{B2}^{-z}$, on the other hand, the trajectories are slightly different (see Fig. 5.30(c)) becoming very steep at $\theta_{D1}^{z} \approx 2.16^\circ$ ($Ra_c > 326565$) and $\theta_{D1}^{-z} \approx 1.68^\circ$ ($Ra_c > 252717$), respectively. Again, the rolls which are unfavoured by the inclination disappear more quickly than the rolls favoured by it.

After determining a critical angle, we can verify the stability of the system by calculating the bifurcation diagram at an inclination just before and after this critical angle. For example, the critical angle corresponding to the $-\theta$–rolls is $\theta_{cri} \approx 4.68^\circ$, so we can choose to calculate the bifurcation diagrams at $\theta = 4.5^\circ$ and $5^\circ$. These diagrams depict the stability of the system just before and after the presumed disappearance of the stable
Figure 5.32: Bifurcation diagram of a fluid $(Pr = 5.9)$ inside a tilted cubical cavity at $\theta = 4.5^\circ$ for $Ra \leq 55000$. The vertical velocity $u_2$ at a representative point inside the cavity $(x_2, y_2, z_2) = (0.9, 0.652, 0.652)$ is plotted as a function of the Rayleigh number $Ra$. The flow at different points is indicated by the white background insets.

$-\theta$-rolls.

Figure 5.32 shows the bifurcation diagram at $\theta = 4.5^\circ$ in the range $Ra \leq 55000$. At this inclination, it is found that (i) the leading branch is predominant for this $Ra$ range, (ii) there is a significant shift for $C_{R4 \pm}$ to a higher $Ra$ (visible for $R4-$ in this figure), and most importantly (iii) the range of existence of the $-\theta$-roll solutions is significantly reduced in comparison to the case of $\theta = 0.1^\circ$. Figure 5.33(a) shows a close-up of the stable $-\theta$-roll solution branches. Notice that the ordinate of the bifurcation diagram in Figs. 5.32 and 5.33(a) is taken as the velocity $u$ at the reference grid point $(x_2, y_2, z_2) = (0.9, 0.652, 0.652)$, whereas, in Fig. 5.33(b) the grid point $(x_1, y_1, z_1)$ is used as in previous bifurcation diagrams to ease the comparison. Again, the reference point can arbitrarily be selected for the sake of convenience. In order to compare the evolution of the bifurcation
3 Steady convection in a tilted cubical cavity with a horizontal edge

Figure 5.33: Bifurcation diagram of a fluid ($Pr = 5.9$) inside a tilted cubical cavity at $\theta = 4.5^\circ$ for the stable range of the $B_z$ solutions. (a) The vertical velocity $u_2$ at a representative point inside the cavity ($x_2, y_2, z_2$) = (0.9, 0.652, 0.652) is plotted as a function of the Rayleigh number $Ra$. (b) The vertical velocity $u_1$ at ($x_1, y_1, z_1$) = (0.9, 0.79, 0.9) is taken in the ordinate axis to compare with the results shown in Fig. 5.28. The flow at different points is indicated by the white background insets. The gray background insets indicate the eigenfunction at the bifurcations $S_z$ and $S_1B_z$. Notice that solid gray lines are used to distinguish the branches that evolve from $S_1B_z^\pm$ in both diagrams.

points with the inclination, Figs. 5.28 ($\theta = 0.1^\circ$) and 5.33(b) ($\theta = 4.5^\circ$) were plotted using the same parameter in the ordinate. These results show that the stabilizing pitchfork bifurcation $S_z$ shifts towards a higher $Ra$, while the destabilizing Hopf bifurcations shifts towards a lower $Ra$. All the solution branches that emerge from the pitchfork bifurcations at $S_1B_z$ and $S_1B_z^\pm$ are shown in Fig. 5.33 (only one was plotted in 5.28). These bifurcations are expected to simultaneously collide at $\theta_{crr} \approx 4.68^\circ$ for $Pr = 5.9$. Finally, the solutions that emerge from the saddle-node point $C_{y-z}$ have already disappeared at $\theta_{ycr} \approx 2.27^\circ$ and, therefore, they no longer exist in the bifurcation diagram shown in Fig. 5.32.

In Fig. 5.32, two interesting interconnections between the branches are observed. In the first interconnection, the stable branches that emerge from $S_1B_z$ are destabilized once at $S_1B_z^+\pm$ and $S_1B_z^-$, then these unstable branches develop passing through a turning point (saddle node), and finally arrive at $S_3$ forming a closed loop. In the second interconnection, the unstable branches consisting of semi-diagonal rolls that emerge from $S_z$ are
Figure 5.34: Bifurcation diagram of a fluid \((Pr = 5.9)\) inside a tilted cubical cavity at \(\theta = 5.0^\circ\) for \(Ra \leq 50000\). The stable solutions in the \(B_z\) branch completely disappear after the bifurcation points \(S_1B_z\) and \(S_z\) have crossed each other at \(\theta_{c_{RI}} \approx 4.68^\circ\). The only stable solutions remaining after the critical angle are those in the branches \(B_{-z}\) and \(B_{R4\pm}^{-}\).

destabilized once more, and the emerging unstable branches are connected to the destabilized branches after the Hopf bifurcations \(H_1B_{z11}^+, H_1B_{z11}^{++}, H_1B_{z11}^{+-}\), and \(H_1B_{z11}^{--}\), which in turn develop from \(S_1B_{z1}^+\) and \(S_1B_{z1}^{-}\), forming another closed loop. The Hopf bifurcations delimit the stable \(-\theta\)–roll solutions, these are depicted in the insets of Fig. 5.33(a).

Figure 5.34 shows the bifurcation diagram at \(\theta = 5^\circ\). From this figure, it is clear that the secondary bifurcation points \(S_z\) and \(S_1B_z\) on the disconnected branch \(B_z\) have crossed each other, resulting in the disappearance of the stable \(-\theta\)–roll solutions. The crossing of \(S_z\) and \(S_1B_z\) has occurred at the critical inclination angle \(\theta_{c_{RI}} \approx 4.68^\circ\). At \(\theta = 5^\circ\), there are three types of stable solutions: (i) those belonging to the leading branch \((B_{-z}\) branch, \(\theta\)–rolls), (ii) two symmetrical four-roll stable solutions (only one of the solutions is plotted in the figure), and (iii) four diagonal-roll solutions beyond \(C_1B_{2}^{-}\) (these are
above the range of $Ra$ shown in the bifurcation diagram of Fig. 5.34). Furthermore, the collision of $S_z$ and $S_1B_z$ results in the disappearance of $S_1B^+_z$ and $S_1B^-_z$ (see Figs. 5.32 and 5.33). The results also indicate that the unstable branches that emerge from $S_1B_z$ are still directly connected to the secondary bifurcation point $S_3$, forming a closed loop.

Another interesting collision that is worth investigating in more depth is the one that occurs at $\theta_{\pm ycri} \approx 2.27^\circ$ for the bifurcation points belonging to the original $\pm y$-roll solutions. Figure 5.35 shows the bifurcation diagram at $\theta = 2.2^\circ$, focusing on the solution branch $B_y$ and its derivative branches just before the collision at $\theta_{\pm ycri}$ of the saddle-node point $C_{y-z}$, the bifurcation point $S_1B_y$, and the Hopf bifurcation points $H_1B_{y11}^\pm$. It is interesting to see that the bifurcation diagram consists of two closed loops, each with a stable and unstable part. Also, from the comparison with Fig. 5.22 we see that the position of the solutions emerging from $C_{y-z}$ has changed, the stable $B_y$ solution being now on the upper branch. The insets of Fig. 5.35, as those of Fig. 5.33(a), show that near the collision at a critical angle the flow structure on the different stable branches is almost identical.
Stable solution diagram

In the first part of §3.4, the locus of the bifurcations shown in Fig. 5.28 was discussed. For that, the stability diagram presented in Fig. 5.31 has shown the trajectories of the bifurcations that evolve from $P_1, S_1B_2, S_1B_3$, and from the interesting bifurcation points on all the derived branches, providing a thorough description of the stability of the system in the $Ra - \theta$ parameter space. In the stability diagram, we can find the $Ra - \theta$ regions where diverse stable solutions exist. However, numerous trajectories make it difficult to identify the various stable regimes. In order to make a clearer description of the stability of the system, we filter the results shown in Fig. 5.31 and propose the stable solution diagram. In this diagram, we only plot the locus of the bifurcation points where stable solutions emerge for a certain solution group. We then identify the different stable regimes with their corresponding flow patterns and label them. Figure 5.36(a) shows the stable solution diagram for the $\pm \theta$-rolls, i.e. those rolls on $B_{\pm z}$. Figure 5.36(b) shows the stable solution diagram for the solutions whose rolls initially have their axes of rotation perpendicular to $\Theta$, i.e. those rolls on $B_{\pm y}$. The stable solution diagram for the diagonal-roll and four-roll solutions can easily be deduced from Fig. 5.31, above the $C_{1B_2}^\pm$ lines and the $C_{R4}^{\pm z}$ line, respectively.

Solutions on the branches $B_{\pm z}$ or their derivatives. In Fig. 5.36(a), the black lines and gray lines indicate the loci for the bifurcation points related to $B_z$ and $B_{-z}$, respectively. Different stable regimes can be identified between these lines. These lines also intersect and determine zones, which correspond to one or more stable regimes and are labelled. For each zone, the corresponding flows are sketched in the tables within Fig. 5.36(a). These patterns are a sketch of the velocity $u$ on the $yz$-midplane at $x = 1/2$, as in the insets previously used, with the gray and white regions representing positive and negative values of $u$, respectively. Notice that these sketches only show one representative of the flow pattern solution. The number of stable solutions corresponding to each flow pattern is indicated within the sketch.
Figure 5.36: Stable solution diagram ($Pr = 5.9$). The stable solutions are given in the $Ra - \theta$ domain for $Ra \leq 110000$. (a) The group of solutions $B_{\pmz}$ consisting of stable $\pm \theta$-rolls, and (b) the group of solutions $B_{\pmy}$ consisting of stable $\pm y$-rolls. The flow patterns found in (a) and (b) are shown in the adjacent table as the sketch of the velocity $u$ on a $yz$-midplane, with the gray and white regions representing positive and negative $u$, respectively. For each flow pattern, the number of equivalent stable solutions is indicated by the number inside the flow pattern.
Zone 1 in Fig. 5.36(a) corresponds to the $\theta$–rolls before the secondary bifurcation $S_1 B_{-z}$, whose locus evolves as $dRa_c/d\theta \to \infty$ at $\theta_{Bcri} \approx 24.461^\circ$. This means that the solutions in Zone 1 are the only stable solutions that exist after tilting the cavity by $\theta > \theta_{Bcri}$. As a consequence, Zone 1 also corresponds to the stable steady solutions found in the limiting case of $\theta = 90^\circ$, i.e. the heated-from-the-sides configuration. These $\theta$–rolls can coexist with stable flow patterns coming from the $-\theta$–rolls in Zones 4, 5 and 6. These patterns, however, only exist for angles $\theta < \theta_{zcri}$ and are on disconnected branches. They can then be naturally avoided if following the path: Zone 1 $\rightarrow$ Zone 2 $\rightarrow$ Zone 3 $\rightarrow$ Zone 10 (above the locus of $H_1 B_{z11}$), which leads successively to the different flow patterns coming from the $\theta$–rolls. Zone 10 exists for the very small inclination range, $\theta < 0.0776^\circ$, and corresponds to the zone where there are no steady solutions. Zone 9 is the zone with the larger number of stable solutions (eight stable solutions), if considering all solutions for each flow pattern. This zone is fragmented due to the oscillatory region between $H_1 B_{111}$ and $H_2 B_{111}$. Zones 4, 7, and 9 have two, four, and eight stable solutions, respectively.

