

Thermal diffusion in liquid mixtures and polymer solutions

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2004 J. Phys.: Condens. Matter 16 R357

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TOPICAL REVIEW

Thermal diffusion in liquid mixtures and polymer solutions

Simone WiegandForschungszentrum Jülich, Institut für Festkörperforschung-Weiche Materie, Leo-Brandt Straße,
D-52428 Jülich, GermanyE-mail: s.wiegand@fz-juelich.de

Received 23 December 2003

Published 27 February 2004

Online at stacks.iop.org/JPhysCM/16/R357 (DOI: 10.1088/0953-8984/16/10/R02)**Abstract**

Thermodiffusion, also called thermal diffusion or the Ludwig–Soret effect, describes the coupling between a temperature gradient and a resulting mass flux in a multicomponent system. Although Ludwig and Soret discovered the effect in the 19th century, there is so far no molecular understanding of thermodiffusion in liquids. In the past decade the Ludwig–Soret effect has attracted growing interest due to improved experimental techniques, especially modern optical methods, which will be discussed and compared. On the basis of theoretical models, simulations and recent experiments we elucidate some properties and mechanisms contributing to the Soret effect.

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1. Introduction

The prediction of transport properties in liquid mixtures, polymer solutions and colloidal dispersions are of great technical importance [1–5]. In the last decade non-equilibrium effects have become the focus of fundamental research in the field of soft matter. For instance, colloidal model systems in external fields are used to understand non-equilibrium phenomena on a microscopic level [6].

One transport property that has attracted growing interest in the last decade is thermodiffusion, also called thermal diffusion or the Ludwig–Soret effect [7]. This effect describes the coupling between a temperature gradient and a resulting mass flux in a multicomponent system. In an binary fluid mixture with non-uniform concentration and temperature, the mass flow J_m of component 1 contains both contributions stemming from the concentration and from the temperature gradient [8]:

$$J_m = -\rho D \nabla c - \rho c(1-c) D_T \nabla T. \quad (1)$$

D denotes the collective diffusion coefficient, D_T the thermal diffusion coefficient, ρ the mass density, and c the concentration of component 1 in weight fractions. In a stationary state where the diffusion flow J_m vanishes, the Soret coefficient S_T is given by

$$S_T \equiv \frac{D_T}{D} = -\frac{1}{c(1-c)} \frac{|\nabla c|}{|\nabla T|}. \quad (2)$$

Although the discovery of the effect by Ludwig [9] and the first systematic investigations by Soret [10–12] date back roughly 150 and 130 years, respectively, there is so far only a limited microscopic understanding for liquids. While at the beginning of the 20th century the focus was on gases, simple fluids and electrolytes [13], in the last decade the interest has been extended to more complex systems such as polymers, colloidal dispersions and magnetic fluids.

One major technical issue is the modelling of the separation of crude oil components under the influence of thermal diffusion and convection in geological fields [14]. Today the effect is also used in technical instruments, such as thermal field flow fractionation for polymer characterization [15, 16]. Primarily, the growing interest in recent years is due to improved experimental techniques, like state-of-the art thermogravitational columns [17], modern optical methods [18, 19], flow channels [20], and microgravity experiments [21], to mention only a few. In addition, simulation techniques for non-equilibrium properties have been improved, which have led for the first time to a reasonable agreement between simulations and experiments [22, 23].

A summary of the classical experiments for measuring the Soret coefficient can be found in the book by Tyrell [13]. There are two kinds of instrument. The first kind serves mainly an analytical purpose. The experimental challenge in those instruments is to establish stable thermal and mechanical conditions and to avoid convection processes which lead to a re-mixing of the components. Thermal diffusion cells belong to this category. The cells are cooled from below and heated from above. The concentration profile can either be monitored by optical detection using the Schlieren method [24–26] or by analysing samples which have been sucked out from the cell [27, 28]. Early experiments were performed by Tanner in 1927 [24] and later by Nachtigall and Meyerhoff [25, 26]. They employed an optical analytical method, which

is obviously preferable because it does not disturb the transport process. Nevertheless this is not absolutely necessary. It is also possible to divide the solution carefully into different layers by suction with a microsyringe [27, 28]. In modern thermal diffusion cell experiments, the deflection of a laser beam is analysed [29, 30]. Over the last few years a transient holographic grating technique, which is based on forced Rayleigh scattering, has been utilized to study the thermal diffusion process in liquid mixtures, polymer solutions and colloidal suspensions [18, 19]. In these experiments an intensity grating is created by the interference of two laser beams. The generated temperature grating and the resulting concentration grating are probed by the diffraction signal of a third laser beam.

The intended purpose of the second kind of instrument is to achieve large separation ratios. The prime example for the second class are thermogravitational columns, which consist of two vertical concentric cylinders with the annular space being filled with a gaseous or fluid mixture. In many mixtures the separation ratio is enhanced due to an overlaying convection process, which drives the fluid at the hot wall to the top and at the cold wall to the bottom. In some mixtures, e.g. in cyclohexane/toluene, the concentration density gradient is opposite to the temperature density gradient and results in a poor separation ratio or a transport of the fluid at the hot wall to the bottom [31]. This effect is also termed the *forgotten effect*. The functionality of a 36 m-high gravitational column was first demonstrated by Clusius and Dickel [32, 33]. Modern state-of-the-art gravitational columns have typical lengths between 30 and 50 cm. Convection can be accounted for, so that the determined values for the Soret coefficient compare well with those of other instruments [34–36].

This topical review is organized as follows. In section 2 we give a short survey of theoretical concepts and simulations for liquid mixtures, polymer solutions and colloids. Then, in section 3 we discuss several optical methods to study thermal diffusion. Recent experimental results which gain some insight into the nature of thermal diffusion are discussed in section 4. In the last section we will summarize and discuss some aspects which determine the thermophoretic behaviour. Based on these observations it might be possible to develop a microscopic understanding of the Soret effect within the next decade.

2. Recent theoretical approaches and simulations

2.1. General

Thermal diffusion in liquid mixtures is not well understood. Classically, the Onsager formalism is used to describe the Ludwig–Soret effect [8]. The thermal diffusion process in gaseous mixtures can be described by the Chapman–Enskog theory. In classical theory for hard-sphere mixtures some trends for the thermal diffusion coefficient can be derived: (i) in mixtures of different mass species, the heavier component diffuses towards the cooler region; (ii) if the species have roughly equal masses, then the larger component diffuses into the cooler region. These trends are no longer valid if soft interactions are involved. Sign changes in the dependence of temperature can be observed for gaseous mixtures [37, 38]. Attempts to extend the Chapman–Enskog theory from gaseous mixtures to explain the complex thermodiffusive behaviour in the liquid state have not been successful [39].

For liquids with specific interactions such as hydrogen bonds in particular, it is often not possible to predict the sign of S_T correctly. For some systems, Prigogine *et al* [40] explained qualitatively a sign change of S_T in low molecular mixtures using a free energy concept. They found that a model based on potential energies of nearest-neighbour interactions alone led to contradictions when applied to alcohol mixtures, where the Soret coefficient changes sign. They emphasized that it is not sufficient to only discuss energetic contributions and argued that the entropic contributions also need to be considered. By assuming that alcohol

molecules form complexes whose disruption results in a loss of local energy and a gain in local entropy, they were able to explain qualitatively the sign change of the Soret coefficient for these systems. This is a phenomenological approach, however, that does not lead to a microscopic understanding of thermal diffusion.

So far, for dense systems limited work has been done to express such Onsager coefficients for temperature gradients induced diffusive mass transport in terms of molecular interaction potentials. For molecular mixtures, where interaction potentials are inherently temperature independent, Bearman *et al* [41] derived microscopic expressions for the Soret coefficient on the basis of the binary Liouville equation. The results of this work are not in a form that allows for a direct comparison with experiments.

