PHYSICAL REVIEW E **75**, 040401(R) (2007)

Thermophoresis of microemulsion droplets: Size dependence of the Soret effect

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(Received 22 September 2006; revised manuscript received 6 February 2007; published 2 April 2007)

Thermophoresis, akin to thermal diffusion in simple fluid mixtures, consists of particle drift induced by a temperature gradient. Notwithstanding its practical interest, the dependence of thermophoretic effects on particle size R is still theoretically and experimentally debated. By performing measurements of water-in-oil microemulsion droplets with tunable size, we show that the thermal diffusion coefficient, at least for a suspension of small particles in a nonpolar solvent, does not appreciably depend on R.

DOI: 10.1103/PhysRevE.75.040401 PACS number(s): 82.70.Uv, 47.57.jd, 66.10.Cb

When a macromolecular solution or a colloidal suspension is placed in a uniform-temperature gradient the dispersed particles migrate, focusing at either the cold or hot side. This effect, akin to thermal diffusion (the Soret effect) in simple fluid mixtures [1], is known as thermophoresis. Taking the temperature gradient along the z axis, the total mass flow J_m of a solute in the presence of thermal diffusion can be written as

$$J_m = -\rho\left[D\frac{dw}{dz} + w(1-w)D_T\frac{dT}{dz}\right], \tag{1}$$

where ρ is the solution density, w is the mass fraction of the solute, D is the usual Brownian diffusion coefficient, and D_T is called the coefficient of thermal diffusion. In the absence of convection, Soret coupling of heat and mass transfer leads therefore to a steady-state concentration gradient given by

$$\frac{dw}{dz} = -w(1-w)S_T\frac{dT}{dz}, \tag{2}$$

where $S_T = D_T/D$ is called the Soret coefficient.

While for common fluid mixtures S_T is of the order of a few $10^{-3}\ \mathrm{K}^{-1}$, the Soret coefficient of disperse systems ranges from $10^{-2}\ \mathrm{K}^{-1}$ for small micelles to several K^{-1} for large latex particles. Macromolecular thermophoresis is therefore a much stronger effect than thermal diffusion in simple systems. As an appealing consequence, it can be exploited in efficient separation methods such as thermal field-flow fractionation [2], and since it does not bring about Joule heating, it is also particularly promising for microfluidic manipulation of highly conducting suspensions [3]. Yet the practical design of separation devices still requires a deeper understanding of the microscopic mechanisms driving particle thermophoresis in liquids, in particular for what concerns their selectivity to the size and nature of the macromolecular solute. Consequently, in the last few years a lot of effort has been devoted to study thermophoresis in disperse systems ranging from polymers [4,5] to surfactant micelles [6], latex particles [7,8], proteins [9], and DNA [10], while several attempts to provide physical understanding of the observed behavior have been presented [11–13]. A common feature of all recent experimental results is the striking dependence of particle thermophoresis, not only for what concerns its amplitude, but also its *sign* (i.e., the direction of particle drift), on the specific nature of the investigated system. Getting basic information such as the dependence of S_T on particle size is then far from being easy. In the case of ideal polymer chains in a good solvent, scaling arguments [14], fully supported by experimental data [4], suggest a molecular-weight-independent thermal diffusion coefficient. For rigid colloids, and in particular for charged latex particles, the situation is much more debated. For instance, while Duhr and Braun [8] found that D_T is positive and scales linearly with R, a comprehensive study performed by Putnam and Cahill [7] suggests a complex dependence of thermophoretic effects on pH, ionic strength, and surface charge. In particular, D_T is often found to be negative (particles move to the *hot* side) and no simple scaling on R is evidenced.

The problem of extracting the size dependence of the Soret effect in charged colloidal dispersions is complicated by the occurrence of *two* mesoscopic length scales: namely, the particle size and the Debye-Hückel screening length λ_{DH}. In addition, it is not easy controlling crucial parameters such as the particle charge, degree of surface ionization, or surface potential over different batches. Finally, care should be taken in avoiding collective effects, which are known to be very pronounced, at least for small particles [6] (this applies in particular to the data presented in [7]). Studying colloidal dispersions in nonpolar fluids, where elusive electrostatic effects are absent and particle-solvent interactions are generally short ranged, is for sure appealing. It would be also particularly useful singling out a system where the particle size can be tuned without modifying the particle-solvent interfacial properties. To this purpose, water-in-oil (w/o) microemulsions, spontaneously formed by the addition of water to solutions of the surfactant Aerosol OT (AOT, docusate sodium salt) in nonpolar solvents, could make up a kind of benchmark system. The phase diagram and water solubilization properties of AOT solutions have been thoroughly investigated in the past [15–17]. AOT w/o microemulsions droplets can be depicted as a water core, embodying a globally neutral charge distribution, shielded from contact with the solvent by the surfactant layer. Thanks to the presence of two hydrocarbon "tails," acting as a kind of "variable wedge," AOT intrinsic curvature spontaneously adapts to the requirements imposed by the droplet geometry, allowing AOT inverted micelles to swell up to more than 10 times their de-

