Preface

In September 2000, the University of Bayreuth, Germany, hosted the Fourth International Meeting on Thermodiffusion (IMT4).

The IMT conferences were born from the idea of bringing together researchers in the field of thermodiffusion. Under the auspices of the *European Group of Research in Thermodiffusion* (EGRT) the conference series started in 1994 with IMT1 in Toulouse and has been continued every other year with IMT2 (Pau, 1996), IMT3 (Mons, 1998), and IMT4 (Bayreuth, 2000). The next conference, IMT5, will be held in 2002 in Lyngby, Denmark.

Thermodiffusion, also called thermal diffusion or the Ludwig-Soret effect, describes the coupling between a temperature gradient and a resulting mass flux. Although the effect was already discovered in the 19th century by Ludwig and Soret, it has gained growing interest during the last years due to improved experimental techniques like state-of-the-art thermogravitational columns, modern optical methods, flow channels, and microgravity experiments, to mention only a few. We are still far from a detailed microscopic picture, but analytical theories have been improved and the availability of fast computers and efficient algorithms for nonequilibrium molecular dynamics simulations has provided valuable input from the theoretical side.

The IMT conferences cover all aspects of thermodiffusion from fundamentals to new applications. Traditionally, the focus has been on the fluid state, ranging from mixtures of simple liquids to more complex systems such as critical mixtures, electrolytes, polymers, colloidal dispersions, or magnetic fluids. IMT4 tried to widen the scope by including a plenary lecture about thermodiffusion in ionic solids. Scientific input comes from diverse disciplines such as physics, chemistry, engineering, and geophysics.

Sadly, Leo Kempers passed away while this book was being prepared. Many of us have lost a friend and respected colleague. His manuscript has been brought into its final state by A. Shapiro, whom we want to thank here.

IMT4 would not have been possible without help from many people, ranging from the scientific committee to students, secretaries, and technicians helping with the local organization. We are grateful to the University of Bayreuth for hosting the conference and for financial support from the Deutsche Forschungsgemeinschaft, the Bavarian State Ministry of Education, Culture, Science and Art, the Emil Warburg Foundation, Wyatt Technology Germany, and the Max Planck Institute for Polymer Research.

Bayreuth, Mainz,
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Werner Köhler
Simone Wiegand

Organization of the Book

Since reviews about thermodiffusion research are scarce, it was our intention to provide a comprehensive overview of the current activities in the field in book form. Consequently, the contributions within this volume are not merely the papers presented at IMT4 but were written with the aim to contain both a review-like introduction together with recent research results. Hence, the book should be of value for both the experts and interested scientists working in different areas. It is organized in three Parts, but the classification is not always sharp.

In the First Part, general concepts, theoretical aspects and computer simulations are discussed. **Bjørn Hafskjold** reviews simulation methods to study thermal diffusion. Equilibrium molecular dynamic simulations using Green-Kubo formalism as well as non-equilibrium methods using linear response theory to derive the transport coefficients are discussed. **Jutta Luettmer-Strathmann** provides a summary on the asymptotic and crossover behavior of thermodiffusion and other transport properties close to the critical point. **Konstantin I. Morozov** develops a theory of the Soret effect on surfacted and ionic colloids. He shows that the double layer thickness and the electric potential of the particle surface determine the sign of the Soret coefficient. **Alexander A. Shapiro** and **Erling H. Stenby** discuss to what extent the concept of principle of entropy maximization can be transferred from the framework of equilibrium thermodynamics to non-equilibrium steady states. **Leo J.T.M. Kempers** uses a thermodynamic approach, which includes kinetic contributions to predict the Soret effect in multicomponent mixtures. Comparison with mixtures relevant to the chemical and petroleum industry shows agreement within a factor of two over four decades. **Ryszard Wojnar** derives a kinetic theory for Brownian particles under the influence of a gravity and a temperature field. He applies this theory to the thermodiffusion process in porous media. **Jan V. Sengers** and **José M. Ortiz de Zárate** demonstrate that the Soret effect induces long-range concentration fluctuations in a binary liquid system which is in a stationary thermal non-equilibrium state. **Jürgen Janek**, **Carsten Korte** and **Alan B. Lidiard** summarize the current state of thermodiffusion in ionic solids. Model experiments as well as theoretical approaches are discussed. The last contribution of the first Part is a song which was performed by **Florian Müller-Plathe** during his presentation. It gives a historic overview and presents recent results from computer simulations.

