Topical issue on Thermal non-equilibrium phenomena in fluid mixtures

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When a temperature difference, or gradient, is applied over a bulk fluid mixture at equilibrium, the phenomenon known as thermodiffusion, or the Ludwig–Soret effect, may occur. When the thermal gradient is applied to a colloidal suspension, the colloids drift toward cold or hot regions. This phenomenon is commonly referred to as thermophoresis. The thermal force induced by the temperature gradient will in general act differently on the components in the mixture, which will respond by migrating in different ways toward cold or hot regions, until the thermal force is balanced by concentration gradients. The result is a measurable concentration gradient in the fluid. If the fluid is soaked in a porous medium, an additional effect known as thermo-osmosis may occur. Thermo-osmosis leads to a pressure difference. These thermal-coupling effects are different from normal diffusion and osmosis, where a concentration difference is the driving force. If the permeability of the porous medium sustains the pressure difference, such as in biological or artificial membranes, the pressure difference is typically of the order 100 mbar K$^{-1}$ and 1 bar K$^{-1}$ in soil (frost heave). In bulk fluids, thermo-osmosis is usually neglected due to the lack of a permeable medium. Whereas thermodiffusion or thermophoresis occurs in a mixture or suspension, thermo-osmosis occurs in both pure components and mixtures. In both cases, the temperature difference is the driving force.

In addition to thermodiffusion/phoresis and thermo-osmosis, gravity may also give rise to concentration and pressure differences in a stagnant fluid mixture. Gravity is a body force; it acts on the components’ different masses. As such it is different from thermodiffusion, which in addition acts on the components’ difference in intermolecular interactions. It is also different from thermo-osmosis, which acts on the interactions between the membrane and the fluid. Gravity is often unwanted in studies of thermodiffusion because it is difficult to separate its effect from the Ludwig–Soret effect. Measurements have therefore been conducted in space at zero gravity, the most prominent example being the DCMIX project of ESA for the investigation of Fickian diffusion and thermodiffusion in ternary mixtures.

These effects may give spectacular observable phenomena, such as Rayleigh–Bénard instabilities in liquids heated from below, fluid composition gradients in oil and gas reservoirs, and frost heave damaging roads at springtime. They are also found in industrial processes, such as isotope separation, coupled heat- and mass transport in fuel cell membranes, desalination of water by membrane distillation, and formation and growth of salt lenses in the carbon cathode during aluminum electrolysis.

A series of international meetings on thermodiffusion (IMT) was started in 1994 in Toulouse, France, as a biannual event. The 14th in the series, IMT 14, was held by web in 2021 (delayed 1 year due to the Covid-19 pandemic). An impressive progress has been made over these years, both in experimental techniques and in the number of studied systems. Good progress has also been done on the theory of thermodiffusion, but it has proved to be rather difficult to extend the formal results to quantitative and predictive models. However, based on experimental and simulation data, some models for specific purposes are now available.

The topics of this issue reflect what was presented at the IMT14 meeting held in Trondheim in May 2021. The complexity of acquiring, understanding, and modeling thermodiffusion data increases dramatically with the number of components in the fluid. Already at three components, this is a challenge. Even the sign of the Soret coefficient is hard to predict. Several ternary systems have been measured in recent years both on ground and in space, and new results are included in this issue. Systematic selections of components and compositions give trends in the data that show the effects of the components’ chemical nature. Three papers in this issue cover Thermodiffusion in multi-
component fluid mixtures and solutions. Schraml et al. [1] have studied the highly polar and hydrogen bonding ternary DCMIX3-system water/ethanol/triethylene glycol and their binary borders. They found that the magnitude of the Soret coefficient was related to negative excess volumes of mixing and showed that at least one ternary composition must exist, where all three Soret coefficients vanish simultaneously. In the closely related paper by Ndjaka et al. [2], they study mass (Fickian) diffusion and thermodiffusion in the binary water/triethylene glycol. The effect of gravity may be especially important for multicomponent mixtures. García-Fernández et al. [3] used an ingenious combination of heating the sample from above and shadowgraphy to measure the Soret coefficient in a polystyrene-toluene-cyclohexane mixture. The results were found to be compatible with a positive sign of the Soret coefficient of the polystyrene in the mixed toluene-cyclohexane solvent. Aqueous solutions are important in many industrial processes, and the effects of temperature gradients in salt solutions were reported by Mohanakumar and Wiegand [4] with special attention to hydrogen bonding in the so-called Hofmeister series spanning the range from hydrophilic to hydrophobic salts.