2.2. Simulations of liquid mixtures

Molecular dynamics (MD) simulations have become an important tool in the investigation of thermodiffusion in small-molecule liquids. For a detailed review on simulation methods see [22]. During the 1980s, many approaches based on irreversible thermodynamics and non-equilibrium statistical mechanics have been developed to compute the Soret coefficient in binary mixtures using MD methods. The corresponding transport coefficients can be obtained from the Green–Kubo (GK) formulae and equilibrium molecular dynamics (EMD) [42] or synthetic non-equilibrium molecular dynamics (S-NEMD), also called homogeneous non-equilibrium molecular dynamics [23, 43, 44]. One can also mimic the real thermal diffusion experiment by modifying the conditions at the boundaries of the simulation box [45]. This method is called boundary driven non-equilibrium molecular dynamics (BD-NEMD) or direct NEMD. However, most of the work has been devoted to the improvement of simulation methods which than have been applied to Lennard-Jones (LJ) fluid mixtures [45–48]. The attempt to reveal at least the nature of thermal diffusion leads to the result that heavier species, smaller species and species with higher interaction strengths, tend to accumulate at the cold side [45, 46]. The size influence on the Soret effect is so far not understood and is controversially discussed [49]. Bordat *et al* confirmed [47] that the larger species move to the warm side regardless of the shape of the chosen Lennard-Jones potential. They noticed that the Soret effect is considerably smaller at supercritical densities compared to dense liquid. Furthermore, details of the attractive tail of the Lennard-Jones potential are important. The Soret coefficient decreases by changing from a full Lennard-Jones potential to a cutoff LJ potential with a much shorter range. This results agree with experimental results in gaseous systems [37, 38].

There have been two attempts to compute the Soret coefficient in molecular liquids: one comes from the work of Hoheisel and co-workers on CF_4/CH_4 mixtures and benzene/cyclohexane using EMD [50, 51]. The authors report some data on mutual diffusion coefficients but only qualitative values were obtained for the Soret coefficients due to strong uncertainties even with long simulation runs. More recently, Simon *et al* [52] were able to compute the Soret coefficient in methane/decane mixtures using BD-NEMD with higher statistical sampling than Hoheisel.

Only in 2001 did Perronace *et al* [53] find reasonable agreement between simulation and experiments. Soret coefficients and mass diffusion coefficients of three weight fractions of *n*-pentane/*n*-decane mixtures were measured with a transient holographic grating technique (see section 3.3) and compared with results from molecular dynamics simulations. From figure 1 it follows that the experimental Soret coefficient only exhibits a weak dependence on the composition of the mixtures. It can be seen that the values of the Soret coefficient obtained by synthetic S-NEMD and BD-NEMD methods are in remarkable agreement with the experimental results [53].

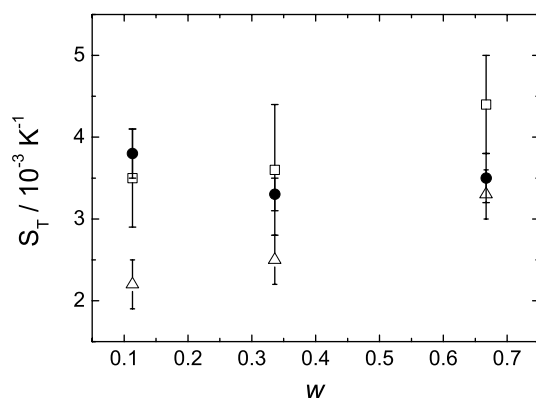


Figure 1. Experimental (●), synthetic S-NEMD (□) and BD-NEMD (△) data of the Soret coefficient S_T of n -pentane/ n -decane mixtures as a function of the n -pentane weight fraction at 300.15 K. Error bars represent the standard deviation of the mean [53].

Recently, Soret coefficients of aqueous solutions have been calculated by molecular dynamics simulations [54, 55]. The obtained data for ethanol/water and methanol/water showed quantitative agreement with experimental data. The subsequent theoretical analysis of the data revealed that large specific interactions are required to show a sign change in the thermophoretic behaviour. Cross interactions have to be larger than the interactions between the pure compounds. They argued that if crossed interactions are stronger than pure interactions, the minor component, for example 1, will tend to concentrate in the cold region due to the fact that this will lower the total energy of the system. When component 1 is very dilute, only the cross interaction ϵ_{12} will compete with the pure interaction (ϵ_{22}) of the other constituent 2. On the other hand, if the concentration of 1 increases to the point of being in the majority, then the constituent 2 will also tend to concentrate in the cold region for the same energetic considerations. In this case, the thermal diffusion factor changes its sign when the concentration of the mixture is changed between these two limiting cases. A similar energetic argument was also derived from a two-chamber lattice calculation [56] for ethanol/water mixtures and poly(ethylene oxide) in a ethanol/water mixture [57, 58].

2.3. Theoretical concepts for polymers

Several scaling concepts have been developed to explain the independence of D_T on the degree of polymerization. The question to be addressed in this topical review is whether these scaling concepts which are typically applicable for polymers with at least 100 repeating units, are necessary to explain the independence on the degree of polymerization. If this is a polymeric property, one should observe deviations for sufficiently short chains. If D_T remains constant down to very small molecular weights, no polymer concept is needed (compare with section 4.3).

A microscopic approach, based on the Smoluchowski equation for a single polymer chain, has been used by Khazanovich [59] to describe thermodiffusion of non-interacting polymers. He predicts that D_T depends on the polymer segmental diffusion coefficient D_{seg} , the activation energy for the solvent viscous flow U_S , the gas constant and the temperature, as $D_T = U_S D_{\text{seg}} / (RT^2)$. The theoretical concept is based on the Rouse model. In this bead-spring model the polymer consists of n beads which are connected by springs. The beads are far enough apart so that they act essentially independently of one another which means

that hydrodynamic interactions between the beads can be neglected. If such a coil is forced to move through a viscous fluid, each bead will be subjected to a frictional resistance that is independent of the other monomers. The effective friction coefficient f of the coil as a whole will be proportional to the number of monomers in the coil, and thus proportional to M . Similarly, the thermophoretic force F_{th} , the force on the chain due to a temperature gradient, is proportional to the number of chain segments. The velocity U_{th} associated with this motion which we call thermodiffusion, can be represented by $U_{\text{th}} = F_{\text{th}}/f$ which is consequently independent of M . Recently, Schimpf and Semenov [60] extended the treatment and derived the following expression for the thermal diffusion coefficient:

$$D_{\text{T}} = -\frac{16\alpha_{\text{T}}r_{\text{m}}^2 A}{27\eta v_0} \quad (3)$$

for dilute solutions of flexible polymers. The parameters α_{T} , η and v_0 are the thermal expansion coefficient, viscosity and molar volume of the solvent, respectively. The effective radius of a polymer segment is given by r_{m} , and A is the Hamaker constant for the polymer–solvent interactions. Using this approach [60, 61] it is found that the Hamaker constants calculated from experimental D_{T} values are several times smaller than the tabulated ones, which is equivalent to overestimating the thermal diffusion coefficient.

De Gennes's explanation of the independence of U_{th} from M in polymers is based on the Dufour effect [62] that describes a temperature change caused by concentration gradient. He formulated the heat flux in a concentration gradient that arises from two factors, the friction of each monomer in the pearl-necklace model and the flow of the solvent. A uniform flow of solvent does not produce any heat flux in diluted polymer solutions. The expressions for heat flux indicate that it is the second-order spatial derivative of the solvent velocity that is responsible for heat flux which is localized around the source of friction at each monomer, and not the entire chain. Consequently, the heat flux associated with mass flux (the so-called *Dufour effect*) is independent of the number of monomers. Using the Onsager reciprocity relationship, the mass flux associated with heat flux must also be independent of the number of monomers. Thus, the solvent acts with each monomer essentially independently in a temperature gradient.

