Thermal Diffusion

Motivation:

A temperature gradient applied to a liquid mixture not only causes a heat flux but also gives rise to a diffusion current of the constituent components. The resulting separation of the components causes a concentration gradient parallel or antiparallel with respect to the temperature gradient. This cross-effect between temperature and concentration is known as thermal diffusion or Ludwig-Soret-effect. Since its discovery by Ludwig (1856) and the first systematic investigations in liquid mixtures by Soret (1879), the effect has been subject to experimental and theoretical studies. Furthermore, the effect is relevant in technical applications as polymer characterization, the analysis of petrol reservoir characterization and for accumulation of uranium.

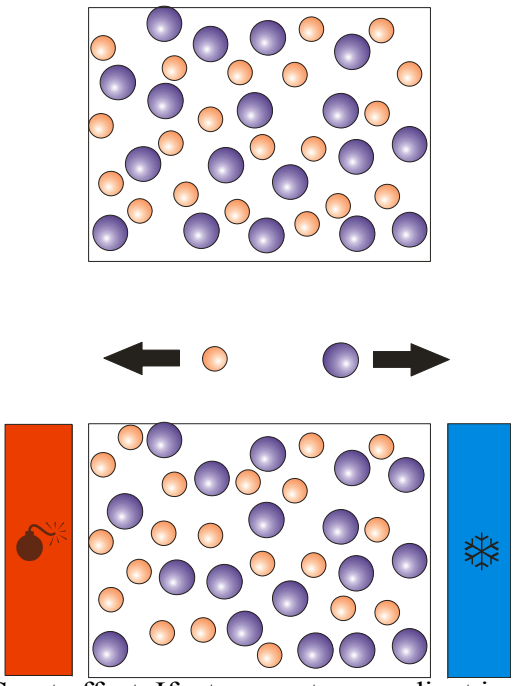

Fig. 1: Illustration of the Soret effect. If a temperature gradient is applied to a mixture, this results in a concentration gradient.

The investigation of the Soret-effect in liquid mixtures is based on the determination of the transport coefficients D (mutual diffusion coefficient), DT (thermal diffusion coefficient) and S_T (Soret coefficient). Therefore, the motivation of our work is to determine these properties experimentally by means of **T**hermal **D**iffusion **F**orced **R**ayleigh **S**cattering (**TDFRS**) [1] and, hence, to provide a "database", enabling a comparison with values obtained, for example, by means of **M**olecular **D**ynamic (MD)-simulations.

Principle of TDFRS:

A grating created by the interference of two laser beams is written in 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. Analyzing the time dependent diffraction efficiency, the transport coefficients can then be obtained.