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*Electronic address: roberto.piazza@polimi.it hydrated size by changing the water/AOT molar ratio r, while still retaining a system of weakly polydisperse droplets [15]. Regardless of the droplet size, their interfacial free energy is anyway set by the short-range dispersion forces between AOT hydrophobic tails and the continuous nonpolar phase. The main purpose of this paper is to show that measurements of the Soret effect in the AOT-water-isooctane system may allow a settling of the question of the size dependence of thermophoretic effects for small colloidal particles dispersed in a nonpolar phase. Albeit we shall retain the common expression "microemulsion droplets," AOT w/o microemulsions can be regarded as a model system for *rigid* colloidal particles, rather than for simple liquid droplets. The surfactant layer, indeed, hinders both momentum transfer to the internal fluid and interfacial Marangoni effects, playing a major role in droplet thermophoresis [18,19].

Microemulsions with a water/AOT molar ratio variable between $r=0$ and $r=50$ were prepared by adding water to an isooctane solution of carefully dehydrated AOT (Sigma-Aldrich, BioChemika Ultra), which was then diluted to keep the total water+AOT concentration in mass/volume c (and therefore the droplet volume fraction) fixed. In order to detect possible concentration effects, we have prepared three series of samples at $c=20$, 40, and 100 g/l corresponding, for $r=0$, to $w=0.029$, 0.057, and 0.138, respectively. Measurements were performed using a "beam deflection" (BD) setup [20], which exploits the deflection of a laser beam due to the concentration (and, therefore, refractive index) gradient induced by the imposed temperature field. After a small temperature difference (typically $\Delta T=0.4$ °C) has been rapidly imposed between two metal plates spaced by $h=0.8$ mm, the beam undergoes a first rapid angular deflection $(\Delta\vartheta)_{th}$ due to the temperature dependence of the solvent refractivity, followed by a much slower change $\Delta\vartheta_s(t)$ due to thermal diffusion, eventually leading to an additional steady-state deflection $(\Delta\vartheta)_s$. The wide differences of time scales allows evaluating S_T as

$$S_T=-\frac{1}{w(1-w)}\frac{\partial n/\partial T}{\partial n/\partial w}\frac{(\Delta\vartheta)_s}{(\Delta\vartheta)_{th}}, \tag{3}$$

where $\partial n/\partial T$ and $\partial n/\partial w$ are, respectively, the temperature and concentration dependence of the refractive index. In addition, the time dependence of $\Delta\vartheta_s(t)$, which reaches its steady-state value exponentially with a time constant $\tau=h^2/(\pi^2 D)$, allows evaluating the particle diffusion coefficient and, therefore, both $D_T=S_T D$ and the particle hydrodynamic radius $R=k_B T/6\pi\eta D$. A precision Abbe refractometer (Atago model 4T, Japan) was used to obtain both the temperature dependence of the solvent refractive index $dn/dT=4.6\times10^{-4}$ K^{-1} and dn/dw for each value of r. Since for $r\gtrsim15$ and sufficiently high T (decreasing from $T\simeq70$ °C at $r=20$ to $T\simeq45$ °C at $r=50$) AOT microemulsions display a liquid-liquid phase separation, all measurements were performed at $T=25$ °C, a temperature value where critical effects are found to be negligible up to $r=60$ [15].

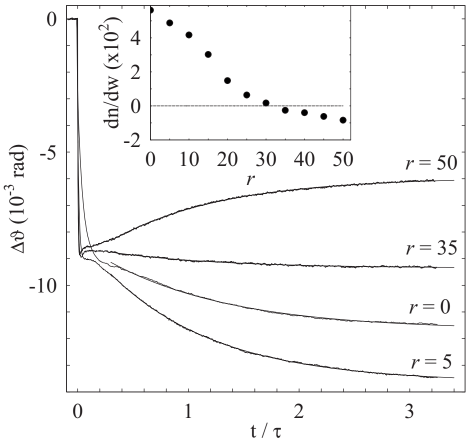

FIG. 1. BD signals from AOT w/o microemulsions at $c=100$ g/l for different values of r, plotted as a function of the rescaled time t/τ, where $\tau=172$ s ($r=0$), 604 s ($r=5$), 1300 s ($r=30$), and 2080 s ($r=50$). Inset: specific refractive index increment as a function of r.