**Solutions on the branches $B_{\pm y}$ or their derivatives.** The stable solution diagram shown in Fig. 5.36(b) accounts for the disconnected branches related to the semi-transverse rolls $B_{\pm y}$. It is interesting to notice that the locus of the saddle node evolving from $S_1 B_{11}$, i.e. $C_1 B_{\pm y1}$, has a positive slope throughout its evolution. Furthermore, the slight inclination has eliminated the Hopf bifurcations $H_1 B_{111}$ and $H_2 B_{111}$ for this disconnected branch starting from $C_1 B_{\pm y1}$ (see Fig. 5.28). In contrast the loci of the solutions evolving from $P_1$, $S_1 B_1$, and $H_1 B_{111}$ converge at $\theta_{\pm ycri} \approx 2.27^\circ$. The upper Zone A corresponds to the solutions stabilized at the bifurcation point $S_2 B_{\pm y}$. Zone E corresponds to the zone where the stable solutions for this group do not exist. Moreover, Zone C has the largest number of stable solutions for this group (eight stable solutions), if we consider all stable solutions for each flow pattern.

Notice that the trajectory of the bifurcation point evolving from $H_2 B_{111}$ is inconclu-
sive, so that Zone C is not clearly defined. The reason is that the calculations for this Hopf bifurcation point suddenly stopped to converge at some inclination angle. This could suggest that there has been a collision with another bifurcation point.

3.5 Effect of the Prandtl Number: \( \theta_{cri} - Pr \)

In §3.3 and §3.4, we conducted a thorough instability analysis of steady natural convection inside a tilted cubical cavity filled with water. Detailed bifurcation diagrams and stability diagrams are presented for \( Pr = 5.9 \). Nevertheless, a comparison between the bifurcation diagrams calculated for the horizontal case in the validation section for \( Pr = 0.71 \) (see Fig. 4.10) and in the result section for \( Pr = 5.9 \) (see Fig. 5.21), indicates that \( Ra_c \) corresponding to secondary bifurcations strongly depends on the Prandtl number (note that the primary bifurcations are independent of \( Pr \)). Puigjaner et al. [168, 169] also showed the difference between the stability properties obtained for air and silicone oil, i.e. \( Pr = 0.71 \) and \( Pr = 130 \), respectively, in a horizontal cubical enclosure heated from below. Therefore, the locus of the bifurcation points (see Fig. 5.31) is also expected to vary with \( Pr \) and, hence, the transition between the bifurcation points at different \( Pr \) needs to be clarified. The best way to describe the effect of the Prandtl number on the stability of this system is to determine the critical angles \( \theta_c \) as a function of \( Pr \).

Let us first consider the locus of the first saddle-node point \( C_z \) for different Prandtl numbers in the range \( 0.71 \leq Pr \leq 130 \). This saddle node is of particular interest because, even though it is not directly related to stable solutions, the \(-\theta\)-rolls (stable and unstable) only exist beyond its critical Rayleigh number. Figure 5.37(a) shows the results for the locus of \( C_z \) calculated with different values of \( Pr \). These results show that for fluids with higher values of \( Pr \) the \(-\theta\)-rolls disappear at lower critical angles \( \theta_c \). Moreover, for \( Pr = 14.2 \) and \( Pr = 130 \) the critical angle seems to be almost the same, suggesting an asymptotic variation of \( \theta_c \) at large \( Pr \). In Fig. 5.37(b), the critical angle is plotted against the inverse of the Prandtl number. It is found that the critical angle at which the unstable \(-\theta\)-rolls disappear is inversely proportional to the Prandtl number in the form
Figure 5.37: Effect of the Prandtl number on the locus of the saddle-node point $C_z$. (a) The trajectories for five different values of $Pr$ in the range $0.71 \leq Pr \leq 130$. (b) The critical angle $\theta_c$ for $C_z$ is inversely proportional to $Pr$. The fit of the curve is shown in the figure.

$\theta_c = 0.82Pr^{-1} + 17.332$.

As mentioned in §3.4, there are two interesting angles for the stable solutions, i.e. $\theta_{zcri}$ and $\theta_{\pm ycri}$. Let us now consider the influence of $Pr$ on these angles.

**Prandtl dependence of the critical angles $\theta_{\pm ycri}$.** Figure 5.38(a) shows the locus of the saddle-node bifurcation point $C_{\pm y-z}$ (whose limit corresponds to $\theta_{\pm ycri}$) for ten different values of $Pr$. This saddle node is related to the stable semi-diagonal rolls emerging from the primary bifurcation $P_1$ at $\theta = 0^\circ$. Notice that the critical angle $\theta_{\pm ycri}$ is larger for the case where the Prandtl number is small, and it seems to reach a constant value when the Prandtl number is sufficiently large. Again, this suggests that there is an asymptotic variation between the critical angle and $Pr$. Figure 5.38(b) shows $\theta_{\pm ycri}$ as a function of $Pr^{-1}$. A fit of the numerical results, which were conducted for eleven values of $Pr$, yields the function $\theta_{\pm ycri} = 1.153Pr^{-2} + 0.843Pr^{-1} + 2.085$. It is interesting to notice that for the limiting case where $Pr \to \infty$, the critical angle becomes $\theta_{\pm ycri} \approx 2.085^\circ$. 

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Figure 5.38: Effect of the Prandtl number on the locus of the saddle-node points $C_{\pm y-z}$. (a) The trajectories for ten different values of $Pr$ in the range $0.71 \leq Pr \leq 130$. (b) The relation between the critical angle $\theta_{\pm y_{cri}}$ and $Pr$. The fit of the curve is shown in the figure.

$$\theta_{z_{cri}} = 1.153 Pr^{-2} + 0.843 Pr^{-1} + 2.085$$

Figure 5.39: Effect of the Prandtl number on the critical angle $\theta_{z_{cri}}$. This point is calculated by following the intersection between the loci of $S_z$ and $S_1B_z$. The solid black lines shows the calculation results; the gray dashed line shows the fit. The equation of this fit is shown.

$$\theta_{z_{cri}} = 3.55 Pr^{-5} - 14.9 Pr^{-4} + 20.8 Pr^{-3} - 7.86 Pr^{-2} + 3.28 Pr^{-1} + 4.2562$$
Prandtl dependence of the critical angle $\theta_{\text{cri}}$. Since the interesting critical angle $\theta_{\text{cri}}$ does not occur when $dRa_c/d\theta \to \infty$, but rather when the secondary bifurcations collide (see Fig. 5.31), we need to find the intersection of two loci corresponding to secondary bifurcations. Following the intersection between the trajectories of $S_z$ and $S_1B_z$ seems the best choice because we know that for $Pr = 0.71$ there is no secondary bifurcation $S_1B_z$ (see Fig. 4.10). The results for this interesting critical angle are shown in Fig. 5.39. This time, the curve has been fitted to the fifth power of $Pr^{-1}$. The resulting fit is shown in the figure. The critical angle $\theta_{\text{cri}}$ decreases with increasing $Pr$, and in the interesting limiting case where $Pr \to \infty$, the critical angle becomes $\theta_{\text{cri}} \approx 4.256^\circ$.

3.6 HEAT TRANSFER CHARACTERISTICS: $Nu - \theta$

After describing the dynamics of the system for a wide range of inclination angles $\theta$ and Prandtl numbers $Pr$, it is interesting to investigate the dependence of the average Nusselt number $Nu$ with $\theta$, as in the case analysed for the truncated duct (see Fig. 5.15). The relation $Nu - \theta$ might have interesting industrial applications, since we can optimize the $Nu$ by a simple inclination of the cavity without increasing the temperature difference $\Delta T$, which would require more energy resulting in an increase of heat loss.

Figure 5.40 shows $Nu$ as a function of $\theta$ for a cubical cavity at $Ra = 8000$ ($Pr = 5.9$). The transverse rolls favoured by the inclination exist throughout the whole inclination range, as discussed in §3.4. This result has the same trend as in the case of the truncated duct shown in Fig. 5.15, where the longitudinal rolls exist for $\theta \leq 90^\circ$ with a maximum Nusselt number $Nu_{\text{max}}$ at $\theta \approx 49.55^\circ$. $Nu_{\text{max}}$ for the cubical case at $Pr = 5.9$ and $Ra = 8000$ is at the inclination $\theta \approx 48.1^\circ$. If we increase the Rayleigh number until $Ra = 50000$, we find that $Nu_{\text{max}}$ has shifted to $\theta \approx 60.6^\circ$. These calculations suggest a relation between $Nu_{\text{max}}$ and $Ra$.

Ozoe et al. [146] conducted a numerical study to determine the relation between $Nu_{\text{max}}$ and $Ra$ for different aspect ratios in a two-dimensional rectangular enclosure. However, their two-dimensional calculations do not take into account the additional shear force
Figure 5.40: Average Nusselt number $Nu$ as a function of the tilt $\theta$ in a cubical cavity at a constant Rayleigh number. (a) $Nu$ as a function of $\theta$ at $Ra = 8000$ for the three solutions that evolve from the primary bifurcation (see Fig. 5.18). $Nu$ is maximum at $\theta \approx 48.1^\circ$. The stable four-roll solutions are omitted. (b) The velocity profile and isotherms at the mid-vertical plane $x = 1/2$ for the $B_{-z}$ solutions.
exerted by the sidewalls. This effect is prominent for cavities with small aspect ratios, such as the cubical cavity considered in this section. Moreover, they conclude that "the computed value of \( Nu \) showed general agreement with the experimental results [148] except at small angles of inclination for which a different mode of circulation prevails". This lack of agreement between the experimental and numerical works at small angles is due to their two-dimensional numerical approach which cannot determine other stable solutions than the rolls favoured by the inclination.

In contrast, the continuation method proposed in Chapter IV can be used to determine the relation between \( Nu \) and \( \theta \) for the various stable solutions. In a real situation where the boundary conditions are nearly ideal, the flow would eventually reach either of the stable solutions. This was observed in [148], where formation of oblique roll cells are more likely to occur for small inclinations. A random initial flow state would also influence the development of these supercritical convection patterns. A stochastic bifurcation analysis of Rayleigh–Bénard convection was performed by Venturi \textit{et al.} [207]. They investigated the effectiveness of a stochastic approach to simulate the onset of convective instability and the influence of random initial flow states on the development of supercritical convection patterns within two-dimensional square enclosures.

\section{Steady convection in a tilted cubical cavity without any horizontal edge}

As mentioned in §2.5, the advantages of the current numerical method is the detection of multiple stable three-dimensional solutions. We discussed in detail the stability of natural convection inside a truncated square duct tilted around its longest axis (see §2), as well as for a cubical cavity tilted around a lower edge(see §3). In both cases, one axis of the cavity was kept horizontal. Nevertheless, a tilt in another direction, or in two directions might occur. Remember that one of the motivations of this study is to clarify the effect that a small tilt involuntarily imposed to the system might have on the stable solutions. This tilt
Figure 5.41: Dimensionless geometry of the cubical cavity tilted by the angles $\theta$ and $\alpha$. The respective inclination vectors are $\Theta$ and $\Omega$. Here, $\alpha$ plays for the $z$ axis the same role that $\theta$ plays for the $y$ axis. For $\alpha = 0^\circ$ we obtain the cavity shown in Fig. 5.17.

should not be limited to one direction, but must concern two directions and involve two inclination angles. The three-dimensional continuation method developed in Chapter IV allows us to investigate in more depth this situation.

