Thermophoresis and Thermal Diffusion

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Motivation:

It turns out that a simple nonequilibrium environment created by a temperature gradient can be used to monitor the reaction kinetics of large proteins with small substrate molecules. This is probably caused by a change in the hydration layer of the protein which is influenced by subtle conformations changes induced by the binding substrate molecule. The underlying effect is thermophoresis or thermal diffusion, which is the mass transport induced by a temperature gradient applied to a liquid mixture. The resulting separation of the components causes a concentration gradient parallel or antiparallel with respect to the temperature gradient. Beside the recently detected biophysical applications it is relevant in polymer characterization, and analysis of petrol reservoir characterization. Additionally the effect is also discussed as an accumulation mechanism for a hydrothermal emergence of life in the early stage of the earth and in the deep sea close to black smokers.

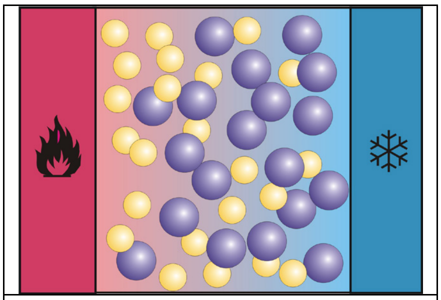

Fig. 1: Illustration of the Soret effect. If a temperature gradient is applied to a mixture, this results in a concentration gradient.

The investigation of the thermophoresis and thermal diffusion in liquid mixtures is based on the determination of the transport coefficients *D* (mutual diffusion coefficient), D_T (thermal diffusion coefficient) and S_T (Soret coefficient). Experimentally we are determining these properties by **T**hermal **D**iffusion **F**orced **R**ayleigh **S**cattering (**TDFRS**) [1-3] and, hence, to provide a "database", enabling a comparison with values obtained, for example, by means of **M**olecular **D**ynamic (MD)-simulations. Presently, we are also developing a set-up to study larger synthetic and biological colloids with an imaging method.

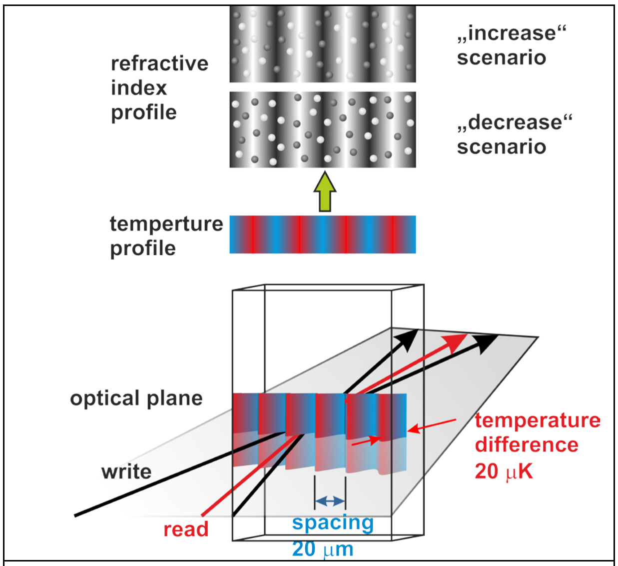

Fig. 1: Schematic drawing of the holographic grating experiment. The two IR-beams (black) writing beams intersect in the sample cell and create a sinusoidal interference grating with a fringe spacing on the order of 20 μm and a temperature amplitude of approximately 20 μK due to absorption of the laser light in the sample. The temperature grating causes a refractive index grating. After equilibration of the temperature the diffusion process starts. This leads depending on the movement of the components to an increase or decrease of the refractive index contrast of the grating. The build up and contrast variation of the refractive index grating is probed by a read-out laser beam (red).

References:

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Thermal Diffusion of Stiff Rod-Like Mutant Y21M fd-virus

We investigated the thermal diffusion phenomena of a rodlike mutant filamentous fd-Y21M virus in the isotropic phase by means of an improved infrared thermal-diffusion-forced Rayleigh scattering (IR-TDFRS) setup optimized for measurements of slowly diffusing systems. Because this is the first thermal diffusion study of a stiff anisotropic solute, we investigate the influence of the shape anisotropy on the thermal diffusion behavior. Additionally we studied the system at low and high salt content.