The BD signals plotted in Fig. 1 highlight a nontrivial trend of $(\Delta\vartheta)_s$ versus r. By increasing the water content, the downward deflection observed for pure AOT inverted micelles becomes first more pronounced, but then decreases in absolute value, eventually switching sign for $r\gtrsim30$. This behavior, however, does not entail any change in the direction of droplet thermophoretic drift, but rather originates from changes in the optical contrast dn/dw. The refractive index of isooctane ($n=1.387$) is indeed intermediate between those of AOT ($n=1.446$) and water ($n=1.333$). Therefore (see the inset of Fig. 1) dn/dw monotonically decreases by increasing r, vanishes at $r_0\simeq30$ (corresponding to perfect index matching of the droplets), and becomes negative for larger values of the water/AOT molar ratio. This unfortunately means that, close to the matching point, BD signals are rather weak. Unfortunately, getting large AOT w/o droplets in aromatic solvents having a much higher refractive index difference with water is very hard [17], so that using isooctane or optically similar solvent sounds like a fixed option.

Figure 2, where measurements at three different weight fractions are compared, leads us to conclude that the general

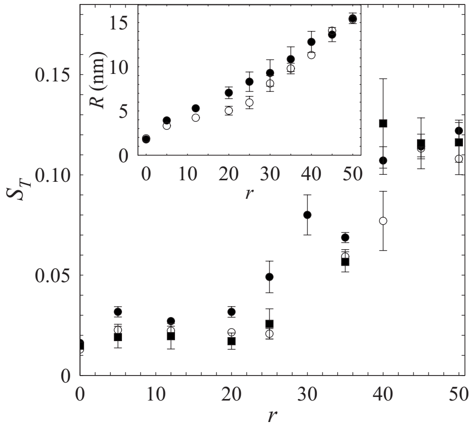

FIG. 2. Soret coefficient versus r for $c=20$ (■), 40 (○), and 100 g/l (●). Error bars in this and the following graphs are obtained from the standard deviation of measurements performed on different samples. Inset: average droplet radius versus r obtained from the BD transients (●) or by DLS (○) for $c=100$ g/l.

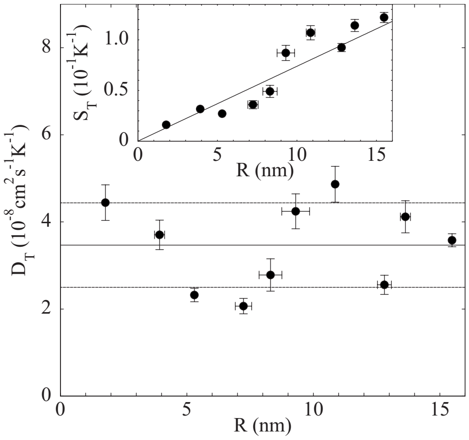

FIG. 3. Inset: size dependence of the Soret coefficient for AOT w/o microemulsions at $c=100$ g/l. The straight line is a tentative linear fit to the data. Main part: thermal diffusion coefficients D_T derived as $D_T=DS_T$ ($c=100$ g/l). The solid line indicates the average value of D_T, while dashed lines correspond to ± one standard deviation of the data points.

trend of S_T versus r weakly depends on droplet concentration. Such a moderate sensitivity of the Soret coefficient on interparticle interactions is consistent with assuming that AOT microemulsion droplets behave essentially as hard spheres. Indeed, according to the results presented in Refs. [6,21], collective effects on the Soret coefficient turn out to be roughly proportional to the osmotic compressibility, which, for hard sphere suspensions at a volume fraction of the order of 0.1, does not differ too much from its dilute limit. In what follows, therefore, we shall only consider the results obtained at $c=100$ g/l, where the stronger signals yield more reliable values for τ and, therefore, for D_T.