Figure 5.41 shows a dimensionless cubical cavity tilted in two directions by the angles $\theta$ and $\alpha$. The boundary conditions are the same as in §3. Here, $\theta$ is defined as the angle between the $y$ axis and the horizontal plane, i.e. the same as in Figs. 4.1, 5.1, and 5.17. $\alpha$ is defined as the angle between the $z$ axis and the horizontal plane. Therefore, $\alpha$ plays for the $z$ axis the same role that $\theta$ plays for the $y$ axis. In this way, we have a cavity equally tilted from both directions when $\theta = \alpha$, i.e. the vector $(1, 1, 1)$ rises along a fixed vertical plane. When $\theta = \alpha = 45^\circ$, the $x$ axis is on the horizontal plane and the isothermal walls of the cubical cavity are in the vertical position (the cavity is heated from the sides). Notice that the inclination vector $\Theta$ ($\Omega$) is on the horizontal plane in the direction of $-z$ ($y$) when $\alpha = 0^\circ$ ($\theta = 0^\circ$).

The governing equations for a fluid in such a cavity are slightly different from Eqs. (4.1). Here, we need to introduce the vertical gravity vector in the conservation equation
of momentum as follows

\[
\frac{\partial u}{\partial t} + (u \cdot \nabla) u = -\nabla p + Pr \nabla^2 u + Pr Ra T \left[ \cos(\theta) \sqrt{1 - \frac{\sin^2(\alpha)}{\cos^2(\theta)}} e_x + \sin(\theta) e_y + \sin(\alpha) e_z \right]. \tag{5.5}
\]

So when \( \alpha = 0^\circ \) we obtain Eq. (4.1b) for the single inclination vector \( \Theta = -\theta e_z \). The equations of continuity and energy conservation are the same as Eqs. (4.1a) and (4.1c), respectively. The solution of these governing equations follows the same procedure as the one explained in Chapter V.

In this section, the effect of this double tilt on secondary bifurcations is not investigated. Our interest here is to clarify the effect that a double tilt has on the stability of the flows that emerge from the primary bifurcation \( P_1 \), as what was shown in Fig. 5.18 for a single tilt.

Figure 5.42 shows the bifurcation diagram for water (\( Pr = 5.9 \)) in a cubical cavity slightly tilted by \( \theta = \alpha = 0.1^\circ \). This diagram is plotted for the range \( Ra \leq 8000 \), as in Figs. 5.18 and 5.22. The red solid line indicates the leading branch for the case where \( \theta = 0.1^\circ \) and \( \alpha = 0^\circ \), i.e. the case shown in Fig. 5.22. This branch corresponds to \(-z\)-rolls, or \( \theta \)-rolls. The orange solid line indicates the leading branch for the case where \( \theta = 0^\circ \) but \( \alpha = 0.1^\circ \), and the leading branch corresponds now to \( y \)-rolls, or \( \alpha \)-rolls. These two situations (red and orange solid lines) follow the same logic and the whole diagram can even be deduced from one case to the other by some permutation of the axes. The black lines are those branches obtained for \( \theta = \alpha = 0.1^\circ \). Notice that the results for \( \theta = \alpha = 0^\circ \) are shown in light gray to ease the comparison between the horizontal and tilted cases.

Figure 5.42 shows that we obtain a completely different flow near \( P_1 \). We can also see that, as for \( \theta = 0.1^\circ \) and \( \alpha = 0^\circ \), the influence of a slight tilt is more prominent near the
first instability threshold than at higher $Ra$. These results show that the leading branch when $\theta = \alpha = 0.1^\circ$ is the branch $B_{y-z}$ corresponding to the diagonal-roll solutions which are favoured by the inclination. This diagonal solution is destabilised once at the pitchfork bifurcation $S_{y-z}$, resulting in two stable branches that, as $Ra$ increases, become closer to the branches $B_y$ and $B_{-z}$ found in the horizontal case.

It is interesting to notice from these results that there are three disconnected branches. We can think of the branch that has the saddle node $C_{-y+z}$ in Fig. 5.42 as an analogue to the disconnected branch that has the saddle node $C_z$ in Fig. 5.22. This means, that when

![Bifurcation diagram for water ($Pr = 5.9$) in a cubical cavity slightly tilted by $\theta = \alpha = 0.1^\circ$. The abscissa indicates $Ra$ and the ordinate indicates the vertical velocity $u_1$ at the representative grid point $(x_1, y_1, z_1) \approx (0.9, 0.79, 0.9)$. The diagram is plotted for $Ra \leq 8000$, focusing on the solutions around the first primary instability threshold $P_1$ found at $\theta = \alpha = 0^\circ$. The red and orange solid lines indicate the leading branches for $(\theta, \alpha) = (0.1, 0)^\circ$ and $(\theta, \alpha) = (0, 0.1)^\circ$, respectively. The light gray lines in the background are those obtained for $\theta = \alpha = 0^\circ$, shown more clearly in Fig. 5.18. These are included to ease the comparison.](image-url)
there is a slight tilt, we will obtain a leading branch consisting of rolls (transverse, diagonal, or mixed) that are favoured by the inclination, and a disconnected branch consisting of opposite rolls that are unfavoured by the inclination. We can also see from these results that the thresholds for the secondary bifurcation points $S_2$ and $S_3$ do not vary significantly with a slight tilt (but the very weak flow structure at these points does change with the type of tilt considered).

Finally, we see that there are two other disconnected branches after the saddle-node bifurcations points $C_{y+z}$ and $C_{-y-z}$. It is interesting to notice that each of these disconnected branches has an unstable part that corresponds to a semi-diagonal roll, i.e. $B_{-y-z}$ for $C_{-y-z}$ and $B_{y+z}$ for $C_{y+z}$. These semi-diagonal rolls have their axes of rotation perpendicular to the axis of rotation of the rolls belonging to the leading branch. This follows the same logic as in the case $\theta = 0.1^\circ$ and $\alpha = 0^\circ$ (Fig. 5.22), where there are two disconnected branches with the stable and unstable solutions evolving from a saddle node and with their stable part consisting of rolls whose axis of rotation is perpendicular to the axis of rotation of the rolls belonging to the leading branch.

The results presented in this section illustrate the importance of a bifurcation analysis to state the stability of the solutions for cavities slightly tilted in two directions. This is of relevance in a three dimensional situation where the cavity is intended to be horizontal but small defects result in slight tilts. The results presented here also show that the influence of slight inclination angles ($\theta$ and/or $\alpha$) is mainly relevant near the first primary instability threshold $P_1$ found in the horizontal case. By using the code developed in Chapter IV, we can deepen our calculations when $\theta \neq 0^\circ$ and $\alpha \neq 0^\circ$, as in §3. However, in a real physical situation it is quite uncommon to tilt a cavity in both directions for large inclination angles. These results would then rather be interesting for scientific reasons than for practical applications. Therefore, this section was limited to slight inclinations of $\theta$ and $\alpha$ around the first instability threshold.
5 CONCLUDING REMARKS

In this chapter, the continuation method developed from a three-dimensional spectral finite element code described in Chapter IV has been applied to study steady natural convection in a tilted truncated square duct and a tilted cubical cavity. In §1, a brief literature review on the problem has been given. In §2, the stability of the solutions in a truncated duct with a square cross-section and an aspect ratio \( A_z = \text{length}/\text{height} = 2 \) is studied. The finite-length square duct is tilted around its longest axis. In §3, a thorough bifurcation analysis of steady natural convection in a tilted cubical cavity is conducted. The solutions are studied from their initiation at low Rayleigh numbers \( Ra \) to their transition to periodic states, for the range of the Prandtl number \( 0.71 \leq Pr \leq 130 \). In §4, the analysis is extended to a cubical cavity slightly tilted in two directions, i.e. without horizontal edges.

The conclusions for this chapter are listed in the following, first for the truncated square duct (§2) and then for the cubical cavity (§3 and §4).

The conclusions for the bifurcation analysis of steady natural convection in the truncated duct filled with a fluid of \( Pr = 1 \) are the following:

1. A precise bifurcation diagram has been obtained for the horizontal case (\( \theta = 0^\circ \)) featuring all the different branches issued from the first ten primary bifurcations and at subsequent secondary bifurcations.

2. For \( \theta = 0^\circ \), the branches of interest are those initiated at the first two primary bifurcations \( P_1 \) and \( P_2 \) because of the existence of stable solutions on these two branches. The first branch initiated at \( P_1 \) corresponds to transverse rolls with axis perpendicular to the axis of the duct (\( T \) solution) and is stable right from its onset at \( Ra_{P_1} = 2726.53 \). The second branch initiated at \( P_2 \) corresponds to a longitudinal roll with its axis parallel to the axis of the duct (\( L \) solution) and is stabilized at a secondary bifurcation point \( S_1B_2 \) (\( Ra_{P_2} = 2818.78, Ra_{S_1B_2} = 3213.62 \)).

3. For \( \theta = 0^\circ \), the branches and sub-branches initiated beyond \( P_2 \) were found unstable.
in the whole $Ra$ range studied. The flow structure for these branches is clarified.

4. The differences between the stability of the solutions found in a truncated square duct and those found in a cubical cavity [168, 169] are clarified.

5. The calculations were extended from the Rayleigh-Bénard situation ($\theta = 0^\circ$) to the case where a tilt is imposed to the finite-length duct around its longest axis. This tilt can be a slight defect of the experimental device or can be imposed on purpose.

6. For $\theta \neq 0^\circ$, the stable no-flow diffusive solution is replaced by a stable $L-$ solution.

7. For $\theta \ll 1^\circ$, the transition that occurred at $P_1$ for $\theta = 0^\circ$ is maintained, so that there is a destabilisation of the $L-$ solution (now at a secondary bifurcation called $S_0$) leading to stable perturbed $T$ solutions denoted as $O\pm$ solutions, which will become clear oblique roll solutions for larger values of $\theta$.

8. For $\theta \ll 1^\circ$, the bifurcation at $P_2$, which leads to $L$ solutions for $\theta = 0^\circ$, is replaced by an imperfect bifurcation. Here, the leading branch of $L-$ solutions continuously evolves for increasing $Ra$, with an increasing intensity of the flow, whereas there is a disconnected branch of $L+$ solutions (with opposite sense of rotation), which appears above a saddle-node point $N_d$.

9. In the tilted case, the leading branch of $L-$ solutions and the disconnected branch of $L+$ solutions are eventually stabilized at secondary bifurcation points $S$ and $S_d$, respectively, souvenirs of the secondary bifurcation points $S_1B_2$ found in the horizontal case.

10. When $\theta$ is increased up to $\theta_c \approx 0.2714^\circ$, the $S_0$ and $S$ points on the leading branch will collide and disappear, so that, for larger $\theta$ (up to $\theta = 90^\circ$), the $L-$ solutions on the leading branch become continuously stable in the studied $Ra$ domain. Another consequence of this collision is that the stable branches of $O\pm$ solutions now belong to disconnected branches above saddle-node points $N\pm$. 