In general, all scaling concepts for polymers fail for short chains with less than 100 repeating units [63]. If a similar value for D_{T} was observed in dilute solutions of oligomers as for long chains with 100 or more repeating units, this indicates that a different non-polymer concept would be needed to explain the effect. Furthermore, it remains to be answered if and at what point the end groups and the structure of the oligomer, i.e. the arrangement of the smallest units of the oligomer chain, influence the thermodiffusive behaviour. Besides the polymer concepts, another working hypothesis would be to assume that the microscopic mechanism underlying the thermal diffusion process depends on the heat transport between the polymer and the surrounding solvent. Due to the fact that the process is insensitive to an attached repeating unit and its position, it is probably of the order of a monomer diameter. Therefore, we might also expect the same behaviour for chain molecules as alkanes which have the advantage of being much better defined than the oligomers.

Recently, Luettemer-Strathmann [56, 57] developed a two-chamber lattice model for thermodiffusion in liquid mixtures and dilute polymer solutions. She applied this model for mixtures of poly(ethylene oxide) (PEO), ethanol and water. In this model the compressibility and hydrogen bonding between PEO and water molecules are taken into account. Soret coefficients have been calculated for a given temperature, pressure and solvent composition. It was found that the Soret coefficient of PEO changes sign from negative (polymer enriched in warmer region) to positive (polymer enriched in cooler region) as the water content of the solution is increased. This is in good agreement with experimental data [58, 64].

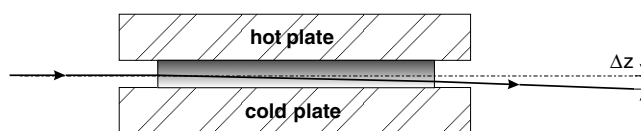


Figure 2. Schematic drawing of a thermal diffusion cell.

2.4. Thermal diffusion of colloids

Thermal diffusion of ionic ferrocolloids and colloids stabilized by a surfactant layer and charge stabilized colloids has been theoretically investigated by Morozov [65, 66]. In this work interactions between colloids are not taken into account. The prediction is that the colloids move to the cold side.

Bringuier and Bourdon derived expressions for Soret coefficients of colloids in a solvent using the kinetic theory of Brownian motion [67]. They find that particle movement is strengthened or reversed by a temperature-dependent interaction potential. They consider diluted and concentrated colloidal suspensions but no hydrodynamic interactions.

Very recently Dhont [68, 69] developed a microscopic approach to thermodiffusion, where the contribution of inter-colloidal interactions to the thermal diffusion coefficient are considered. This contribution to the thermal diffusion coefficient is expressed in terms of the pair-potential of mean force. The temperature dependence of the potential of mean-force is shown to give rise to sign changes of the Soret coefficient on changing the temperature and/or concentration under appropriate conditions.

2.5. Thermal diffusion close to the critical point

Theoretically a divergence of $S_T = D_T/D$ is expected when the critical point is approached. The mutual diffusion coefficient D varies with $t_{\text{red}}^{\nu(1+z_\eta)}$ in the asymptotic range [70, 71]. Here, $t_{\text{red}} = (T - T_c)/T_c$ denotes the reduced temperature and $\nu = 0.63$ and $z_\eta \approx 0.063$ are the critical exponents for the correlation length and viscosity, respectively. According to theory, the thermal diffusion coefficient D_T shows no critical enhancement [70, 71].

3. Working principles of experimental methods

In this topical review we will focus on optical techniques to investigate the thermal diffusion processes in liquid mixtures, polymer solutions and colloidal suspensions. Most of the methods work in the absence of convection. Exceptions are laser Doppler velocity experiments in Rayleigh Bernard cells [72] and thermogravitational columns [73]. In order to analyse the thermogravitational data, a correction factor which accounts for convection needs to be determined by a numerical simulation. In practice it was demonstrated that for both geometries the obtained values compare well with those obtained in convection free cells. A drawback of these experiments are long equilibration times even for low molecular mixtures of several hours. If those gravitational columns are additionally packed with porous media, the equilibration takes up to 40 days [14].

3.1. Diffusion cells

In thermal diffusion cells the thermal gradient in the mixture under consideration is induced by a heated top and a cooled bottom plate. The concentration changes induced by the temperature

gradient are probed nowadays by the deflection of a laser beam, which traverses the sample parallel to the plates. A schematic sketch of a thermal diffusion cell is shown in figure 2. Typically the gap distance is $h = 2$ mm. The time constant τ to reach the steady state is given by $\tau = h^2/(\pi^2 D)$. For low molecular mixtures, this results in equilibration times of approximately $\tau = 10$ min and for polymeric systems of 10 h and more. These fairly long equilibration times require excellent temperature control and stability of the cells. One important issue is a constant temperature over the full probing length of the laser. Due to the unavoidable temperature gradient end effects at the edge of the plates it is preferable to use larger plates hanging over the part containing the sample, as schematically sketched in figure 2. Putnam and Cahill [75] have developed an ac beam deflection technique for measurements of thermodiffusion in liquid mixtures. Due to a micrometre-scale geometry the apparatus speeds up equilibration times by a factor of approximately 300. The determined values for a 50 wt% binary mixture of dodecane and 1,2,3,4-tetrahydronaphthalene [76] agreed within a few per cent with the results obtained in a benchmark test by different methods for the same mixture [36].

Thermal diffusion cells have been used to investigate low molecular mixtures [29, 74, 77] and polymer solutions [30]. Giglio and Vendramini performed systematic measurements to study the critical behaviour of an aniline/cyclohexane mixture [78] in a thermal diffusion cell. For carefully designed cells the data obtained for low molecular mixtures, e.g., toluene/*n*-hexane [29], compare well with other techniques as thermogravimetric columns [17] and holographic grating techniques [79], which will be discussed in detail in section 3.3.

3.2. Thermal lens method and Soret feedback

There are very few experiments which utilize the thermal lens effect to measure the Soret coefficient. In contrast to the previously discussed thermal diffusion cells with boundary heating and cooling, in a thermal lens experiment the laser beam itself is used for heating and detection simultaneously. Figure 3 illustrates schematically a typical thermal lens set-up. The local heating of the laser beam usually creates a concave lens in liquids, if the refractive index is decreasing with increasing temperature. An exception is the thermal lens in water which changes a converging lens to a diverging lens with temperature [80]. Due to the Soret effect one additionally observes the formation of a concentration lens. The sample is either fixed in position or it is moved through the focal region in a so-called *Z*-scan experiment [81].

Giglio and Vendramini [82] were the first to notice that the thermal lens in a binary mixture was noticeably larger than in the two pure components. Hardcastle and Harris [83] observed, with the thermal lens set-up, an increase of the Soret coefficient in the mixture 2,6-dimethylpyridine/water close to the critical point. Arnaud and Georges studied in several papers the influence of the Soret effect on the thermal lens [84–86], but their working equations lead only to a qualitative understanding of the Soret coefficient. Recently Alves *et al* [81] performed a *Z*-scan experiment and generalized the thermal lens formalism by including third order non-linear optical effects.

An advantage of the thermal lens method compared to the diffusion cell is the shorter equilibration times of $\tau \approx \omega_F^2/(4D)$ due to smaller distances in the order of the focal beam width $2\omega_F$. For polymeric systems with typical diffusion constants of the order $D = 10^{-7}$ cm² s⁻¹ this leads to equilibration times of $\tau < 100$ s for a focal beam width of $2\omega_F = 100$ nm. As already observed in thermal diffusion experiments in pure liquids [87], the onset of convection leads to a skewed Gaussian profile. It has been suggested that these convection effects might be reduced by a horizontal arrangement of a very thin sample cell ($d = 0.1$ mm) [88].