As mentioned above, modeling the Soret effect is challenging. Two papers contribute to Theories and empirical models. Hoang and Galliero [5] have reviewed existing models for the Soret coefficient (or equivalently the thermal diffusion factor) for hard-sphere and Lennard-Jones fluids. They confirm that a thermodiffusion model can be made by adding one term related to the isotope effect and one term related to the “chemical” effects. Furthermore, a kinetic term is required to quantify thermodiffusion from the gas state to the liquid state. They also confirm that although some models work in limited regions of the phase diagram for binary mixtures, a generic model able to accurately predict the Soret coefficient in simple binary mixtures from the gas state to the liquid state is still missing. Díaz-Marquez and Stirnemann [6] used molecular dynamics simulations and showed that the Soret coefficient in dilute aqueous solutions of trimethylamine N-oxide (TMAO), urea, and methanol is sensitive to the relative mass difference between the solute and the solvent, but not to their absolute mass. They found that the mass effect can compensate for the other contributions to the Soret coefficient.

Many experimental techniques have been used to determine Soret coefficients. Most measurements performed today rely on optical detection combined with heating at the boundaries, such as the well-established optical beam deflection (OBD) or optical digital interferometry (ODI), which was also used in the DCMIX microgravity experiments onboard the International Space Station. Multicolor versions of these techniques allow to tackle not only binaries, but also ternaries. Sometimes light is also employed for heating the sample, such as in the transient holographic grating technique TDFRS or in optical lensing. Even the well-understood thermogravitational column technique has recently been miniaturized and equipped with interferometric optical detection. Despite the availability of these and a number of similar methods, there is still a need for Methodological developments. One example for more recent developments is the already mentioned determination of Soret and diffusion coefficients from giant non-equilibrium fluctuations by means of dynamic shadowgraphy. A new, innovative technique was presented by Lee et al. [7]. They used heating of a microwire on a chip to induce a temperature gradient. The concentration of dyed polystyrene particles was detected by confocal microscopy, and the Soret coefficient could be extracted. The authors claim that the chip offers a simple way to study the thermophoretic behavior of biological systems in multicomponent buffer solutions quantitatively. In their paper, Zapf et al. [8] show that shadowgraphy experiments may give incorrect Soret coefficients if the applied temperature difference is larger than the inverse of the Soret coefficient. They also show how the raw data can be processed with a local model that treats the measured shadowgraph signal as a superposition of the contributions from every layer of the sample and how correct results can be extracted.

Thermophoresis of colloids has been a topic of great interest in recent years due to the phenomenon’s importance for understanding transport processes in biological systems, nanomachines, and so-called microswimmers, as well as in the design of analytical devices to test biomolecular binding. Roca-Bonet and Ripoll [9] have developed a model to simulate phoretic Brownian dynamics of swimmers, which helps to understand the subtle interplay of steric interactions, propulsion, and phoretic effects and identify the importance of hydrodynamic interactions in systems of self-phoretic swimmers. Two papers discuss the properties of Janus particles. Avital and Miloh [10] present a theoretical analysis of a laser-heated particle with two conducting hemispheres of different thermal and electric conductivities embedded in a quiescent fluid. The theory was used to map the inner and outer temperature fields in the particle, the heat flux vectors in the two-phase Janus, the light-induced velocity and vorticity fields in the ambient solute, and a new practical estimate for the self-propelling velocity. Bresme et al. [11] used molecular dynamics simulations to study Janus nanoparticles in solution under thermal fields. They showed that mass anisotropy plays a crucial role in driving the thermal orientation of the Janus nanoparticles, contributing substantially to the Soret coefficient of the nanoparticles. A significant enhancement of the Soret coefficient occurs near the solvent critical point, which leads to the complete alignment of a Janus particle in the thermal field. Cherepanov and Smorodin [12] studied flow patterns in a convective cell filled with a colloidal suspension of nanoparticles. The mechanisms of thermodiffusion and gravity settling were analyzed with finite-difference numerical simulations. The spatiotemporal characteristics of stable traveling waves were determined, including how the Rayleigh number depends on
the Lewis number of the stable traveling wave at the limit of the wave’s existence.

Porous systems have been used from the very beginning of experimental work on thermodiffusion. Two papers deal with Thermodiffusion in porous systems. Sioud et al. [13] present an analytical and numerical analysis of species separation in vertical and horizontal porous, cylindrical annular cells. Velocity, temperature, mass fraction fields, and time to reach steady state were determined. They found that the efficiency in terms of species separation was higher for the horizontal column than the vertical column, but the time necessary time to reach steady state in the horizontal column was almost twice as long as for the vertical column. Hafskjold et al. [14] used molecular dynamics simulations to study the combined effects of thermodiffusion and thermo-osmosis in a porous matrix. They showed that both the Soret coefficient and the thermo-osmotic coefficient depend strongly on the porosity for low porosities and that caution should be made in analyzing data from experiments with packed columns.

Overall, this topical issue presents a series of articles providing a flavor of key development in the area of thermodiffusion, thermophoresis and thermo-osmosis in complex fluid mixtures.

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Guest editors

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