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11. In the tilted case, three types of stable solutions have then been found: the leading longitudinal roll $L^-$ solutions, the longitudinal roll $L^+$ solutions, and the oblique roll $O\pm$ solutions. The domains of existence of these different stable solutions were determined in the $Ra-\theta$ parameter space.

12. Interesting comparisons with previous studies dealing with convection in inclined ducts have been obtained. These previous studies involved two-dimensional calculations [47], three-dimensional stability studies [1], and experimental measurements [146]. The results presented in §2 confirm and complement the results obtained in these previous studies. This good agreement suggests that our results are also valid for longer square ducts.

The conclusions for the bifurcation analysis of steady natural convection in the cubical cavity are the following:

13. For $\theta \neq 0^\circ$ ($\alpha = 0^\circ$), the pitchfork bifurcation at $P_1$ (where four stable and four unstable solutions simultaneously emerge for $\theta = 0^\circ$) is broken, resulting in a leading branch, three disconnected branches, and a secondary branch. The leading branch consists of stable rolls in the direction of the inclination. One disconnected branch consists of rolls opposite to the inclination; this branch is stabilized at a pitchfork bifurcation that is related to the secondary branch consisting of unstable diagonal solutions. These unstable diagonal solutions have a component of their rotation vector opposite to the inclination vector. The other two disconnected branches that emerge from $P_1$ are symmetric to one another and consist of unstable semi-diagonal and stable semi-transverse rolls favoured by the inclination.

14. These results indicate that the two groups of stable and unstable solutions, which were seemingly unrelated at $\theta = 0^\circ$, are now connected when a slight tilt is imposed.

15. There is a shift in the $Ra$ domain of the secondary bifurcations when the cavity is slightly tilted, e.g. $\theta = 0.1^\circ$. The position of these points determine the ranges
of existence in the $Ra – \theta$ parameter space for the different solutions. The groups of solutions that have a component of their rotation vector perpendicular to the inclination vector have other disconnected branches at higher $Ra$.

16. A thorough stability diagram in the $Ra – \theta$ domain was presented for $Pr = 5.9$. This diagram is constructed from the loci of the bifurcation points related to stable solutions. The stability diagram provides a comprehensive description of the stable regimes as a function of $Ra$ and $\theta$. It was found that the loci of the secondary bifurcations related to the leading branch evolve towards higher $Ra$ and $\theta$, whereas the loci of the solutions related to the disconnected branches converge at critical angles.

17. The stable semi-transverse rolls whose rotation axis has a main component perpendicular to the inclination vector disappear after tilting the cavity beyond a critical angle $\theta_{ycri}$. As an exception, four other disconnected branches that evolve from a tertiary bifurcation disappear at a smaller critical angle.

18. The stable transverse-roll solutions with a component of the rotation axis opposite to the inclination vector disappear at the critical angle $\theta_{zcri}$. Interestingly, the secondary, tertiary, and Hopf bifurcations simultaneously converge at the same $\theta_{zcri}$ and $Ra_c$.

19. Stable solutions diagrams are proposed as a tool to clearly describe the various stable regimes in the $Ra – \theta$ domain. In this diagram, zones that account for different flows patterns are depicted.

20. The effect of the Prandtl number on the stability of the convective flow inside the tilted cubical cavity was determined. The interesting critical angles $\theta_{ycri}$ and $\theta_{zcri}$ were determined as a function of the Prandtl number. The angles for the limiting case where $Pr \to \infty$ were determined.
21. The relation between the average Nusselt number $Nu$ and the inclination $\theta$ was clarified. The results were qualitatively compared with the numerical and experimental results of Ozoe et al. [146, 148]. These results indicate that there is a maximum $Nu$ at $\theta \approx 48.1^\circ$ for $Ra = 8000$ and $Pr = 5.9$.

22. A bifurcation analysis near the first instability threshold $P_1$ (found in the horizontal case) was conducted for a cubical cavity tilted in two directions by $\theta = \alpha = 0.1^\circ$. The results indicate that there is a leading branch that consists of rolls (transverse, diagonal, or mixed) which are favoured by the inclination, a disconnected branch that consists of opposite rolls which are unfavoured by the inclination, and two disconnected branches with a stable and unstable part after a saddle-node point. These two disconnected branches consists of rolls whose axis of rotation is originally perpendicular to the axis of rotation of the rolls belonging to the leading branch. A last branch can appear as a secondary branch in cases where symmetries of the flows are involved (e.g. $\theta \neq 0^\circ$ and $\alpha = 0^\circ$, or $\theta = \alpha$) or as a disconnected branch in more general cases.

This bifurcation analysis study is the first of its kind to fully address, from the primary instability threshold to the oscillatory state, the influence of a tilt on the stability of three-dimensional convective flows inside rectangular enclosures.

Some of the results presented in this chapter were published in [197].
VI

**Measurement of Convection in Rectangular Parallelepiped Cavities**
OVERVIEW

In Chapter II, a high-resolution phase-shifting interferometer was developed and validated for the measurement of Fickian and Soret coefficients. Molecular dynamics theory can only predict mass diffusion coefficients in limit cases [196]. Therefore, experimental studies of mass diffusion are essential to understand mass transport in mixtures. In contrast, for the case of natural convection, the flow can be numerically studied to a better approximation by solving the Navier-Stokes equations. The conditions considered in this study are not complex, i.e. steady laminar flow with constant thermophysical properties, but multiple stable solutions are known to exist. In Chapter IV, a three-dimensional continuation method to study such flows was developed. The results obtained with our continuation study usually give an array of possible steady solutions, as illustrated in Chapter V. Nevertheless, in a real physical situation, only one stable solution is reached. The heating configuration, the initial conditions, possible disturbances, and the veracity of the boundary conditions are some determining factors for the stable solutions that occur [207]. It is then important to conduct an experimental investigation of such flows in order to assess the influence of these factors on the resulting stable solution.

In this chapter, a measurement technique to study natural convection inside a cubical cavity differentially heated is developed. This technique consists of simultaneous measurements of temperature and velocity fields by phase-shifting interferometry (PSI) and particle image velocimetry (PIV), respectively. The focus is mainly on the development of a novel measurement technique, rather than to investigate all the solution patterns obtained in Chapter V. This experimental technique would allow us to partially determine the solution \((u, v, w, T, C)\) of a convective flow within a binary mixture, given the contrast factors \(\frac{\partial n}{\partial T}\) and \(\frac{\partial n}{\partial C}\) are known (see Chapter II §4). In this study, the working fluid is limited to liquids and, therefore, the pressure dependence of the refractive index can be neglected (only important for gases). In this chapter, the working fluid is further limited to pure liquids, i.e. only \(\frac{\partial n}{\partial T}\) is considered in the optical measurement of the refractive
In §1, a brief introduction of the experimental techniques available to measure convection in enclosures is presented. In §2, the experimental method, which consists of an optical system, a Rayleigh-Bénard cell, and an image processing software, is described. In §3, the conclusions of this chapter are presented.

1 INTRODUCTION

Even though numerical studies have been conducted to deepen our understanding of natural convection in enclosures (e.g. see results in Chapter V), experimental investigations of this phenomenon are required in order to assess the accuracy and validate the results of such studies. Compared to numerical studies, the experimental work for natural convection in enclosures is rather scarce. In this section, some representative experimental works concerning the measurement of natural convection in enclosures are discussed. This presentation is divided in different parts according to the heating configuration.

CAVITIES HEATED FROM THE SIDES

Hiller et al. [80] conducted experiments on thermal convection in a 38 mm $\times$ 38 mm $\times$ 38 mm cubical cavity with two opposite vertical walls kept at prescribed temperatures. This is the same heating configuration as in the numerical work of Wakashima et al. [208], which is used in the accuracy assessment in Chapter IV §3.2. The velocity and temperature fields were measured with the help of liquid crystals suspended as small tracer particles in the medium. This technique is called digital particle image thermometry/velocity (DPIT/V). Dabiri [56] gives a comprehensive review of the simultaneous measurement of temperature and velocity fields by means of DPIT/V. In contrast to interferometric techniques, a large visualization area can be measured with DPIT/V because it is not limited by the size of a beam splitter. Hiller et al. [80] investigated the flows for Rayleigh numbers in the range $10^4 \leq Ra \leq 2 \times 10^7$ and Prandtl numbers in the range $5.8 \leq Pr \leq 6000$. 
The working fluid is a glycerol-water solution so $Pr$ can be fixed by adjusting the concentration ratios. Their observations show that the convection within the cubical cavity is strongly three-dimensional. Moreover, the three-dimensional steady-flow structures in the convective flow were defined by a set of critical points and interconnecting streamlines. They showed that the flow structure undergoes a change from a one-roll to a two-roll flow pattern. This indicates the presence of a bifurcation. For $Pr = 6000$, this bifurcation occurs at $Ra \approx 60000$.

DPIT/V is amply sufficient to resolve the relevant flow and thermal structures without the ambiguities that might be found in a non-simultaneous measurement. The experimental technique is overall simple, has low cost, and the possibility of simultaneously recording the flow and temperature fields makes it particularly suitable for broad-range parametrical studies, e.g. to investigate the influence of aspect ratios, inclination angle and thermal boundary conditions on free convection. Nevertheless, the experimental uncertainty associated with this experimental technique was estimated to be of the order of 10% both for the fluid velocities and for the (relative) temperatures. This accuracy is lower than that allowed by most specialised techniques such as laser-Doppler velocimetry, conventional particle image velocimetry (PIV) with laser-generated light beams and dedicated tracers, and local temperature measurements.

**Cavities heated from below**

Pallares et al. [149] conducted a systematic PIV study of Rayleigh-Bénard convection in a horizontal cubical cavity of dimensions $12.5 \text{ mm} \times 12.5 \text{ mm} \times 12.5 \text{ mm}$ at moderate Rayleigh numbers ($Ra \leq 8 \times 10^4$) using silicone oil ($Pr \approx 130$). They considered two boundary conditions for the sidewalls: adiabatic and conducting. They performed this experimental study after a thorough investigation by a three-dimensional numerical study (Pallares et al. [151]), which clarified the stable solutions that can be expected (note that their numerical study does not employ a continuation method, so it is not as detailed as the results presented in Chapter IV §3.3 and Chapter V §3.2). For a cavity with adiabatic
sidewalls, they showed that the sequence from the conductive state consists of a toroidal roll that evolves to a diagonally oriented single roll with increasing Rayleigh number. This diagonal roll, which is stabilized by the effect of the small but finite conductivity of the walls, shifts its axis of rotation towards two opposite walls, and back to the diagonal orientation to allow for the increase in circulation that occurs as the Rayleigh number is further increased. The topology and the velocity fields of all structures are in good agreement with numerical results. An experimental technique that provides additional measurements of temperature fields would, however, clarify the relation between the velocity and temperature fields, as well as to assess the boundary conditions of the cavity.