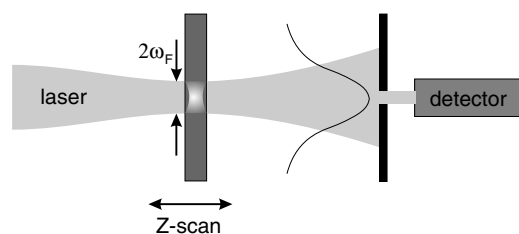


Figure 3. Schematic drawing of a thermal lens experiment.

Unfortunately, the data base for Soret coefficients obtained with the thermal lens method is rather small. The data Alves *et al* [81] determined for an ionic ferrofluid agreed with those they measured in a forced Rayleigh scattering experiment [81]. In contrast, Voit [88] did not find agreement with other methods. The Soret coefficient S_T of the binary mixture *n*-dodecane/1,2,3,4 tetrahydronaphthalene was more than 40% smaller [88] than the literature values, which had been confirmed in a benchmark by several groups with several methods [36]. In the case of a polymer solution polystyrene/toluene, the value obtained in the thermal lens experiment is only one third of the literature value [88, 89].

A special case of the thermal lens method is the investigation of strongly absorbing fluids. Luo *et al* and Tabiryian *et al* investigated the lensing effect in absorbing ferrofluids [90–92]. They observed a bleaching of the sample and suggested a Soret-type motion of the magnetic colloids out of the heated path of the laser beam. This so-called Soret feedback eventually limits the achievable temperature within the laser beam. Starting from this picture, Hoffmann and Köhler derived an analytical expression that connects the time-dependent optical transmission with the sought-after Soret coefficient. Additionally, they proved that the bleaching is caused by thermophoretic migration of the absorbers out of the laser beam and not by a photo reaction. Within the accuracy of this simple model, their thermal diffusion coefficients agree well with the values obtained for similar ferrofluids in thermogravitational columns [93].

Recapitulating one can say that thermal lens experiments have the advantage of much shorter equilibration times compared to diffusion cells and thermogravitational cells. The disadvantage of the method seem to be its sensitivity to convection and the fact that no single scattering vector q can be selected, as in the case of the grating experiments (cf section 3.3). In particular, in the last five years many experimental aspects of the thermal lens method have been investigated and the theoretical treatment has been improved. Certainly, further improvements in experiment and theory are necessary to obtain reliable values for the thermophoretic properties by thermal lens experiments in all systems.

3.3. Holographic grating techniques

In the last decade many experiments have been performed to study the thermal diffusive behaviour with a transient holographic grating technique. This technique might also be called thermal diffusion forced Rayleigh scattering (TDFRS) because of the thermophoretic contribution. Figure 4 shows a schematic sketch of a set-up. The measurement principle is the following: a grating created by the interference of two laser beams is written into a sample. A small amount of dye present in the sample converts the intensity grating into a temperature grating which in turn causes a concentration grating by the effect of thermal diffusion. Both gratings contribute to a combined refractive index grating, that is read out by diffraction of a third laser beam. Analysing the time dependent diffraction efficiency, three transport

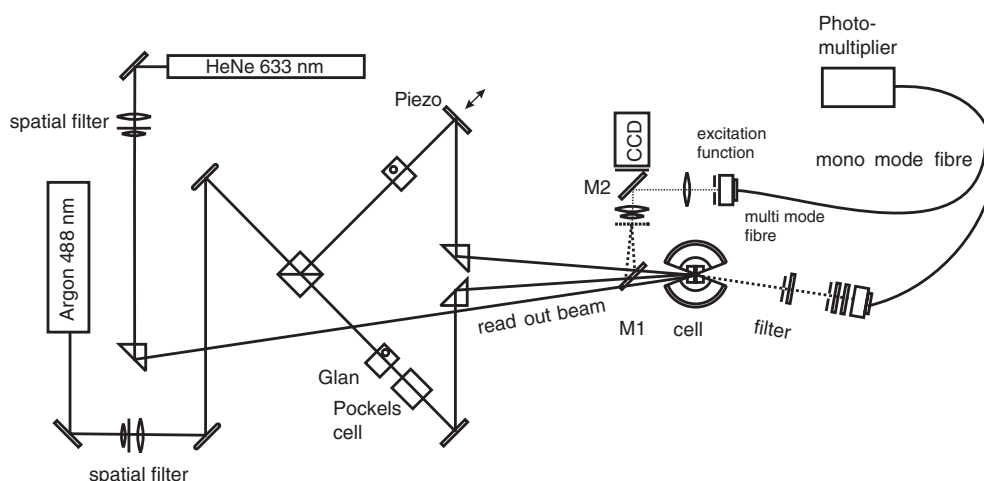


Figure 4. Schematic drawing of a thermal diffusion forced Rayleigh scattering (TDFRS) set-up.

coefficients can be obtained: the thermal diffusivity D_{th} , the translational diffusion coefficient D and the thermal diffusion coefficient D_T . The thermal diffusivity is the diffusion coefficient that controls the dynamics of heat dissipation in the heat equation. It can be expressed as $D_{th} = \kappa / \rho c_p$ with the thermal conductivity κ , the density ρ and the specific heat c_p . The ratio of the thermal diffusion coefficient and the translational diffusion coefficient also allows then the determination of the Soret coefficient S_T .

Thyagarajan and Lallemand [94] were the first to observe a fast heat and a slow concentration mode in a forced Rayleigh scattering experiment which had previously been predicted by Allain and Lallemand [95]. The slow mode stems from a concentration grating, which is induced by the holographic temperature grating that is written into the solution. Later, Pohl studied a critical mixture of 2,6-lutidine/ H_2O with the same technique [96]. Over the last few years the TDFRS has been improved [18, 19] and has been employed for the investigation of different systems such as liquid mixtures [79] and liquid mixtures near the critical point [97, 98], mono- and polydisperse polymer solutions [99], and colloidal suspensions [100, 101]. Recently, studies on magnetic colloids have been reported utilizing forced Rayleigh scattering [102, 103].

A conceptually different grating technique to study the thermodiffusive mode has been developed by Takagi and Tanaka [104]. By frequency modulation of the writing laser beam they create a moving grating. From the half-width at half maximum of the resonance they can determine the thermal diffusivity D_{th} . This method also allows the determination of the Soret coefficient [105, 106], but it has not been realized yet.

The TDFRS method has been validated within the framework of a benchmark test, which was initiated to compare experimental results of the investigation on thermal diffusion in binary organic and aqueous solvent mixtures by different techniques. The Soret, diffusion and thermal diffusion coefficients of three binary mixtures of dodecane, isobutyl benzene and 1,2,3,4 tetrahydronaphthalene for a concentration of 50 wt% at a temperature of 25 °C have been measured [36]. The experimental techniques applied by the five participating laboratories were transient holographic gratings [107, 108], annular and parallelepipedic thermogravitational columns [34, 35] and vertical parallelepipedic columns with velocity amplitude determination by laser Doppler velocimetry (LDV) [34]. The agreement between the different experiments

was fairly good, the deviations are of the order of a few per cent in most cases (8.5% at most) for all three thermophoretic coefficients [36].

The spacing between the high temperature region and the low temperature region in the TDFRS experiment, given by the fringe spacing of the grating, is of the order of several micrometres for small angles of a few degrees between the two writing beams. This leads as in the thermal lens method to fast equilibration times of several hundred milliseconds. The temperature modulation of the grating is typically of the order of 20 μK . The relative concentration changes, which are detectable, are of the order of $\delta c/c \approx 10^{-5}$. Therefore the TDFRS method is a reliable sensitive method to investigate the thermophoretic behaviour of liquids. The equilibration times for systems with slow dynamics, as polymer solutions and colloidal suspensions, remain quite reasonable.

4. Some results for liquid mixtures and polymer solutions

4.1. Liquid mixtures

In the past the experimental methods were often not reliable due to convection problems. Only in recent years has it been possible to investigate the thermal diffusion behaviour of liquid mixtures and solutions systematically.