The inset of Fig. 2 shows the average droplet hydrodynamic radii obtained from the transient behavior of the BD signal. The full data set is moderately well fitted by a linear trend $R=2.0+0.26r$ (in nanometers). As a further check, we also performed measurements of the droplet average hydrodynamic radius by dynamic light scattering (DLS), obtaining results that are in good agreement with transient BD results except close to index matching. Here, as already pointed out and extensively discussed in [16], the intrinsic droplet polydispersity and the strong dependence of the scattering signal on R concur to yield a rather marked apparent deviation from a linear dependence of the hydrodynamic radius on r.

The dependence of S_T on the droplet radius is shown in the inset of Fig. 3. Notwithstanding the scattering of the data points and the limited investigated size range, covering just one decade, the graph suggests a quasilinear scaling of the Soret coefficient on the microemulsion droplet size. Notice that the apparent steeper slope in the region corresponding to $r \simeq r_0$ may still be due to polydispersity effects. Due to different weighting, the average size derived from the time dependence of the BD signal may indeed slightly differ, in particular close to the matching point, from the effective value yielding the average steady-state value (in some sense, this is equivalent to the distinction between molecular-weight and Z averages when comparing static and dynamic light scattering data). This practical hitch will unfortunately turn out in any experimental investigation of particles in the few-nanometer-size range, where polydispersity is unavoidable. Yet size effects are better appreciated by considering the thermal diffusion coefficient D_T. The main part of Fig. 3 shows that, within the investigated size range, D_T is essentially constant, with a relative standard deviation of the data points of about 30%–40%. Therefore, w/o microemulsions seem to resemble much more polymers than charged colloids for what concerns the dependence of D_T on particle size.

The survey of thermophoretic effects in dispersed systems consequently seems to be rather complex, at least for what concerns size effects. So far, theoretical models have mainly focused on charged colloids [6,11,13,19], so they do not apply to the case we are considering. Unfortunately, general approaches to thermophoresis in liquids are still rather unsatisfactory. Developing a purely hydrodynamic theory of thermophoresis is well known to be precluded, since the Navier-Stokes equations for a fluid in a constant-temperature gradient embodying a rigid sphere admit a single rigorous solution: a constant-pressure field and no fluid motion [18]. Attempts to get around this negative result have followed different routes. Rigorous statistical mechanics approaches [22–24], trying to analyze Brownian motion in the presence of temperature gradients, often yield cumbersome results and are generally unable to catch the strong system and specificity of thermophoretic effects. The latter shortcoming is shared by endeavors stressing the contribution of hydrodynamic fluctuations [25] or critically reconsidering the structure of transport equations [26].[1] More promising approaches have focused on solid-liquid interfacial properties [12,27,28], basically envisaging thermophoresis as a consequence of the temperature dependence of the particle-solvent interfacial tension, which yields an effective slip velocity of the fluid in a thin layer of thickness $\delta \ll R$ close to the particle surface, similarly to what happens for other particle "phoretic" transport processes [28]. A common feature of most theoretical models is nonetheless the prediction of a size-independent thermophoretic velocity and, therefore, of a linear scaling of S_T on R (with the noteworthy exceptions of Refs. [27] and [25], respectively yielding $u_T \sim R$ and $u_T \sim R^{1/2}$). In particular, in the "interfacial" models the steepest pressure (and therefore velocity) gradients develop on spatial scales comparable not to R but to δ, acting as a new dominant length scale. Therefore, balancing the magnitude of the two members of the Navier-Stokes equation $\eta \nabla^2 u = \nabla p$, one gets in the quasiplanar approximation a thermophoretic velocity $u \sim (\delta^2/\eta)(dp/dT)\nabla T$ which does not depend on R [12]. Albeit not pretending to be exhaustive, the evidence we have presented gives experimental support to this prediction, at least when the range of particle-solvent interactions is much smaller than R and no charge effects are present. Having performed measurements on a model system where the par-

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[1] We should nonetheless point out that Brenner's approach predicts a size-independent $D_T = \lambda D_s \alpha$, where D_s and α are the solvent self-diffusivity and thermal expansivity, and λ is a system-specific correction factor of $O(1)$. This simple expression yields anyway the right order of magnitude, $D_T \sim 10^{-12}$ m^2/(s K), observed for most systems.

ticle size is the only varying parameter strengthens to our view our conclusions. From a practical point of view, a size-independent thermophoretic velocity implies that any separation method based on thermophoresis will be sensitive only to the nature of the macromolecular solute and not to its molecular weight, a rather peculiar feature that could be fruitfully exploited. Whether this conclusion holds only for very small particles or has more general soundness is of course to be further investigated.

We thank S. Iacopini for help in preliminary measurements, and A. Parola for illuminating insights.

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