Ciofalo et al. [46] used DPIT/V to study Rayleigh-Bénard convection in shallow rectangular enclosures having an aspect ratio 1:2:4 at a Rayleigh number of $Ra \approx 14500$. They visualized and quantitatively characterized the flow by using glycerol as working fluid and suspended thermochromic liquid crystal tracers. They were able to reconstruct the 3D flow and thermal fields by interpolating the experimental velocity and temperature distributions obtained on parallel planes. Their results are of great interest to experimentalist working on Rayleigh-Bénard convection. Furthermore, Ozawa et al. [144] employed DPIT/V to measure temperature and flow fields of natural convection in a Hele-Shaw cell. This cell is similar to a Rayleigh-Bénard cell, i.e. both are parallelepiped cavities heated from below. Nevertheless, a Hele-Shaw cell (HSC) is characterized by having a very small aspect ratio and, therefore, it is only useful for studying two-dimensional natural convection. Moreover, Ciofalo et al. [46] and Ozawa et al. [144] used DPIT/V, whose accuracy is much inferior than the accuracy of optical digital interferometry.

Lee and Kim [106] investigated variations of temperature and velocity fields in a HSC using digital holographic interferometry and a 2D PIV system. Their method is a good example of the implementation of both measurement techniques to study convection in enclosures. However, they did not conduct simultaneous measurements nor analyse three-dimensional flow structures (due to the HSC constraint). In contrast, Skarman et al. [185, 186], proposed for the first time simultaneous PIV and temperature mea-
measurements using a CCD based holographic interferometry (with a phase-shift method) to investigate Rayleigh-Bénard convection. They compared their results with DPIT measurements and showed a considerable improvement. Nevertheless, they use the same CCD camera for the PIV and digital holographic interferometry measurements, and adjust the focus of a lens to set the measurement area of the PIV measurement. This is a drawback because there is an extra error caused by the uncertainty of the position of the measurement area, which in conventional PIV is determined with a higher accuracy by simply setting a laser sheet.

**TILTED CAVITIES**

Ozoe et al. [148] have conducted an extensive PIV experimental study in tilted cavities. Some of their experimental results were compared with the numerical results on a truncated square duct (see Chapter V §2.4).

**CAVITIES HEATED UNDER MICROGRAVITY CONDITIONS**

Even though a microgravity environment is not considered in this study, the interferometric techniques developed for thermodiffusion studies in the International Space Station (ISS) are the most accurate to this date. Ahadi et al. [2–6] used an FFT method to measure concentration and temperature fields in a rectangular enclosure. Shevtsova et al. [181, 182] studied the nonlinear dynamics occurring in a non-uniformly heated fluid with Soret effect inside a rigid-wall container subject to translational vibrations under microgravity conditions. The experiments of Ahadi et al. [5] and Shevtsova et al. [182] were conducted in the ISS with the same FFT method used by Mialdun et al. [121, 125]. In Chapter IV the advantages and disadvantages of the phase-shifting interferometry (PSI) in contrast to FFT methods were discussed. Since PSI allows us to conduct a real-time measurement of the phase-map within the convective cell, it might be a more suitable measurement technique for such convective systems than FFT-based methods.
VI MEASUREMENT OF CONVECTION IN RECTANGULAR PARALLELEPIPEDI CAVITIES

OBJECTIVES

In this chapter, we propose a novel optical setup capable of conducting simultaneous measurements of two-dimensional temperature and velocity fields of natural convection inside a rectangular cavity. The method is applied to study Rayleigh-Bénard convection in a cubical cavity. The measurement apparatus consists of the phase-shifting interferometer developed in Chapter II and a conventional PIV setup. The objectives of this chapter are the following:

1. Construct a cubical Rayleigh-Bénard cell suitable for parametric measurements of steady natural convection.

2. Conduct simultaneous measurements of temperature and velocity fields.

The experimental device proposed in this chapter can be used for a parametric study of natural convection in parallelepipped cavities. These systematic measurements should yield results comparable with the bifurcation diagrams found in the result sections of Chapter V.

2 NATURAL CONVECTION EXPERIMENT

2.1 SIMULTANEOUS PSI AND PIV MEASUREMENTS

The experimental device is shown in Fig. 6.1. It consists of a phase-shifting interferometer and a PIV system. The interferometer is the same as the single phase-shifting interferometer described in Chapter II (see Fig. 2.2). The PIV systems consists of a light source (a laser with the same wavelength as the laser in the interferometer, $\lambda = 633$ nm), two cylindrical lenses to form the laser sheet, and a CCD camera to record the tracer movement inside the Rayleigh-Bénard cell. Notice that the measurement region of the
Figure 6.1: Sketch of the phase-shifting interferometer and PIV system. The interferometer is the same as the single phase-shifting interferometer shown in Fig. 2.2. The insets indicate the polarization state of each beam section of the interferometer. The PIV system consists of a laser sheet and a CCD camera to register the traces of the particles. (1) He–Ne laser, $\lambda_{\text{beam}} = 633$ nm, (2) polarizing plate, (3) ND filter, (4) mirror, (5) objective lens, (6) pinhole, (7) collimator, (8) polarizing beam splitter, (9) Rayleigh-Bénard cell, (10) focus lens, (11) quarter-wave plate, (12) rotating polarizer, (13) CCD camera, (14) stepper motor, (15) cylindrical lenses.

PIV is designated by the location of the laser sheet, whereas the phase-shifting interferometer measures the integral of the temperature (related to the refractive index) in the OP direction. Therefore, in order to compare a two-dimensional temperature profile obtained by numerical calculations, e.g. those conducted in Chapters IV and V, we first need to integrate the temperature field in the OP direction.

The working fluid in these experiments is distilled water. The Prandtl number for distilled water is strongly dependent on temperature, as shown in Table 6.1, with the temperature dependence becoming weaker at higher temperatures. This table also shows the temperature dependence of the dynamic viscosity, kinematic viscosity, and the volumetric expansion coefficient for water.
Table 6.1: Some thermophysical properties of water at different temperatures.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Dynamic viscosity [Pa · s × 10^{-3}]</th>
<th>Kinematic viscosity [m^2/s × 10^{-6}]</th>
<th>Expansion coefficient [1/K × 10^{-4}]</th>
<th>Prandtl number [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.31</td>
<td>1.304</td>
<td>0.88</td>
<td>9.47</td>
</tr>
<tr>
<td>15</td>
<td>1.14</td>
<td>–</td>
<td>1.51</td>
<td>8.24</td>
</tr>
<tr>
<td>20</td>
<td>1.0</td>
<td>1.002</td>
<td>2.07</td>
<td>7.01</td>
</tr>
<tr>
<td>25</td>
<td>0.89</td>
<td>–</td>
<td>2.57</td>
<td>6.22</td>
</tr>
<tr>
<td>27</td>
<td>0.85</td>
<td>0.853</td>
<td>2.76</td>
<td>5.90</td>
</tr>
<tr>
<td>30</td>
<td>0.798</td>
<td>0.789</td>
<td>3.03</td>
<td>5.43</td>
</tr>
<tr>
<td>35</td>
<td>0.719</td>
<td>–</td>
<td>3.45</td>
<td>4.88</td>
</tr>
<tr>
<td>40</td>
<td>0.653</td>
<td>0.653</td>
<td>3.85</td>
<td>4.34</td>
</tr>
</tbody>
</table>

Figure 6.2: The test section in the optical apparatus shown in Fig. 6.1. The cubic volume of 10 mm × 10 mm × 10 mm filled with water is enclosed in the Rayleigh-Bénard cell shown in Fig. 6.3. A laser sheet is passed through the cell to measure the velocity field. The test beam is that of the phase-shifting interferometer.
A sketch of the test section is shown in Fig. 6.2. The laser sheet is perpendicular to the test beam of the interferometer. This allows us to have the same visualization region for both two-dimensional temperature and velocity measurements. The velocity field is that of the tracers inside a laser sheet whose width is 2 mm, as shown in Fig. 6.2. The tracer (density 1.03 g/cm$^3$, mean diameter 48-52 µm) concentration was chosen such that it is suitable for the PIV processing while allowing enough light to pass through the sample in order to conduct accurate interferometric measurements. Notice that the coordinate system is the same as the coordinate system used for the numerical analysis of the flows in a cubical cavity in Chapters IV and V, and it differs from the coordinate system used in the previous experimental work in Chapters II and III. Moreover, as indicated in Fig. 6.2, the optical axis of the lens of the CCD camera used for the PIV measurements has an inclination $\sigma$ with the measurement area (this optical axis is horizontal). The distance from the CCD camera to the measurement area is set to 10-15 cm. The aberrations due to the angle $\sigma$ and distance perspective are corrected using the PIV processing software DaVis 8.0 (LaVision), which is a commercial software used in this study to determine the velocity fields.

2.2 Rayleigh-Bénard cell

The Rayleigh-Bénard cell designed for this study is shown in Fig. 6.3. This cell follows the same concept as the Soret cell designed in Chapter II (see Fig. 2.39), i.e. a parallelepiped (in this case cubical) space between quartz sidewalls and an upper and lower copper boundary. The lateral sidewalls allow the passage of light, while the copper boundaries allow a fast temperature control. Notice that the lateral sidewalls are not made of an insulating material so the adiabatic condition considered in Chapters IV and V cannot be realized. The thermal conductivity of the quartz glass is 1.4 W/(m·K), which is a much smaller than the value for copper 401 W/(m·K) but larger than the value for water 0.58 W/(m·K). The assessment of these boundary conditions is done in §2.4 by analysing the two-dimensional temperature profile determined from the phase-shifted data.
The temperature control of the Rayleigh-Bénard cell uses the same PID temperature control system as the one described in Chapter II §4.2. Also notice that the cavity is designed so that its height is adjustable. This can allow us to study natural convection in parallelepiped cavities with different aspect ratios.

In this chapter, the cavity is kept horizontal since the objectives are to create Rayleigh-Bénard convection in the cell and to conduct simultaneous measurements of the temperature and velocity fields. Nonetheless, the experimental apparatus was designed so that the cavity can be tilted by an angle $\theta$, as described in Chapter V. When tilting the cavity, the upper part of the laser sheet that enters the cell is blocked by the upper copper edges. This is an obstacle for the PIV configuration (where the laser sheet is fixed) because the PIV measurement cannot be conducted over the whole square section. However, the PSI measurement is unaffected, since this beam is perpendicular to the walls of the cavity. On the other hand, if we change the position of the CCD camera and tilt the cavity by the angle $\alpha$, as shown in Fig. 5.41, then the PIV measurement for the tilted case could be conducted but the PSI measurement would not be possible.

**Adjustment of the Rayleigh Number**

The Rayleigh number $Ra$ within the cell is controlled by adjusting the temperature difference between the upper and lower copper walls $\Delta T = T_H - T_C$. Therefore, the Rayleigh number becomes

$$Ra = \frac{g \beta h^3 (T_H - T_C)}{\nu \kappa},$$

where $g$ is the acceleration of gravity, $\beta$ is thermal expansion coefficient, $h$ is the side of the cubic cell, $\nu$ is the kinematic viscosity, $\kappa$ is the thermal diffusivity, $T_H$ and $T_C$ are the temperatures of the lower hot and upper cold copper-liquid boundaries, respectively.

In Table 6.2 the Rayleigh numbers obtained for different $\Delta T$ at $T_m = 27^\circ C$ are listed. The mean temperature within the cell is set to $T_m = T_{room} \pm 3 \text{ K}$ in order to reduce the
heat flux from the lateral sides. In the calculation of the Rayleigh number, the thermal expansion coefficient, kinematic viscosity, and thermal diffusivity of distilled water are taken as $\beta = 2.76 \times 10^{-4} \text{ K}^{-1}$, $\nu = 8.53 \times 10^{-7} \text{ m}^2/\text{s}$, $\kappa = 1.43 \times 10^{-7} \text{ m}^2/\text{s}$, respectively, and the side of the cell is fixed to $h = 0.01 \text{ m}$ (Rayleigh-Bénard cell shown in Fig. 6.3).