Recently, microscale thermophoresis has been used to analyse interactions of proteins or small molecules in biological liquids such as blood serum or cell lysate [1]. This technique is based on thermal diffusion, which describes the mass flow induced by a temperature gradient. Due to its practical importance especially for biological molecules it is important to understand how the molecule size, shape, charge and hydration shell influence the thermophoretic motion. Therefore, a study of the thermal diffusion behaviour of biological relevant small [2] and large molecules [3] is essential.

Therefore, we investigated the thermal diffusion phenomena of a mutant filamentous bacteriophage fd-Y21M with a length of 910 nm and a diameter of 6.6 nm [3]. The wild-type fd-viruses have been widely used as a robust colloidal model system, which has the big to be rather monodisperse and having identical structures with the same physical parameters such as mass, length, and diameter. We investigated the virus in two different buffers of tris-(hydroxymethyl)aminomethane (TRIS), one with low salt content (2 mM TRIS-HCl buffer adjusted to pH 8.2) and another one with higher salt content (20 mM TRIS-HCl+100mM NaCl adjusted to pH 8.2).

To check that all experiments were in the isotropic phase, we characterized qualitatively the isotropic/nematic phase transition of fd-Y21M in both high salt (hs) and low salt (ls) buffers. In the experiment, we placed fd-Y21M solutions of different concentrations between two crossed polarizers (c.f. Fig. 1). We started from a high-concentrated fd-Y21M solution and diluted the solution until we reached the isotropic phase. The object of this experiment is not to determine accurately the isotropic/nematic phase transition but to select the range of fd-Y21M concentrations that are in the isotropic phase. In Figure 1a, the results for the ls buffer are shown. As it can be observed, the isotropic/nematic phase transition is at ~3 mg/mL. Therefore, to be completely sure that we performed the experiments in the isotropic phase, we decided to study the system at concentrations up to 2 mg/mL. In Figure 1b, the results for the hs buffer are shown. In this case, the isotropic/nematic phase transition is ~13 mg/mL, which is in good agreement with the literature value of 13.9 mg/mL.

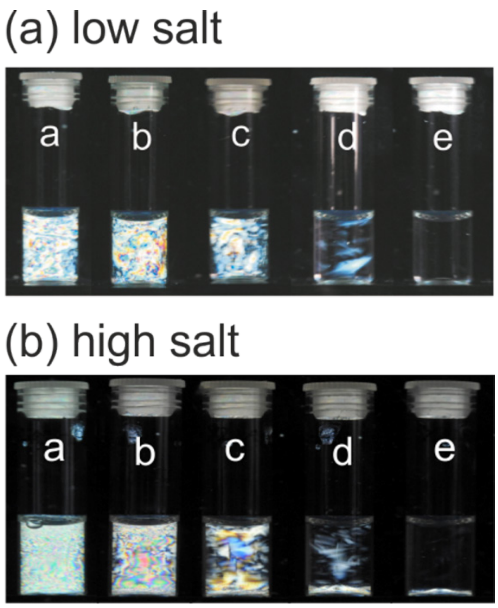

FIG. 1: (a) Isotropic/nematic phase transition for fd-Y21M at low salt content in a 2 mM Tris buffer and (b) at high salt content in a 20 mM Tris+100mM NaCl buffer at room temperature. At low salt content the fd-concentrations are (a) 6.5, (b) 5.2, (c) 3.7, (d) 3.0, and (e) 2.9 mg/mL and at high salt content (a) 19.8, (b) 15.0, (c) 13.5, (d) 13.1, and (e) 12.4 mg/mL. The images were taken between crossed polarizers.

All measurements have been performed with an improved infrared thermal-diffusion-forced Rayleigh scattering (IR-TDFRS) setup optimized for measurements of slowly diffusing systems such as the fd-Y21M. The usage of an IR-laser for heating the sample has the big advantage that no light absorbing dye is needed for aqueous mixtures.