Table 1 summarizes the Soret coefficients for some selected binary mixtures. For components 1 and 2 the difference in molar mass $\Delta M = M_1 - M_2$, density $\Delta\rho = \rho_1 - \rho_2$ and Hildebrandt parameter $\Delta\delta = \delta_1 - \delta_2$ are listed. The solubility of organic compounds can be obtained from the Hildebrandt parameter δ [110], which can be estimated according to $\delta = \sqrt{(\rho(\Delta H_v - RT))/(M)}$ with the gas constant R and enthalpy of vaporization H_v . The solubility parameter concept works reasonably well for non-polar solvent, but it fails for polar solvents and systems with specific interaction. It is intuitively expected that the solubility is related to the Soret coefficient S_T . If two non-polar solvents have a large tendency to separate, indicated by a large difference in δ , we also expect that the two compounds try to separate more easily in a temperature gradient, which corresponds to a large Soret coefficient.

This tendency is reflected for the first three binary systems listed in table 1. The three compounds were chosen so that they can be fairly reasonably mapped onto a Lennard-Jones fluid. Lennard-Jones simulations [116] of the three binaries confirm the trend that the largest Soret coefficient is found for the system *cis*-decalin/2-methylbutane which has the largest difference $\Delta\delta$. For these three systems the component with the larger mass M and larger density ρ moves to the cold side.

The Hildebrandt criterion is only a crude rule of thumb, as can be seen in the second group of systems listed in table 1. The systems selected here are still non-polar but they cannot be so easily mapped to a Lennard-Jones sphere. The component with the larger mass and larger density still moves to the cold side, which is in agreement with the observations and theory in gases, but the largest Soret coefficient is not found for the system with the largest difference $\Delta\delta$ but the largest difference in M .

The third group of systems contains an alkane, a one-ring and a two-ring component. All compounds are non-polar and the three binaries have been extensively investigated in a benchmark test by various methods [36]. For these systems the component with the larger density moves to the cold side, but not the component with the larger mass.

Even the examination of fairly simple solvents without specific interactions shows clearly that there is no simple relation between the Soret coefficient and other physical properties. There are some rules of thumb in that typically the component with the larger mass or higher density moves to the cold side, and that the effect becomes stronger if the components are not easily soluble.

Table 1. Soret coefficients S_T for some selected binary mixtures of those pure liquids in relation to the difference in mass M , density ρ and Hildebrandt parameter δ . The reference book [109–111] used for physico-chemical properties of the pure component is specified for each substance in the table. The concentration of the mixture is either specified by the weight fraction w or the molar fraction x . The reference listed refers to the measurements of S_T .

Component 1/component 2 composition	T (K)	S_T (10^{-3} K^{-1})	ΔM (g mol^{-1})	$\Delta\rho$ (g cm^{-3})	$\Delta\delta$ ($\text{J}^{1/2} \text{ cm}^{-3/2}$)
<i>Cis</i> -decalin [109]/ 2-methylbutane [110, 111] ($w = 0.5$) [112]	295	11.3	63	0.2731	3.9
Cyclohexane [110, 111]/ 2-methylbutane [110, 111] ($w = 0.5$) [112]	295	4.7	9	0.1584	2.8
<i>Cis</i> -decalin [109]/ cyclohexane [110, 111] ($w = 0.5$) [112]	295	3.5	54	0.1146	1.1
Toluene [109]/ <i>n</i> -hexane [109] ($w = 0.517$) [17, 29, 79]	296	4.98	5.9	0.207	3.8
Nonadecane [110, 111]/ <i>n</i> -hexane [109] ($x = 0.15$) [61, 113]	295	7.31 ± 0.11	182.3	0.1306	2.2
<i>n</i> -decane [109]/ <i>n</i> -pentane [109] ($w = 0.663$) [53]	300	3.27 ± 0.23	70.05	0.1049	1.4
1,2,3,4-tetrahydronaphthalene [109]/ <i>n</i> -dodecane [109] ($w = 0.5$) [36]	298	9.5 ± 0.5	−38.1	0.2116	3.4
1,2,3,4-tetrahydronaphthalene [109]/ isobutylbenzene [111] ($w = 0.5$) [36]	298	3.3 ± 0.3	−2	0.1166	4.9
Isobutylbenzene [111]/ <i>n</i> -dodecane [109] ($w = 0.5$) [36]	298	3.9 ± 0.1	−36.1	0.095	1.7
Ethanol [109]/ water [109] ($w = 0.5$) [73, 74, 114]	296	5.55 ± 0.5	28.1	−0.2422	−21.9
Benzene [109]/ cyclohexane [110, 111] ($x = 0.5$) [115]	293	−1.8	−6.1	0.0905	2.1

The situation becomes even more complicated when specific interactions play a dominant role. A well-established example is the mixture ethanol/water. As can be seen in figure 5, the Soret coefficient changes sign at a weight fraction of water $w \approx 0.7$. If the water content is lower, the water molecules move to the cold side and in water rich solutions the water molecules migrate to the warm side. There are quite a number of liquid mixture which change their thermal diffusion behaviour with concentration. As explained in section 2.1, Prigogine *et al* [40] explained qualitatively a sign change of S_T in the alcoholic mixtures

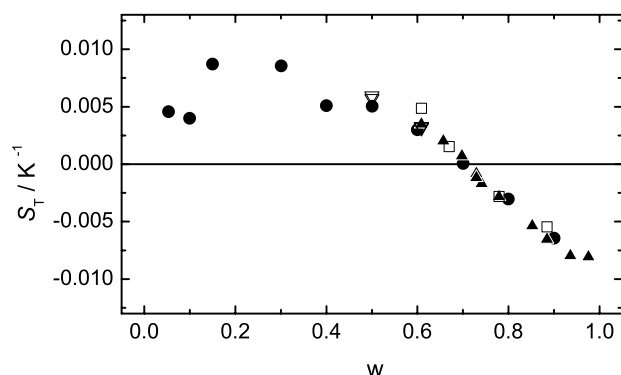


Figure 5. Soret coefficient S_T of water/ethanol as a function of weight fraction of water w for a binary system [114] at 20 °C (●), [74] at 20 °C (▲), [117] at 25 °C (□) and [73] at 22.5 °C (▽).

methanol/benzene, ethanol/cyclohexane and hexanol/cyclohexane using a free energy concept. For aqueous solutions also the potential energy argument discussed in section 2.2 works nicely.

Finally, we want to discuss recent measurements of benzene and cyclohexane and its isotope substitutes. In an experimental study [115] two distinct contributions to the Soret coefficients could be identified. The first contribution, due to differences in the molecules' masses (M_1 , M_2) and moments of inertia (I_1 , I_2 , largest eigenvalue of the inertia tensor), was found to be independent of composition of the mixture. The second, reflecting chemical differences of the molecules, was found to vary with composition and change sign, inducing a sign change of the total Soret coefficient. In [115] the following empirical formula is proposed:

$$S_T = a_M \delta M + b_I \delta I + S_T^0 \quad (4)$$

with $\delta M = (M_1 - M_2)/(M_1 + M_2)$ and $\delta I = (I_1 - I_2)/(I_1 + I_2)$ are the normalized differences of the mass and moment of inertia. The quantity S_T^0 has been added to account for a finite Soret effect that would be still be present even if benzene and cyclohexane could be made identical with respect to mass and moment of inertia. S_T^0 accounts for the chemical difference in the systems and might be called the *chemical contribution* to the Soret coefficient. While the chemical contribution and mass dependence have already been introduced for gaseous mixtures [118] and have been observed in molecular dynamic simulations [46], the dependence of the moment of inertia was never been predicted before. The question that arises here is whether the dependence of the Soret coefficient on the moment of inertia is a universal feature or a specific property of the investigated systems.