These values for the thermophysical properties are also indicated in Table 6.1. Moreover, the upper cold temperature $T_C$ should not be too much below the room temperature $T_{\text{room}}$, e.g. $T_C = T_m - 5 \text{ K}$, since no coolant is used in the heat sink of the Peltier modules and the fins might not be enough to exhaust heat.

The values shown in Table 6.2, indicate that in theory we should be able to de-
Table 6.2: Rayleigh number $Ra$ as a function of the temperature difference $\Delta T$.

<table>
<thead>
<tr>
<th>$\Delta T$ [K]</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
<th>2.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ra [10^3]$</td>
<td>2.22</td>
<td>4.43</td>
<td>6.65</td>
<td>8.87</td>
<td>11.1</td>
<td>22.2</td>
<td>33.3</td>
<td>44.3</td>
<td>55.4</td>
</tr>
<tr>
<td>$\Delta T$ [K]</td>
<td>3.0</td>
<td>3.5</td>
<td>4.0</td>
<td>4.5</td>
<td>5.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Ra [10^3]$</td>
<td>66.5</td>
<td>77.6</td>
<td>88.7</td>
<td>99.8</td>
<td>111</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Detect the instability thresholds calculated in Chapter V. The theory indicates that the primary bifurcation is expected to occur at $Ra_c(P_1) = 3388.5$, a secondary bifurcation at $Ra_c(B_{11}) = 54961.2$, and again a ternary bifurcation at $Ra_c(B_{111}) = 71445.2$ (see Table 5.5). However, these values are expected to change to some extent because the sidewalls are not perfect insulators.

2.3 IMAGE PROCESSING AND MEASUREMENT RESULTS

In this section, the system for simultaneous measurement of two-dimensional temperature and velocity fields is tested. The Rayleigh number was set to $Ra \approx 88700$, corresponding to a temperature difference between the copper blocks of $\Delta T = 4$ K. The initial temperature for both blocks at $t = 0$ s is $T = 25^\circ C$. Here, $t$ is the elapsed time after setting the target $\Delta T$ with the PID temperature control system. During the temperature control process, the upper cold boundary is kept at constant $T_C = 25^\circ C$, while the lower hot copper-liquid boundary is set to $T_H = 29^\circ C$. Therefore, the temperature control at the boundaries is slightly different to those profiles set in the Soret experiments (see Fig. 2.47).

A photo of the test section during this natural convection experiment is shown in Fig. 6.4. The tracers illuminated by the laser sheet passing through the Rayleigh-Bénard cell are clearly visible. The position of the CCD camera is adjusted with the camera holder, such that the lens of the camera is as close as possible to the test beam of the interferometer without blocking the beam. The angle $\sigma$ is adjusted to the minimum allowable angle in order to reduce the optical aberration.

Figure 6.5 shows the images simultaneously acquired with the CCD cameras for the
2 Natural convection experiment

Figure 6.4: Photo of the Rayleigh-Bénard cell during a convection experiment. The lower hot copper-liquid boundary is heated to maintain a constant temperature of $T_H$; the upper cold boundary is set to a constant temperature $T_C$. The tracers within the cell are clearly visible.

Figure 6.5: Simultaneous acquisition of the tracers and phase-shifted data for PSI and PIV measurements, respectively. The scale indicates that the phase-shifted data (modulo $2\pi$) has dimensions of $10 \text{ mm} \times 10 \text{ mm}$, while the snapshot for the PIV measurement has the same height of $10 \text{ mm}$ but a slightly shorter width. This is due to the optical aberration induced by the angle $\vartheta$. 

$Pr = 5.9, \quad Ra = 8.87 \times 10^4$
PIV and PSI measurements at $t = 0$ s, 10 s, and 80 s. From these snapshots, only the phase-shifted data $\phi(y,x)$ has meaningful information, since for the PIV measurement we need consecutive images of the tracers at short time intervals $\Delta t$ in order to extract a velocity or streamline profile.

From the phase-shifted data at $t = 0$ s shown in Fig. 6.5, we can see that there are vertical fringes near the walls. At this initial time, the system is isothermal, i.e. $T_{\text{room}} = T_{\text{lower}} = T_{\text{upper}} = 25^\circ$C. Here, $T_{\text{lower}}$ and $T_{\text{upper}}$ are the temperatures of the lower and upper copper boundaries, respectively. Therefore, the temperature inside the fluid is constant and, as a consequence, an isophase condition (without fringes) should be reached. However, as discussed in Chapter II §2.4, optical defects of the quartz walls caused by a possible deflection due to the weight of the copper block, or the lack of parallelism after manufacturing, will be responsible for the appearance of extra fringes, such as in the case of Fig. 6.5. These optical defects can be suppressed by subtracting the unwrapped phase-shifted data corresponding to the initial condition from subsequent unwrapped phase maps.

Moreover, from the phase-shifted data shown at $t = 10$ s in Fig. 6.5, we see that fringes only appear near the lower boundary. This is because, as mentioned above, only the lower boundary is heated, while the upper boundary is kept at constant temperature.

Figure 6.6 shows the phase-shifted data acquired during the natural convection experiment where the Rayleigh number is set to $Ra = 88,700$, i.e. $\Delta T = 4$ K. Here, the lower boundary is heated to $T_H = 29^\circ$C while the upper boundary is kept at constant temperature $T_C = 25^\circ$C. The results show that the convection within the cavity is unsteady until $t \approx 85$ s. Moreover, the phase-shifted data at $t = 90$ s and $t = 120$ s indicate that the temperature profile within the cell has reached a quasi-steady state. Notice that in the phase-shifted data shown in Figs. 6.5 and 6.6, the tracers used for the PIV measurement are barely visible. This indicates that the tracers do not affect the temperature measurement in a significant way. Moreover, if the phase-shifted data at $t = 0$ s were isophase throughout the whole two-dimensional domain, then the isophase lines corresponding to
the phase-shifted data at \( t > 0 \) s would correspond to the isothermal temperature contours. Nevertheless, as explained above, an optical aberration creates the initial fringes observed in the phase-shifted data at \( t = 0 \) s and, hence, an additional image processing must be conducted to correct this aberration in order to determine the temperature profiles.

After conducting the natural convection experiment, the phase-shifted data is stored for the post-experimental image processing explained in the next subsection.

### 2.4 Two-dimensional unwrapping and initial phase map

Figure 6.7 shows a window of the program written in Processing language in order to conduct the two-dimensional unwrapping of the phase-shifted data and perform the subtraction of the initial phase-map, which takes into account the optical aberrations. This window is divided into 6 frames. At this point, frames 5 and 6 are not used. The phase-
Figure 6.7: Layer selection in the phase-shifted data for the two-dimensional unwrapping. This is the first step in the image processing for obtaining a two-dimensional temperature profile. The window is divided into six frames. At this step, only frames 1, 2, 3, and 4 are used. In frames 1 and 2 the phase-shifted data at \( t = 80 \) s and \( t = 0 \) s are displayed. In frames 3 and 4 the different layers (continuous phase shift \( \phi \) between 0 and \( 2\pi \)) corresponding to the phase-shifted data are identified for subsequent unwrapping.

shifted data \( \phi(y,x) \) at \( t = 80 \) s and \( t = 0 \) s are displayed in frames 1 and 2, respectively. In Chapter II §3, the phase-shifted data of one-dimensional diffusion experiments were unwrapped and averaged in real-time with the self-written image processing program named Emerald (see Chapter II §2.4). This was possible because the algorithm to unwrap the phase-shifted data whose isophase lines are parallel is relatively simple. For the two-dimensional unwrapping, however, an automatic procedure to unwrap the phase-shifted data is rather complex if taking into account the curvature of the fringes and the noise (black or white pixels) near the isophase lines. Therefore, the program shown in Fig. 6.7 for the two-dimensional unwrapping of the phase-map follows some manual input from the operator. Here, the different layers of the phase-shifted data are manually selected, and the hierarchy of the layers is adjusted. Each layer in the phase-shifted data is defined as the continuous value of the phase shift \( \phi(y,x) \) between 0 and \( 2\pi \). Frames 3 and 4 show
Figure 6.8: Two-dimensional unwrapping of the phase-shifted data. This is the first step for the image processing to obtain the two-dimensional temperature profile. The window is divided into six frames. Frames 1 and 2 display the phase-shifted data at $t = 85$ s and $t = 0$ s, respectively. Frames 3 and 4 display the unwrapped phase map for the phase-shifted data displayed in frames 1 and 2, respectively. Frame 5 displays the subtracting results between frames 3 and 4. Frame 6 displays the two-dimensional temperature field.

the different layers corresponding to the phase-shifted data in frames 1 and 2, i.e. $t = 85$ s and $t = 0$ s, respectively. The colours in these frames (frames 3 and 4) indicate the hierarchy of the different layers. Then the layers are connected by successively adding $2\pi$ to each layer and the unwrapped phase map $\psi(y, x)$ is thus obtained.

Figure 6.8 shows the phase-shifted data $\phi(y, x)$ (as in Fig. 6.7), the unwrapped phase map $\psi(y, x)$, the result after the subtraction of the initial conditions, and the obtained two-dimensional temperature profile $T(y, x)$. Remember that these values are not at a location $z$ but rather represent the integral value along $z$. Frames 3 and 4 give the unwrapped phase map $\psi(y, x)$ for the phase-shifted data displayed in frames 1 and 2, respectively. Notice that the phase map for the initial condition at $t = 0$ s (frame 4) gives the wavefront deformation due to the optical aberration, while the phase map for the phase-shifted data at $t = 85$ s (frame 3) gives the wavefront deformation due to the same optical aberrations.
Figure 6.9: Two-dimensional temperature field obtained with the procedure described in Fig. 6.8. (a) The temperature field and the isotherms are shown. (b) A Gaussian filter is applied to the results in order to obtain a smoother temperature profile.

(neglecting the thermal stresses induced in the quartz walls) and the variation of the refractive index caused by the temperature field, which is the focus of this study. In order to remove the optical aberrations, the phase map at \( t = 0 \) s is subtracted from the phase map at \( t = 85 \) s, i.e. \( \psi(t = 85 \text{ s}) - \psi(t = 0 \text{ s}) \). The results are displayed in frame 5 of the program window shown in Fig. 6.8. This phase map corresponds to the wavefront deformation due only to the temperature field. Also notice that in frames 3 and 4, the boundaries between the different layers in the unwrapped phase map are still visible. This is due to some noise near the boundaries of the different layers. This noise passed to the difference shown in frame 5. An additional filtering for this image is performed to remove this noise. After removing the noise the temperature boundary conditions are imposed to the phase map \( \psi(y, x) \) in order to obtain the temperature field \( T(y, x) \). Here the boundary conditions are \( T = 29^\circ \text{C} \) at \( x = 0 \) mm and \( T = 25^\circ \text{C} \) at \( x = 10 \) mm. The obtained temperature field is displayed in the frame 6 shown in Fig. 6.8. The isothermal (isophase) lines are also plotted without any additional filtering.