In Figure 2, the thermal diffusion, collective diffusion, and Soret coefficients are shown as a function with increasing temperature. In ls solutions, D_T is always positive in the studied range of temperatures, which means that fd-Y21M moves to the cold side. To some extent, the temperature dependence of D_T is influenced by the viscosity change with temperature. Additionally, changes in the interactions with temperature influence the thermal diffusion behaviour. This becomes even more evident for the hs solutions, where D_T changes its sign around 26 °C. At temperatures <26 °C, D_T is negative, meaning that fd-Y21M moves to the warm side, whereas at temperatures >26 °C, D_T is positive, which means that fd-Y21M moves to the cold region. The physical mechanism of this sign change with temperature is probably related to the fact that the system minimizes its free energy at low temperature by forming hydrogen bonds, while the system minimizes the free energy at high temperatures by maximizing the entropy..

The addition of salt has a similar effect as lowering the temperature. This induces a higher order in the inner and outer hydration cell around the ions and leads also to a lower D_T, so the reduction of the temperature as well as the addition of salt results in a higher structure of the water molecules, which leads to a more thermophilic behaviour of the fd-Y21M virus. The increasing salt content at constant fd-Y21M concentration as well as an increase in the temperature will decrease the structure between the rod like particles. Regarding these two aspects, we do not find a correlation with the thermal diffusion coefficient. Whereas D_T increases with increasing temperature, it decreases with increasing salt content. Therefore, we conclude that the structural changes of the solvent surrounding the solute particles have a larger influence on the thermal diffusion behaviour than the interactions between the solute particles. This implies that the interparticle interactions, which are certainly present because all investigated concentrations are well above the overlap concentration, influence the dynamics of the solution but are less important for the thermal diffusion behaviour of the system. This finding confirms the importance of the solvent structure on the thermal diffusion.

Considering the collective diffusion coefficient, as one can expect, it increases with increasing temperature because of the decreasing viscosity with increasing temperature. Keeping the temperature constant, D decreases by approximately 60-70% because of the added salt. As expected for this slow-diffusing charged rod like particle, the determined Soret coefficients are almost three orders of magnitude larger than the values obtained for low-molecular-weight mixtures, but the values are comparable to those of other biopolymers such as DNA. Although the Soret coefficient is fairly large, the expected concentration separation in our setup, the IR-TDFRS, is only in the order of $\Delta c = 10^{-4}$mg/mL because of the small temperature difference in the order of $\Delta T = 100$ μK.

Finally, we can conclude that the rod like virus fd-Y21M behaves as colloidal or polymeric model system. We did not find a signature of the anisotropy nor of the virus character in the thermal diffusion behaviour.

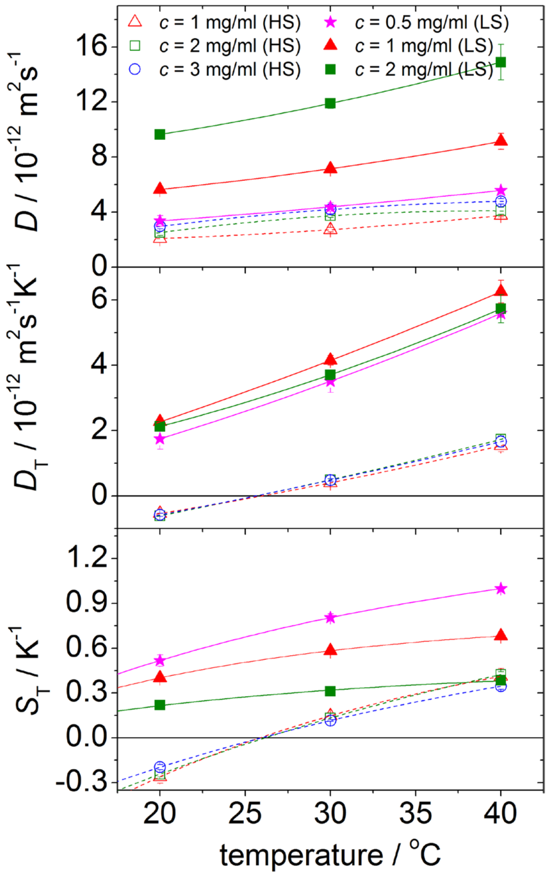

FIG. 2: Temperature dependence of D_T, D, and S_T coefficients of fd-Y21M at different concentrations and in two different buffers. Open symbols correspond to the high salt (hs) buffer of 20mM Tris+100mM NaCl. Filled symbols correspond to the low salt (ls) buffer of 2mMTris.

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