Recapitulating, we can say that the situation is already quite complicated for low molecular weight mixtures. While the behaviour of non-polar systems of fairly spherical compounds is to some extent predictable, simple concepts fail in the presence of specific interaction. Those specific chemical interactions seem to be responsible for sign changes in the thermophoretic behaviour.

4.2. Liquids close to the critical point

The first qualitative measurements of the Soret coefficient in the critical binary mixture nitrobenzene/*n*-hexane were performed by Thomaes [119]. Later, Giglio and Vendramini performed systematic measurements using an optical diffusion cell [78]. For the system aniline/cyclohexane they determined a critical exponent of $\varphi = 0.73$ for the divergence of $S_T \propto (T - T_c)^{-\varphi}$, while the thermal diffusion coefficient D_T remains constant with temperature

(see also [70]). Pohl [96] was the first to apply the holographic grating technique to a critical mixture 2,6-lutidine/water. He showed for two temperatures below and two temperatures above T_c that the dynamical behaviour changed.

Due to the possibility of choosing a very narrow fringe spacing of a few micrometres, and because the temperature difference can be as low as a few microkelvin, the TDFRS technique appears suitable for critical mixtures. The first systematic measurements of the Soret coefficient using the TDFRS technique were recently performed for the binary mixture aniline/cyclohexane [97, 98]. The strong scattering of the sample requires an additional beam as local oscillator for heterodyne phase tracking [19].

The first check for the reliability of TDFRS measurements on critical mixtures is to study the influence of the addition of dye. It is known that a third component modifies the critical concentration, critical temperature and the asymptotic critical behaviour [120]. In order to adjust the optical density (OD) of toluene to $OD = 1$ one needs 0.0035 wt% quinizarin. For the investigated system aniline/cyclohexane it was checked that the critical weight fraction $w_c = 0.470 \pm 0.001$ and temperature $T_c = 302.87$ K remained unchanged within the experimental accuracy. The criticality of the sample was checked by the equal volume criterion 0.01 K below the critical temperature and was also not influenced by the addition of the dye. Therefore we do not expect a change in universal critical behaviour of the system [120].

The temperature stability during the measurements in the TDFRS set-up was 2 mK over 24 h. In order to avoid convection, sample cells with a thickness of 0.2 mm were used. The cells were carefully sealed with a combination of Teflon stoppers, Teflon tape and finally fixed by some glue, which did not come into direct contact with the sample. Nevertheless, although no weight loss was noticed during the measurement, the sample needed to be replaced by a fresh sample from a large critical batch after 2–3 days. The reason was a colour change of the sample from pale yellow to yellow–red due to oxidation of the aniline.

It was shown that the Soret coefficient diverges as $S_T \propto (T - T_c)^{-\varphi}$ with $\varphi = 0.68 \pm 0.03$ [97, 98]. The investigated temperature closest to the critical point was roughly 1.2 K away from the critical temperature. The results obtained very close to the critical point scatter over a large range. The most likely explanation for the poor reproducibility are persistent concentration gradients. Unfortunately, the small sample cells required for convection minimization allow no stirring in order to resolve the gradients. Presumably these gradients are mainly caused by global heating in the beam path during the measurement, which is of the order of 0.5 K and three orders of magnitude larger than the temperature difference between the hot and cold stripes within the beam.

Figure 6 shows the Soret coefficients S_T determined by the TDFRS technique in comparison with S_T values calculated from the thermal diffusion ratios k_T given by Giglio and Vendramini [78] by using the relation $S_T = k_T/(Tc(1 - c))$.

It can be concluded that the TDFRS technique is suitable to study critical mixtures. In order to measure very close to the critical point, it would be advantageous to use some kind of flow cell, which allows the continuous replacement of the sample from a large reservoir, which can be stirred. Much improvement is expected from sapphire windows, which, due to their high thermal conductivity, largely reduce the overall sample heating caused by the absorbed laser light.

4.3. Polymers

4.3.1. Non-polar polymer solutions. An interesting observation is the independence of D_T on the degree of polymerization for polymers in solution. This independence was demonstrated

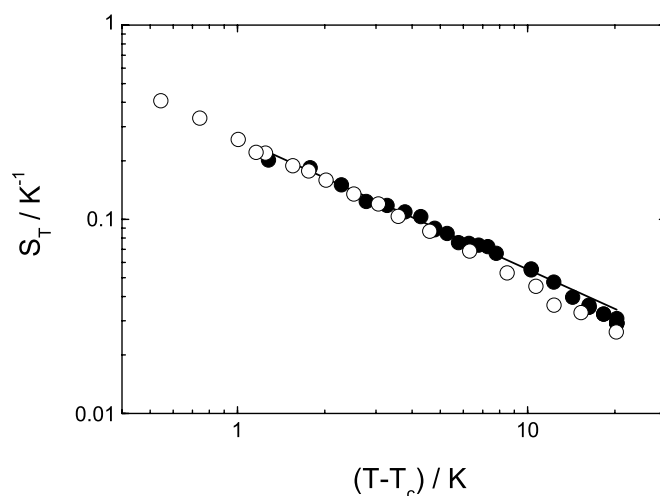


Figure 6. Soret coefficient S_T of aniline in cyclohexane at critical composition (●) measured for the binary critical mixture aniline/cyclohexane versus the reduced temperature. The solid line represents the fit to the experimental data points. For comparison, we show the estimated values for S_T (○) using the displayed thermal diffusion factors α_T in figure 2 of the paper by Giglio and Vendramini [78].

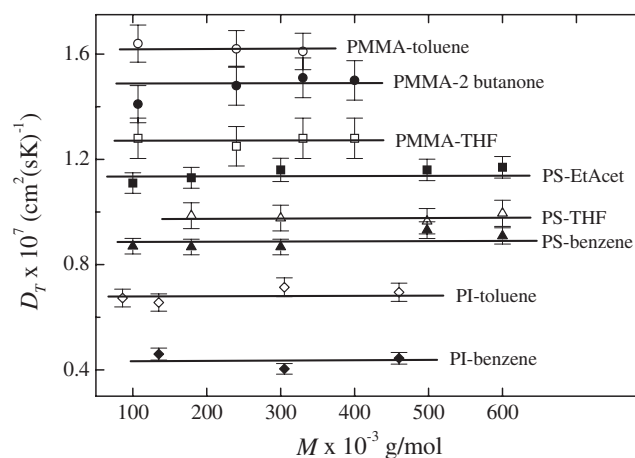


Figure 7. Plot of D_T versus molecular weight M for a representative set of polymer-solvent combinations extrapolated to infinite dilution, illustrating that D_T depends on both polymer and solvent but is essentially independent of M [16]. The picture was taken from [16].

in a study of 17 different polymer-solvent systems [121] using thermal field flow fractionation (ThFFF). Figure 7 displays plots of D_T versus molecular weight for several systems. Although D_T values vary with the composition of both polymer and solvent, no systematic influence of the degree of polymerization is seen. For polystyrene in ethyl benzene it was also shown that D_T is independent of the structure of the polymer [122]. These findings were later also confirmed by TDFRS measurements for the solution of polystyrene in ethyl acetate [99]. The investigation of polystyrene with molar masses $M \geq 71\,700 \text{ g mol}^{-1}$ in ethyl acetate [123] showed that the thermal diffusion coefficient is independent of the degree of polymerization.

Recently, we investigated the thermal diffusion behaviour of highly diluted solutions of low molecular polystyrenes in ethyl acetate, to detect whether D_T remains independent of the chain length for a few repeating units [61, 108]. For solutions of styrene oligomers ($N = 16, 3, 2$) in ethyl acetate, we could show that the thermal diffusion coefficient D_T is independent of the molecular weight and in good agreement with the value obtained for high molecular polystyrenes in the same solvent and concentration range. The measurements demonstrate that the smallest segment governing the thermal diffusion of the polystyrene chain consists of two monomer subunits. Neither the constitution of the identified segment nor the end-groups of the polymer chain have a significant influence on D_T .