In the Second Part of the book, experimental techniques as well as their application to special systems, such as polymers, are discussed. In the first paper, **Simone Wiegand** and **Werner Köhler** summarize the recent applications and developments in optical grating techniques. The influence of convection and the approach of a critical point are discussed in more detail. **Guy Chavepeyer**, **Jean-François Dutrieux**, **Stéfan Van Vaerenbergh**, and **Jean-Claude Legros** describe experimental effects in thermal diffusion flow cells, which perturb the measurement of small Soret coefficients. They discuss numerical simulation results and compare those to experimental data. **Javier Valencia**, **Mohamed Mounir Bou-Ali**, **Oscar Ecenarro**, **José Antonio Madariaga** and **Carlos M. Santamaría** explain the limitations of the Furry, Jones and Onsager thermogravitational column theory. **Michel Martin**, **Charles Van Batten** and **Mauricio Hoyos** give a background in the thermal field flow fractionation technique, which is a standard liquid chromatography technique for polymer fractionation and characterization. **Martin E. Schimpf** reviews thermodiffusion theories. He compares them with experimental results obtained for various polymers by field flow fractionation and presents a recently developed hydrodynamic model.

The Third Part of the book covers theoretical and experimental aspects of thermodiffusion and convection, including thermodiffusion in porous media. In the first contribution, **Jean-Karl Platten**, **Jean-François Dutrieux** and **Guy Chavepeyer** discuss the combination of free convection and thermodiffusion for the measurement of Soret coefficients in Rayleigh-Bénard cells and thermogravitational columns. **Björn Huke** and **Manfred Lücke** summarize their finding about laterally periodic convection structures in binary mixtures in the Rayleigh–Bénard system for positive Soret effect. **Mark I. Shliomis** focuses on the convective instabilities in ferrofluid layers in a Rayleigh–Bénard cell heated from above or from below in the presence of a magnetic field. **Boris L. Smorodin**, **Bela I. Myznikova** and **Igor O. Keller** present a theoretical study of the influence of transverse vibrations on the formation of instabilities in binary mixtures. They show that, depending on the amplitude and frequency of the modulation, the vibrations can stabilize or destabilize the equilibrium state of the liquid. The last three papers in the third section discuss thermodiffusion in porous media. **Pierre Costesèque**, **Daniel Fargue** and **Philippe Jamet** review the experimental, theoretical and numerical studies performed on thermodiffusion and thermodiffusion-convection transport in porous media. **Mohamed N. Ouarzazi**, **Annabelle Joulin**, **Pierre-Antoine Bois** and **Jean K. Platten** study the pattern formation of a binary mixture in a porous medium heated from below in the presence of a horizontal flow. The book concludes with a paper by **Bruno Lacabanne**, **Serge Blancher**, **René Creff** and **François Montel**, who derive a model and perform numerical simulations for the Soret effect in multicomponent flow through porous media.

An attempt has been made to use a uniform nomenclature, but this has proved to be an almost impossible task with contributions from different scientific disciplines. The most important symbols that most authors could agree on are summarized in a global glossary on page XVII. At the end of every contribution there is a supplementary glossary with the symbols not contained in the global one. Some authors preferred to stay with their own established notation and deviated from the conventions in the global glossary. Hence, the reader is always advised to check the supplementary glossary.

There is no agreement in the literature on how to define the sign of the Soret coefficient. The sign convention used in this book does not depend on the densities of the components and is explained in detail on page XVII.

We would like to express our thanks to the contributors to this volume for their enthusiasm and their ready cooperation in making this book a timely reflection of the progress achieved in various theoretical aspects and applications of thermodiffusion.

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Glossary of Symbols

c	concentration (weight fraction)
c_{p}	specific heat capacity at constant pressure
c_{v}	specific heat capacity at constant volume
D	mutual diffusion coefficient
D_{T}	thermal diffusion coefficient
D_{th}	thermal diffusivity
F	Helmholtz free energy
k_{B}	Boltzmann's constant
Le	Lewis number
M	molar mass
Pr	Prandtl number
q	wave vector
t	time
Ra	Rayleigh number
Re	Reynolds number
Sc	Schmidt number
S_{T}	Soret coefficient (see below for sign convention): $S_{\mathrm{T}} = D_{\mathrm{T}}/D$
T	temperature
x	concentration (mole fraction)
u	fluid velocity
α	cubic expansion coefficient: $\alpha = -\left(\frac{1}{\rho}\frac{\partial\rho}{\partial T}\right)_{p,c}$
α_{T}	thermal diffusion factor: $\alpha_{\mathrm{T}} = TS_{\mathrm{T}}$
β	solutal expansion coefficient: $\beta = \left(\frac{1}{\rho}\frac{\partial\rho}{\partial c}\right)_{p,T}$
λ	wavelength of light
λ_{T}	thermal conductivity
μ	difference in chemical potential per unit mass between the two species in a binary mixture
ϕ	concentration (volume fraction)
ψ	separation ratio: $\psi = \frac{\beta}{\alpha}S_{\mathrm{T}}c(1-c)$
ρ	mass density

Sign convention for S_{T} and D_{T}

In a binary mixture of A and B, 'S_{T} of A' (and also D_{T}) is positive if A migrates to the cold side. This implies that S_{T} of B must be negative, since B migrates to the hot side. Usually, one would specify S_{T} for the component that has been used for the definition of the concentration. Note that this definition does not depend on the densities of the two components.