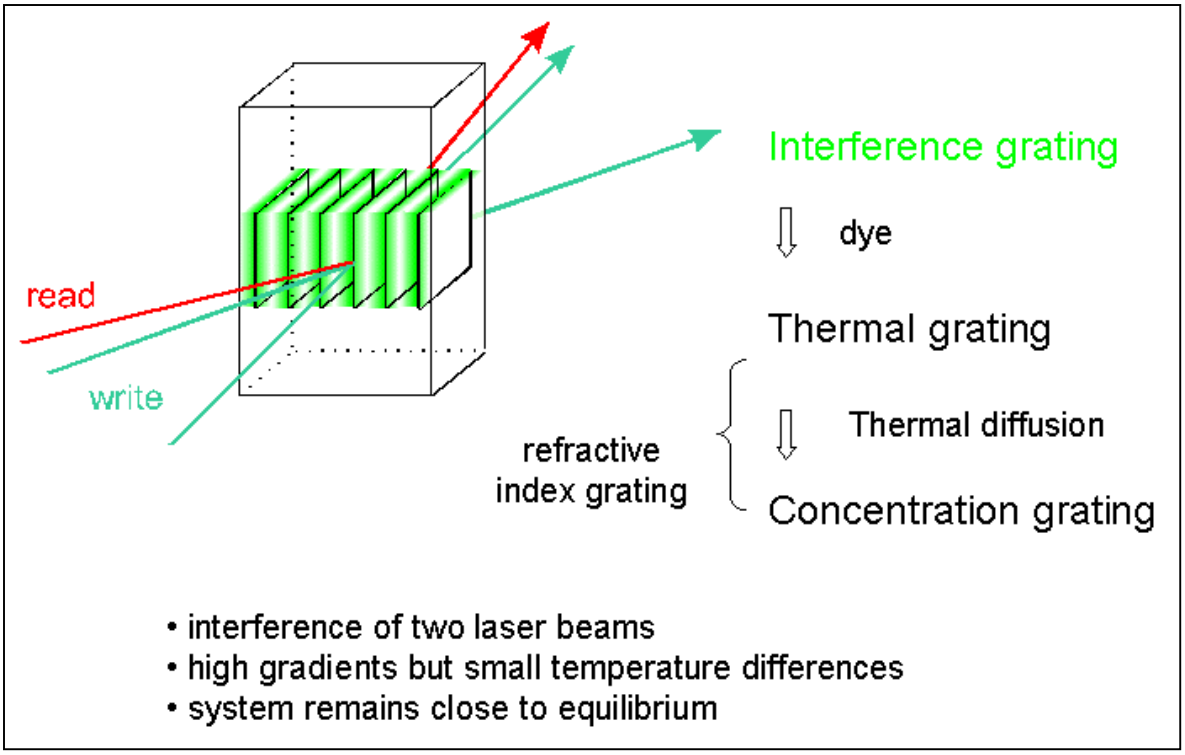

Fig 2.: Principle of the TDFRS experiment

Projects:

Validation of the method

Unfortunately one finds in the literature still contradicting values for the Soret coefficients for the same mixture. This was motivation for a group of researchers from the universities of Bayreuth, Bilbao, Mons, Toulouse and from the Max Planck Institute for Polymer Research in Mainz met in Fontainebleau and started a ground based measurement campaign with the aim to establish a reliable base of Soret, thermodiffusion and isothermal mass diffusion coefficients for the three binary mixtures of dodecane, isobutylbenzene and 1,2,3,4 tetrahydronaphtalene at a fixed concentration of 50 weight-percent and at a mean temperature of 25 °C. The experimental techniques applied by the five participating laboratories are transient holographic gratings, annular and parallelepipedic thermogravitational columns, vertical parallelepipepdic columns with velocity amplitude determination by Laser Doppler Velocimetry (LDV). There is a good agreement between the different experiments with deviations of the order of a few percent in most cases (8.5 % at most) [1,2].

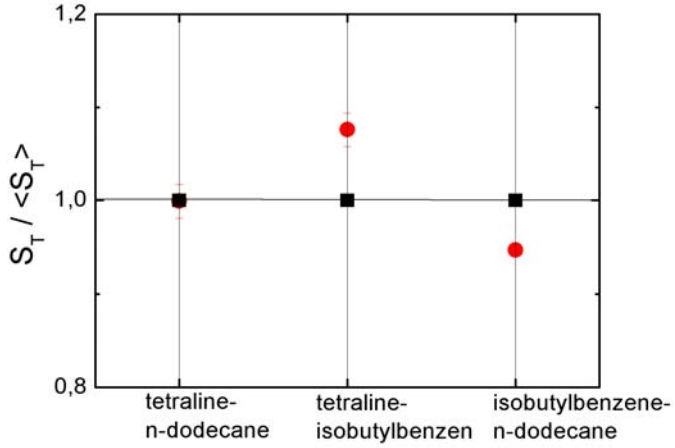

Fig. 3: Comparison of the TDFRS results with the mean value determined by all methods.