In this context we were also interested in the question of whether simple molecules, such as alkanes, that differ from polymers with respect to their well-defined structure and molecular weight, show the same thermal diffusion behaviour in dependence of the molecular weight. Therefore, we investigated binary mixtures of higher n -alkanes in n -hexane at a fixed molar fraction of $x = 0.15$. This investigation also reveals the independence of D_T from the molar mass of the higher n -alkane.

These findings comply with experiments by Chan *et al* [124]. They determined Soret coefficients for aqueous poly(ethylene glycol) (PEG) solutions and binary mixtures of n -alkanes in tetrachloromethane and trichloromethane. It was found that D_T is independent of the degree of polymerization for relatively small PEG oligomers of approximately three repeating units using ThFFF. The thermal diffusion coefficients for solutions of n -hexane, n -heptane and n -octane in tetrachloromethane and in trichloromethane have been measured. With increasing number of carbons from six to eight the limiting thermal diffusion coefficients for infinite dilution in tetrachloromethane and trichloromethane decrease by 20% and 3%, respectively.

These observations might also help to understand thermal diffusion by MD simulations for rather small molecules, which can be easily performed. From those results it is also expected that the negative thermal diffusion behaviour of PEO in ethanol/water mixtures [58, 64], which will be discussed in section 4.3.2, is inherent in a small chemical unit of the PEO. We expect that a monomer or dimer already shows the negative D_T and causes this unusual effect. The experimental findings allude to a rather short length of the thermal diffusion process which might be comparable with the length scale ($\sim 10^{-10}$ m) of the heat transport. MD simulations on small molecules, representing one or several repeating units, could also contribute to a better microscopic understanding of thermal diffusion of complex substances such as oligomers, polymers or even biological systems. Whether one can also identify smallest segments determining thermal diffusion of proteins [125] or DNA remains an open question which has to be clarified in future work.

In a recent paper, Rauch and Köhler [89] demonstrated for the system polystyrene/toluene that the collective diffusion coefficient D and the thermal diffusion coefficient D_T , both decay sharply when the glass transition is approached. In the diluted regime the Soret coefficient S_T increases with the molecular weight M as,

$$S_T \propto M^{0.53} \quad (5)$$

within the dilute regime below the overlap concentration C^* , and becomes mass independent above C^* .

If one compares the behaviour of S_T in polymer solutions with equation (4) found for different isotope substitutes of cyclohexane and benzene, one finds for large mass differences that S_T becomes molecular weight independent as in the case of high polymer concentrations. It might be expected that for very highly diluted low molecular weight mixtures that equation (4)

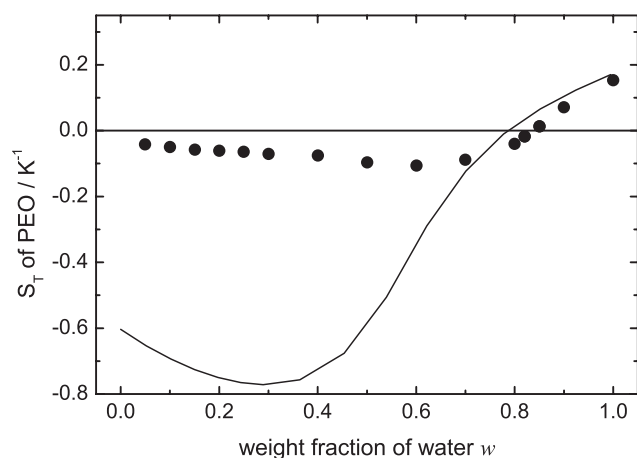


Figure 8. Soret coefficient of 5 g l^{-1} PEO in water/ethanol in dependence of the water weight fraction. The solid line shows the lattice predictions for the Soret coefficient [57, 58].

needs to be modified. Experimentally this range might not be accessible due to the low concentration signal.

4.3.2. Aqueous polymer solutions and ionic systems. As in the case of low molecular liquids the situation becomes more complicated when specific interactions such as hydrogen bonds are involved. Typically it is observed that in liquid mixtures whose components differ widely in molecular mass, such as polymer solutions [126] and colloidal suspensions [127], it is the heavier component that migrates to the cold region. There are, however, exceptions. In 1977, Giglio and Vendramini found a negative Soret coefficient for poly(vinyl alcohol) in water [30]. Recently, we reported results of TDFRS measurements on solutions of PEO in mixtures of ethanol and water [58, 64]. In pure water, PEO exhibits the expected migration to the cold region of the fluid ($S_T > 0$). However, in solutions with low water content, PEO is found to migrate to the warmer region of the fluid ($S_T < 0$). Although changes in sign of the Soret coefficient have been reported for a number of liquid mixtures of small-molecule fluids, including alcohol solutions [73, 128], the PEO/ethanol/water system is the first polymer solution for which such a sign change has been observed. Recently, Iacopini and Piazza [125] also reported a sign change in protein solutions.

Figure 8 displays the Soret coefficient of 5 g l^{-1} PEO in water/ethanol in dependence of the water weight fraction. The solid line shows the S_T values predicted from a lattice model [57, 58]. The interaction parameters between the ethanol and water molecules were adjusted in such a way that the density calculated in the lattice model agreed with experimental values. The agreement was excellent for mixtures with high water content but the deviations between tabulated and calculated values increased with decreasing water content but did not exceed 2% [57]. In order to calculate the thermophoretic properties, two chambers with slightly different temperatures were considered and the probability was calculated to find the polymer in one or the other box. Each box reflected the thermodynamic and structural properties of the mixture. As expected, the agreement of the S_T values for water rich mixtures is good, while the deviations for the ethanol rich mixtures become quite large. Within the model, the concentration where the Soret coefficient changes sign was reasonably well reproduced [58].

Figure 9 shows the temperature dependence of the Soret coefficient of 5 g l^{-1} PEO in water/ethanol with a water weight fraction of $w = 0.82$. As can be seen, the sign of the Soret

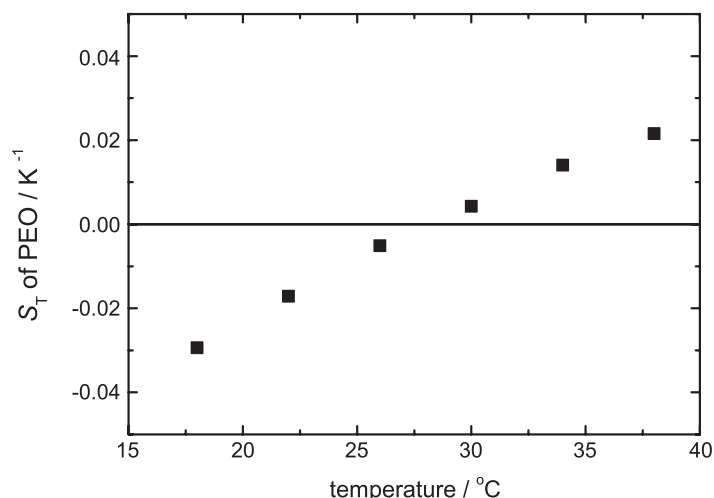


Figure 9. Temperature dependence of the Soret coefficient of 5 g l^{-1} PEO in water/ethanol with a weight fraction of $w = 0.82$.

coefficient changed at a temperature of approximately $29 \text{ }^\circ\text{C}$. Unfortunately it was not yet possible to determine the second virial coefficient B_2 by static light scattering with sufficient accuracy. We expect that a strong temperature dependence of the second virial coefficient should result in a large Soret coefficient.