Figure 6.9 shows the measured two-dimensional temperature field with its corresponding isothermal lines. Figure 6.9(a) shows the temperature field just after applying the boundary conditions to the phase map. Some noise intrinsic to the phase-shifted data is
still present. At this point, it is useful to apply a filter in order to smooth the temperature profile. Figure 6.9(b) shows the results after applying a Gaussian filter to the results shown in Fig. 6.9(a). In this filtering process, a grid with dimensions derived from a bounding box of the scattered data and re-size to a given $\Delta y$ and $\Delta x$ for each mesh is created for plotting and contouring. Here, the grid is equally spaced in $y$ rows and in $x$ columns; the $T$ values are computed as weighted averages or spline interpolations of the scattered points of $T$ values. In other words, a regularly spaced grid is created and a smooth approximation to the raw data is evaluated for all grid points. This approximation is plotted in Fig. 6.9(b).

The temperature measurement results shown in Fig. 6.9 indicate that the isotherms are not symmetrical with respect to the central axis $z$ of the cavity (at $y = x = 5$ mm). This is expected because the Rayleigh number in this case, i.e. $Ra = 88\,700$, is larger than the critical Rayleigh number of the tertiary bifurcation point $S_{1}B_{11}$, i.e. $Ra_{c} = 71\,445.2$ (see Fig. 5.21 and Table 5.5). Therefore, the solutions shown in Fig. 6.9 should correspond to a solution on the branch $B_{111}$ which has no symmetries.

Notice that from the temperature measurements the boundary conditions of the cavity can be assessed. If the sidewalls were perfectly insulating, the isothermal lines would be normal to these vertical walls. This is not exactly the case for the measurement shown in Fig. 6.9. Nevertheless, the normal gradient of the isotherms just at the boundaries (which indicates the heat flux) is not too large. This suggests that even though the walls are not perfectly insulating, a fairly good adiabatic condition is reached. In addition to the poor thermal conductivity of quartz, the mean temperature within the cell $T_{m}$ is not too different from the room temperature $T_{room}$, improving the adiabatic conditions of the sidewalls.

It is worth noting that these phase-shifted data were taken with tracers inside the flow, and therefore, the tracers used for the PIV measurement seem not to significantly affect the interferometric measurement.
Figure 6.10: Streamlines tracing program for real-time or post-experimental processing. This is the same experiment as the one shown in Fig. 6.6. (a) CCD camera recording (for PIV) of the Rayleigh-Bénard cell at $t = 1.2$ s. (b) The operator delimits the area in which the particle tracing is performed; this snapshot is taken at $t = 4.3$ s. (c) The streamlines for $\Delta t = 2$ s at $t = 10.1$ s. (d) The streamlines for $\Delta t = 2$ s at $t = 20.1$ s. Notice that at this time the flow is still in an unsteady state.

### 2.5 Determination of Streamlines

Before proceeding to determine the two-dimensional velocity fields with the commercial software DaVis 8.0 (LaVision), which is a post-experimental image processing, it is useful to have a program capable of visualizing the streamlines of the flow in real-time. As in the case of the real-time display of the one-dimensional diffusion field with Emerald, it is useful to have a real-time visualization of the natural convection within the cell, e.g. to detect possible bifurcation points while gradually increasing $Ra$.

Figure 6.10 shows the window of the program written in Processing language used
to capture the streamlines within the Rayleigh-Bénard cell. This image processing is conducted in real-time or post-experimentally after recording the phase-shifted data (in video or image files). This is the same experiment as the one shown in Fig. 6.6 where the phase-shifted data are shown. Figure 6.10(a) shows the recording with the CCD camera (see Fig. 6.1 for the positioning of the camera) of the Rayleigh-Bénard cell at $t = 1.2$ s. Notice that the perspective of the camera is clearly visible. The operator then delimits the area in which the particle tracing will be performed, as shown in Fig. 6.10(b). Even though there is the problem of the perspective, the tracing of the particles delimited by the laser sheet would give a fairly good two-dimensional result (the perspective is taken into account in §2.6). After selecting the area where the streamlines are to be taken, the program acquires consecutive frames of $640 \times 480$ pixels at intervals of $1/30$ s, and store them in a memory address. The streamlines are then outputted for a time intervals of $\Delta t$, which correspond to the total time of evolution of the tracers. Figures 6.10(c) and (d) show the streamlines for $\Delta t = 2$ s outputted at $t = 10.1$ s and $t = 20.1$ s, respectively (i.e. the position of the tracers is first recorded at $t - \Delta t$ for each streamline output file). Notice that for these times the flow is still in an unsteady state.

Figure 6.11 shows the streamlines when the flow has reached a quasi-steady state. This
measurement was conducted at the same time as the temperature measurement shown in Fig. 6.9. The streamlines shown in Fig. 6.11 indicate that the flow is not symmetric with respect to the central axis $z$ (at $y = x = 5$ mm), i.e. the same qualitative result obtained for the temperature measurement. Also notice that there are two weak vortices in the upper left and lower right corners. These vortices cannot be easily detected with the phase-shifting interferometry and, hence, are a good example of the importance of the simultaneous measurement of both temperature and velocity fields in order to have a thorough description of the flow.

## 2.6 PIV Measurements

In this study, the commercial software DaVis 8.0 (LaVision) was used for PIV measurements. This software allows us to take into account the correction of the perspective problem, as well as to conduct other tasks such as temporal averaging of the velocity fields.

Figure 6.12 shows the PIV measurement results for the velocity field $(u, v)$ at $z = 5$ mm and $t = 85$ s, i.e. the same time as the temperature measurement shown in Fig.
6.9. The velocity is shown in Fig. 6.12(a) as a vector field, whereas in Fig. 6.12(b) the magnitude of the velocity is indicated over the streamlines determined in §2.6. Here, a steady state roll is obtained with a maximum velocity of $V_{\text{max}} \approx 1.6$ mm/s. Again, weak rolls at the corners are also observed. These measurements indicate the close relation between heat and mass transport within the cell, i.e. the water heated along the lower hot boundary moves upward towards the upper cold boundary where it is cooled and subsequently descends; and the same process is repeated.

The velocity fields shown in Fig. 6.12(a) can be compared to those determined by the numerical calculation, e.g. shown in Fig. 5.40. This would allow us to perform an evaluation of the numerical results obtained in Chapter V.

3 Conclusions

In this chapter, the phase-shifting interferometer developed in Chapter II was utilized to measure two-dimensional temperature fields. Particle image velocimetry (PIV) measurements of the velocity field in a mid-vertical plane were simultaneously conducted for a Rayleigh number of $Ra = 88700$, corresponding to a temperature difference between the lower and upper walls of $\Delta T = 4$ K. The conclusions of this chapter are the following:

1. A single phase-shifting interferometer and a PIV system were setup to study natural convection.

2. A Rayleigh-Bénard cell, similar to the Soret cell developed in Chapter II §4.2, was designed as a cubical enclosure with dimensions 10 mm $\times$ 10 mm $\times$ 10 mm. The lateral walls of the cell allow us to perform these simultaneous measurements.

3. A Rayleigh-Bénard experiment was conducted at $Ra = 88700$. One main roll with smaller rolls at the corners was observed in its steady state. This flow corresponds to a solution on the $B_{111}$ branch determined in Chapter V for $Pr = 5.9$ in the horizontal case.
4. The two-dimensional temperature profile is used to evaluate the lateral boundary conditions. As expected, the quartz sidewalls do not give a perfect insulating condition. However, the gradient of the temperature near the walls indicate that departure from the adiabatic condition remains weak.

5. These results give a quantitative description of the convective flow within a parallelepiped cell in terms of velocity and temperature fields. This is important to clarify the relation between these two fields which characterize natural convection in enclosures.

6. This technique can be applied to any system where a two-dimensional information on the temperature and velocity fields at any given time becomes relevant for its characterization.

The technique developed in this chapter provides a tool to deepen our understanding of natural convection in enclosures and can be used to assess numerical calculations, such as the detailed calculations on cubical cavities and truncated square ducts described in Chapter V. Moreover, since the same optical apparatus was proven to be capable of determining thermodiffusion coefficients, then the measurement technique described in this chapter can also be used to study natural convective flows where mass diffusion (Fickian diffusion and thermodiffusion) occur as well.
VII

General conclusions and summary
In order to clarify the heat and mass transfer phenomena in parallelepiped enclosures, an experimental technique and a numerical analysis were developed and applied to different configurations. A novel optical digital interferometry technique was established. This technique was then applied to study isothermal diffusion in binary and ternary systems of inorganic and biological systems, thermodiffusion (Soret effect) in binary inorganic and biological systems, and Rayleigh-Bénard convection in parallelepiped enclosures. Moreover, a numerical technique based on a three-dimensional continuation method was developed and applied to characterize natural convection of pure fluids in parallelepiped cavities. The effect of the inclination on the stability of the different solutions was studied in detail. The main contributions of this study are summarized in this chapter.

In Chapter I, the background of this study and the relevant literature on the problem were presented. Some questions remain concerning the mass diffusion properties of biological systems under isothermal and non-isothermal conditions. In spite of this, few experimental techniques are capable of visualizing and measuring mass diffusion phenomena with a high accuracy. Therefore, there is a need to develop new experimental techniques that can deepen our understanding of mass diffusion in such systems. Furthermore, fundamental questions remain concerning steady natural convection in tilted rectangular enclosures. Several researchers have contributed to solve some of these questions. However, a three-dimensional analysis of the problem that considers a wide range of Rayleigh numbers \( Ra \) and Prandtl numbers \( Pr \) has never been conducted before. The objectives of this dissertation were finally stated following the need to have more accurate optical techniques to study mass diffusion and better numerical methods to investigate natural convection in parallelepiped enclosures.

In Chapter II, a novel yet precise technique to visualize isothermal diffusion and thermodiffusion was developed. The construction of a real-time phase-shifting interferometer
was described. The interferometer comprises a polarizing Mach–Zehnder interferometer, a rotating polariser, a CCD camera, and an original image-processing algorithm. A three-phase algorithm [53] is implemented to obtain the phase-shifted data at time intervals of $\Delta t = 1/10$ s. This optical apparatus is highly accurate and versatile.

A method to determine the isothermal diffusion coefficient as a function of concentration in aqueous solutions was developed. This method uses the phase-shifting interferometer, a solution injection device, a diffusion cell, and an inverse analysis coupled with a numerical calculation in order to conduct highly-accurate measurements of the isothermal diffusion coefficient. The method has a shorter measurement time and uses less amount of sample than similar methods reported in the literature. The method was then validated by comparing the measured concentration dependence of the diffusion coefficient for aqueous solutions of sucrose and NaCl in water and the corresponding literature values [134].

Two phase-shifting interferometers are simultaneously used to visualize and measure thermodiffusion. A Soret cell with lateral transparent walls made of quartz glass and upper and lower boundaries made of copper was built. A rapid temperature control system was applied to control the upper and lower copper-liquid boundary temperatures. Thermodiffusion experiments were conducted with the height of the cell set to 2 mm. This is much less than the height of the cell used by previous research groups that use interferometric methods [51, 122]. A shorter cell height has three main advantages: (i) Reducing the volume sample (directly proportional to the height); (ii) Shortening the measurement time (directly proportional to the second power of the height); and (iii) Increasing the hydrodynamic stability of the system by decreasing the Rayleigh number $Ra$ ($Ra$ is directly proportional to the third power of the height). The measurement method for thermodiffusion was validated by determining the Soret coefficient of two benchmark liquid pairs [162].