Investigation of simple fluids and comparison with simulations

Another subject of our interest is the study is the comparison with simulation results for simple liquids. We compared for instance the concentration dependence of the Soret-effect in pentane/decane mixtures. Experimental results are compared with MD-simulations based on synthetic (S-NEMD) [3] and boundary driven (BD-NEMD) [4] non-equilibrium techniques [5].

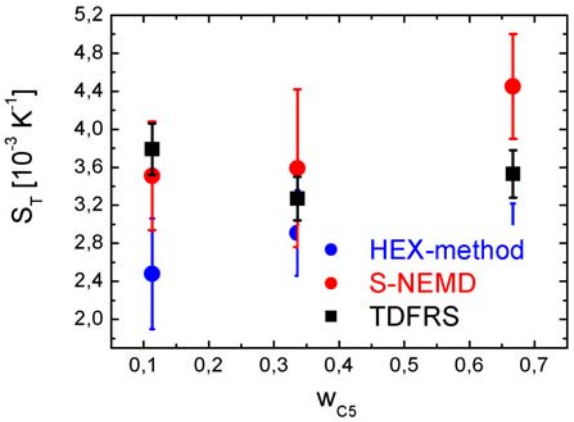

Fig. 4: Experimental, stationary S-NEMD and BD-NEMD data of the Soret coefficient as function of the *n*-pentane weight fraction at 300.15 K. Error bars represent the standard deviation of the mean.

Systematic investigation of chain molecules

For high molecular weight polymers the experimental values for the thermal diffusion coefficient D_T are independent of the molecular weight and shape of the polymer [6, 7]. In this paper we examine whether this experimental finding remains valid for low molecular weight polymers, oligomers and monomers. We find that the thermal diffusion coefficient D_T remains constant down to the dimer. In analogy to the behavior observed in polymers the thermal diffusion coefficient D_T remains constant if we investigate binary mixtures of hexane with alkanes of different chain length, as decane, dodecane, pentadecane and eicosane.

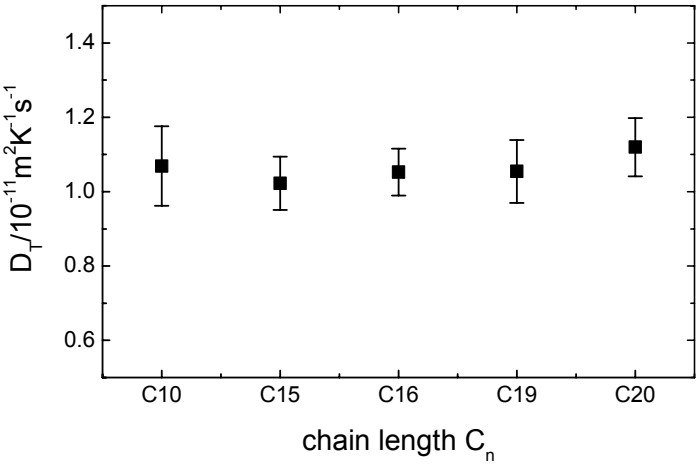

Fig. 5: Thermal diffusion coefficient for different binary mixtures of hexane with alkanes of different chain length C_n.

Investigation of polymer solutions and colloidal dispersions

Polymer solutions

Our current research is focused on the study of the Soret-effect in polymer solutions with the aim of learning more about fundamental questions like the dependence of the thermal diffusion coefficient on molecular weight for polymers consisting of only a few monomer units. A very interesting system is poly(ethylene oxide) in ethanol/water mixtures. The sign of the Soret coefficient in mixtures of low water content is negative, i.e. the poly(ethylene oxide) molecules move to higher temperatures, whereas in pure water the sign is positive as usually found for polymers [8, 9].