Nevertheless, our experimental investigation of PEO in ethanol/water mixtures helps to understand the unusual conditions that lead to unusual thermodiffusion in polymer solutions. The experimental data illustrate the seemingly essential role of solvent quality. Positive Soret coefficients are observed for PEO in pure water, which is an excellent solvent, while negative Soret coefficients are observed for low water content of the solution which corresponds to poor solvent conditions. The negative Soret coefficient reported [30] for poly(vinyl alcohol) in water at $25 \text{ }^\circ\text{C}$ agrees with our findings, since the system is very close to poor solvent conditions [129]. Our investigation leads us to expect other systems to exhibit changes in sign of polymer Soret coefficients. For example, a solution of a random copolymer in a single solvent may change sign as a function of composition of the copolymer, if the chains are composed of two types of segments, one with highly attractive and one with net repulsive segment-solvent interactions. For the PEO/ethanol/water system studied here, hydrogen bonding plays a most important role. Large structural changes that occur in binary mixtures of ethanol and water [130] at high water content (80 wt%) might be responsible for the sign change in the Soret coefficient.

Besides specific interactions as hydrogen bonds, electrostatic effects also have a dramatic influence on thermal diffusion. This was demonstrated in a recent work on charged micelles by Piazza and Guarino [131]. In the diluted regime, they find that the Soret coefficient strongly decreases with the solution ionic strength and scales as the square of the Debye-Hückel length. For higher concentrated solutions the collective effects reverse the behaviour. With a simple model based on the interfacial tension mechanism proposed by Ruckenstein [132] they are able to predict the correct scaling and order of magnitude of the electrostatic contribution to the single particle Soret coefficient.

The recent results in more complicated solutions with specific interactions and charges show that there are many mechanisms contributing to the Soret coefficient.

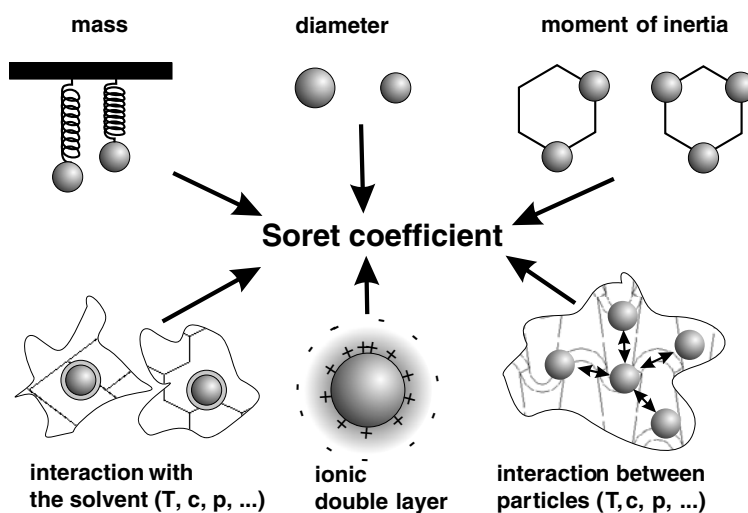


Figure 10. The main features determining thermodiffusion behaviour.

5. Discussion and conclusions

A survey of the literature over the last decade shows an increasing interest in thermal diffusion. This is reflected in the development of, in particular, optical methods, theory and simulations. As stated at the beginning, there is still no microscopic theory to explain the thermal diffusion behaviour of liquids. Starting from the recent experimental and simulation results we would like to summarize some aspects which need to be considered in a theoretical treatment of the thermal diffusion process.

In figure 10 we show the main features that control thermodiffusion behaviour. The first three contributions are easily accessible particle properties such as mass, moment of inertia and size of the considered molecule or particle. The moment of inertia is closely related to the flexibility of the molecule and is certainly of no importance for spherical molecules or highly flexible macromolecules. The other three contributions stem from chemical interactions. We have sketched these as separated contributions, but it is reasonable to expect interference effects. For instance, an extended double layer of a colloidal particle might also interact with the double layer of another colloid. Only in a very limited number of cases can we assume that those contributions are additive.

Conceptually, the highly diluted and the concentrated solutions can be differentiated. In the first case, chemical interactions of the solute and the surrounding solvent are important. In the diluted solutions, temperature, concentration and pressure are important parameters. In addition, it is expected that in charged systems, properties such as the ionic strength and valency of the ions might be important. All structural changes of the solvent surrounding the solute will lead to a change in the thermodiffusion behaviour. Measurements indicate that the first shell of surrounding molecules, in particular, is important. In concentrated solutions the interactions between solute molecules also need to be considered. The interplay of solvent–solute and solute–solute interactions are complicated and a comprehensive theoretical modelling of the thermal diffusive process might only be possible in a full molecular dynamic simulation. In the dilute regime it is common to express the collective diffusion coefficient in a virial expansion $D = D_0(1 + B_2c + O(c^2))$ with D_0 the diffusion coefficient at infinite dilution and B_2 the

second virial coefficient. The Soret coefficient S_T can similarly be expanded as,

$$S_T = S_{T,0}(\mu) + Fc + O(c^2) \quad (6)$$

with $S_{T,0}(\mu)$ the Soret coefficient at infinite dilution as a function of the chemical potential μ which depends on temperature and pressure. F accounts for interactions between the solute particles. Both $S_{T,0}(\mu)$ and F can give rise to sign changes of S_T on changing solvent composition or temperature, and concentration, respectively.

While the Soret coefficient S_T strongly depends on the mass, the thermal diffusion coefficient D_T is independent of the molar mass for various polymers of different structure. The strong dependence of S_T on the mass is caused by the mass dependence of the ordinary diffusion coefficient. For fairly shape-persistent molecules, it was experimentally found that the Soret coefficient depends on the chemical difference, the difference in mass, and the difference in moment of inertia [115]. It is obvious that for sufficiently long flexible chain molecules the moment of inertia dependence must eventually become irrelevant, since such molecules do not perform rigid-body reorientations in the melt. At present it is not clear whether there exists a range of intermediate sized molecules, such as small n -alkanes, where both rigid-body motion and internal transitions simultaneously contribute to the Soret effect, or whether molecules use only either one mechanism with an abrupt change between rigid and flexible molecules.

Recent studies showed that the thermal diffusion coefficient D_T is independent of the molecular weight M for chain-like molecules and for oligomers with two repeating units [61, 113]. Consequently, scaling concepts are not appropriate to explain the effect. A reasonable concept for the explanation of the molecular weight independence of D_T in diluted solutions is to relate the thermal diffusion process to the heat transport between the considered substance and the surrounding solvent. In this concept we assume that the process takes place within a very short distance of the order of a bond length. Structural changes of the surrounding solvent or solvent mixture might change the behaviour. The sensitivity of the thermal diffusion behaviour to the surface compositions of polystyrene and silica particles in aqueous and non-aqueous solvents has already been noticed in thermal field flow fractionation experiments [133].

For many systems that show a sign change in the thermal diffusion behaviour specific interactions, e.g., hydrogen bonding plays a most important role. Lattice simulations for binary systems [54] showed that if cross-interactions are stronger than pure interactions, a sign change can occur. This concept certainly holds for aqueous systems, but as Prigogine noticed in 1952, entropic effects need also to be considered. If those specific interactions show a temperature dependence one might also observe a change in sign with temperature as it was recently for several systems [58, 64, 125]. And as for known gases [37, 38], we also expect for liquids and polymer solutions a high sensitivity of the thermal diffusion coefficient to the interaction potential.

Acknowledgments

I am grateful to J K G Dhont, R Kita, M Kleemeier and C N Likos for a critical reading of the manuscript. Without my postdocs and students many of the results presented here would not have been possible. Special thanks go to B-J de Gans, C Leppla and R Kita. I am also grateful to my colleagues, in particular S Hess, W Köhler, J Luettmer-Strathmann, F Müller-Plathe and J Platten and their coworkers for providing results prior to publication as well as for many fruitful discussions.

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