The optical techniques presented in this chapter are then used to study isothermal diffusion and thermodiffusion of biological systems (see Chapter III), as well as natural convection in parallelepiped enclosures (see Chapter VI).
In Chapter III, the optical system developed in Chapter II was applied to mass diffusion measurements in aqueous protein solutions. The importance of Fickian diffusion and thermodiffusion in biological systems was discussed. The challenges to study these systems were also presented. The focus of this chapter was biomolecular Fickian diffusion in binary and dilute ternary systems, as well as thermophoresis in binary systems.

The mass diffusion coefficients of seven different types of macromolecules (and two inorganic compounds) were determined at infinite dilute concentration. These experiments were conducted in order to investigate the solvent-solute interactions. Here, the same solvent, i.e. distilled water, is used in all solutions. The results show that the diffusion coefficient decreases with molecular mass, as predicted by the Stokes-Einstein equation. It was found that the diffusion coefficient of the protein molecules is seemingly proportional to their molecular mass to the power $-1/3$ by assuming a constant molecular density for the proteins studied. The deduced values of protein density were not always accurate. This might be due to a possible hydration and other intermolecular effects.

The concentration dependence of lysozyme and BSA was determined (pH 7.0, $T = 25^\circ$C). A qualitative comparison between molecular dynamics calculations reported in the literature and the present measurement results was conducted. It was shown that BSA has a hard-sphere-like diffusion behaviour, whereas lysozyme exhibits a soft sphere characteristic.

A dilute ternary system consisting of NaCl-lysozyme-buffer was studied. A buffer solution was used to fix the pH of the solution. It was experimentally proven that, for the dilute ranges of concentration considered in this study, the cross-term effect between the diffusion species is negligible. A general formulation for the inverse analysis in dilute multicomponent systems was then proposed. It was then shown that from a ternary concentration profile the isothermal diffusion coefficient of each substance and their concentration ratio can be determined. These diffusion coefficients were determined within a 8.0% margin of uncertainty. This method could be an alternative to conventional chromatography methods.
The measurement method for Soret coefficients was applied to study thermodiffusion in two dilute protein aqueous solutions: aprotinin-water and lysozyme-water. It was found that for the considered concentration \( C_m = 3 \text{ mg/ml} \) the aprotinin molecules have a thermophilic behaviour \( (S_T < 0) \), whereas lysozyme molecules have a thermophobic behaviour \( (S_T > 0) \). The proposed optical technique was used to visualize, for the first time, thermodiffusion of protein molecules. This optical method can then be used in the future as a tool to deepen our understanding of thermodiffusion in biological systems, and specifically of thermophoresis of protein and DNA molecules.

In Chapter IV, a continuation method was developed from a three-dimensional spectral finite element code [18]. This method is particularly well suited for the studies involving complex bifurcation diagrams of three-dimensional convection in rectangular parallelepiped cavities. This continuation method allows the calculation of solution branches, the stability analysis of the solutions along these branches, the detection and precise direct calculation of the bifurcation points, and the jump to newly detected stable or unstable branches, all this being managed by a simple continuation algorithm. This can be used to calculate the bifurcation diagrams describing the convection in tilted cavities.

An accuracy assessment of the code was performed by comparing with the work of Wakashima et al. [208]. They proposed benchmark solutions for natural convection of air \( (Pr = 0.71) \) in a cubical cavity heated from the sides using a finite difference method having a fourth-order accuracy. The percent difference on the calculated Nusselt number between their results and our results (computed with the mesh used in all our study on a cubical cavity) is within 0.7%. The case studied by Mallinson and Davis [113] was then reproduced with a higher accuracy. Here, natural convection inside a truncated square duct, with its length two times the length of the square side, and heated from the sides was studied.

The code for calculating the solution branches and bifurcation points was validated by reproducing the work of Puigjaner et al. [168]. Here, detailed bifurcation diagrams
were determined for a cubical cavity with adiabatic sidewalls and heated from below. Air ($Pr = 0.71$) was used as working fluid. A very good agreement with their work was obtained, validating the developed continuation method.

The numerical methods developed in this chapter can help deepen our understanding of steady natural convection in tilted cavities (see Chapter V).

**In Chapter V**, the continuation method developed in Chapter IV was applied to study steady natural convection in a tilted truncated square duct and a tilted cubical cavity.

The stability of the solutions in a truncated duct with a square cross-section and an aspect ratio $A_z = \text{length}/\text{height} = 2$ was studied. The finite-length square duct was tilted around its longest axis. A precise bifurcation diagram was obtained for the horizontal case ($\theta = 0^\circ$) featuring all the different branches issued from the first ten primary bifurcations and at subsequent secondary bifurcations. The calculations for the square duct were then extended from the Rayleigh-Bénard situation ($\theta = 0^\circ$) to the case where a tilt is imposed to the finite-length duct around its longest axis. This tilt can be a slight defect of the experimental device or can be imposed on purpose.

In the tilted square duct, three types of stable solutions have then been found: the leading longitudinal roll $L^-$ solutions, the longitudinal roll $L^+$ solutions, and the oblique roll $O^\pm$ solutions. The domains of existence of these different stable solutions were determined in the $Ra-\theta$ parameter space. When $\theta$ is non zero but small, the stable leading branch of $L^-$ solutions is destabilized at a first bifurcation point by the oblique roll branch and re-stabilized at a second bifurcation point, whereas the originally unstable disconnected branch of $L^+$ solutions is eventually stabilized. At a small $\theta_c$, the bifurcation points on the leading branch will collide and disappear, so that, for larger $\theta$ (up to $\theta = 90^\circ$), the $L^-$ solutions on the leading branch become continuously stable in the studied $Ra$ domain. Another consequence of this collision is that the stable branches of oblique solutions $O^\pm$ now belong to disconnected branches above saddle-node points. Interesting comparisons with previous studies dealing with convection in inclined ducts
have been obtained. These previous studies involved two-dimensional calculations [47], three-dimensional stability studies [1], and experimental measurements [146]. The presented results confirm and complement the results obtained in these previous studies. This good agreement suggests that these results are also valid for longer square ducts.

Furthermore, a thorough bifurcation analysis of steady natural convection in a tilted cubical cavity was conducted. The solutions were studied from their initiation at low Rayleigh numbers $Ra$ to their transition to periodic states, for the range of the Prandtl number $0.71 \leq Pr \leq 130$. For this cubical cavity, the pitchfork bifurcation obtained for $\theta = 0^\circ$ at the first primary bifurcation (where four stable and four unstable solutions simultaneously emerge) is broken, resulting in a leading branch, three disconnected branches emerging at saddle-node bifurcations, and a secondary branch. It was shown that there is a shift in the $Ra$ domain for all these secondary bifurcations when the cubical cavity is slightly tilted, e.g. $\theta = 0.1^\circ$. Moreover, a thorough stability diagram in the $Ra - \theta$ domain was presented for $Pr = 5.9$. This diagram is constructed from the loci of the bifurcation points related to stable solutions. The stability diagram provides a comprehensive description of the stable regimes as a function of $Ra$ and $\theta$. It was found that the loci of the secondary bifurcations related to the leading branch evolve towards higher $Ra$ and $\theta$, whereas the loci of the solutions related to the disconnected branches converge and disappear at critical angles. The effect of the Prandtl number was investigated by determining the interesting critical angles $\theta_{ycri}$ and $\theta_{zcri}$ as a function of the Prandtl number. In addition, the relation between the average Nusselt number $Nu$ and the inclination $\theta$ was also clarified. These results indicate that there is a maximum $Nu$ at a given inclination angle. The analysis was also extended to a cubical cavity slightly tilted in two directions, i.e. without horizontal edges. The influence of these inclinations on the three-dimensional flow was discussed.

This bifurcation analysis study is the first of its kind to fully address, from the primary instability threshold to the oscillatory state, the influence of a tilt on the stability of three-dimensional convective flows inside rectangular enclosures.
In Chapter VI, the phase-shifting interferometer developed in Chapter II was utilized to measure two-dimensional temperature fields. Particle image velocimetry (PIV) measurements of the velocity field in a mid-vertical plane were simultaneously conducted for a Rayleigh number of $Ra = 88700$, corresponding to a temperature difference between the lower and upper walls of $\Delta T = 4$ K.

A novel technique for the simultaneous measurement of temperature and velocity fields was proposed. This optical apparatus consists of a single phase-shifting interferometer and a PIV system. A Rayleigh-Bénard cell, similar to the Soret cell developed in Chapter II §4.2, was designed as a cubical enclosure. The transparent lateral walls of the cell allow us to perform these simultaneous measurements. A Rayleigh-Bénard experiment was conducted at $Ra = 88700$. One main roll with smaller rolls at the corners was observed in its steady state. This flow corresponds to a solution on the leading branch (after two pitchfork bifurcations) determined in Chapter V for $Pr = 5.9$ in the horizontal case. Furthermore, the two-dimensional temperature profile is used to evaluate the lateral thermal boundary conditions. As expected, the quartz sidewalls do not give a perfect insulating condition. However, the gradients of the temperature near the walls indicate that the thermal boundary conditions are not far from adiabatic.

These results give a quantitative description of the convective flow within a parallelepiped enclosure in terms of velocity and temperature fields. This is important to clarify the relation between these two fields, which characterize the natural convective flow. The technique can be applied to any system for which two-dimensional temperature and velocity fields at any given time become relevant for its characterization.

The technique developed in this chapter provides a tool to deepen our understanding of natural convection in enclosures and can be used to assess numerical calculations, such as the detailed calculations on cubical cavities and truncated square ducts presented in Chapter V.
Final remarks. Heat and mass transfer is a broad field, and within this field, heat and mass transfer in enclosures is one of the most important and fundamental phenomena in physics, both for its practical application and scientific importance. Understanding these phenomena paves the way to new horizons and important applications. In this dissertation, mass diffusion and natural convection in tilted enclosures are studied thoroughly, both experimentally and numerically. Important contributions were presented regarding optical techniques to measure and analyse mass diffusion and heat transfer, with possible applications to separation of species and more efficient heat transfer mechanisms within enclosures.

The author hopes that the fundamental studies and applications described in this dissertation will contribute to the further development of heat and mass transfer in enclosures and its applications in various fields.


LIST OF PUBLICATIONS,
PRESENTATIONS AND AWARDS
JOURNAL PUBLICATIONS


INTERNATIONAL CONFERENCES


**DOMESTIC CONFERENCES IN JAPAN**


**WORKSHOPS & SEMINARS**


**PRESENTATION AWARDS**

1. **Best Poster Awards.** *The 5th Annual ELyT Laboratory Workshop*, Zao Toogata, JAPAN (20 February 2013)

2. **Outstanding Award.** *The 5th International Young Researchers Seminar on Flow Dynamics*, Sendai, JAPAN (12 July 2012)

3. **Best Poster Award.** *The 10th International Meeting on Thermodiffusion*, Brussels, BELGIUM (7 June 2012)

4. **Outstanding Award.** *The 4th International Young Researchers Seminar on Flow Dynamics*, Sendai, JAPAN (8 July 2011)

5. **Outstanding Presentation Award.** *The 48th Japanese Heat Transfer Symposium*, Okayama, JAPAN (2 June 2011)
6. **Best Student Presentation Award.** *The 30th Japanese Symposium of Thermophysical Properties*, Yonezawa, JAPAN (29 October 2009)

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