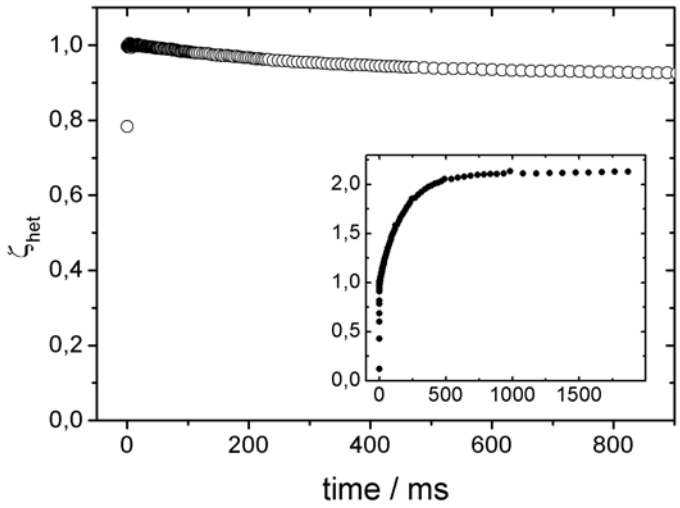

Fig. 6: Typical normalized heterodyne diffraction signal for a solution of PEO in ethanol/water (15.02 % wt H_2O). The inset shows for comparison the signal of PEO in pure water.

Colloidal dispersions

Another area of interest are colloidal dispersions. Unfortunately, experiments in this area are very difficult because of the strong scattering of the colloidal particles themselves. We demonstrated the presence of the Soret-effect in colloidal dispersions using polystyrene latex particles in an mathanol/water mixture. Another problem imposes the adsorbtion of the dye onto the particle surface, as happens in the case of boehmite (γ-AlOOH) needles [9]. The sign of the Soret coefficient of the boehmite rods changes from positive to negative with increasing water content, i.e. at sufficiently high water content the colloidal particles move to higher temperatures.

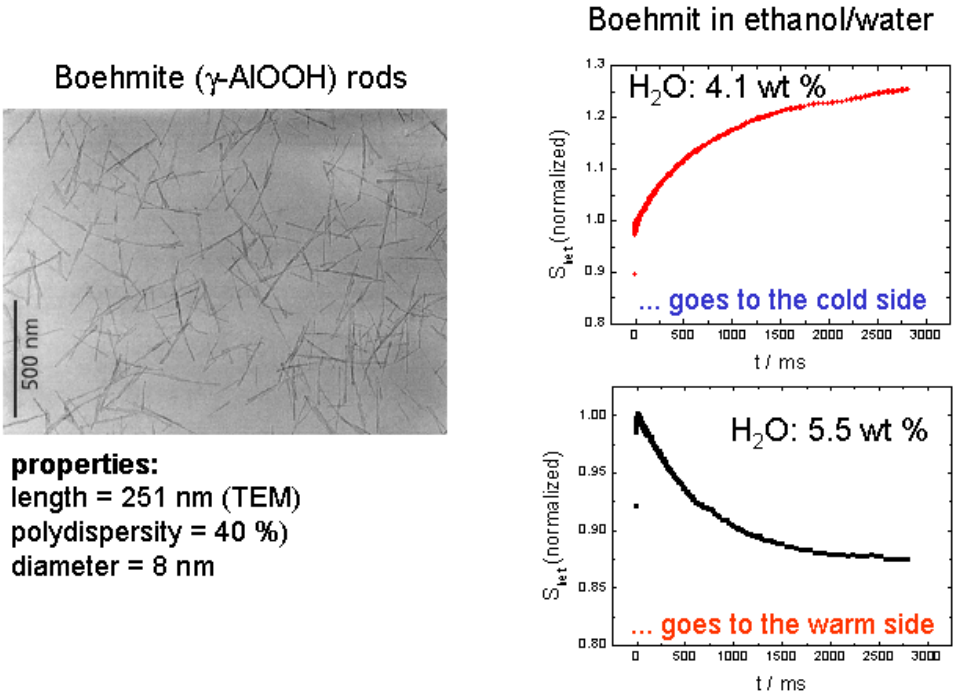

Fig.:7 Unusual thermal diffusion behavior of boehmite rods in ethanol/water mixtures.

References:

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