

Does Thermophoretic Mobility Depend on Particle Size?

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Thermophoresis is particle drift induced by a temperature gradient. By measuring the full temperature dependence of this effect for polystyrene latex suspensions, we show that the thermophoretic mobility (or “thermal diffusion coefficient”) D_T is basically independent on particle size, in particular, when the interfacial properties of the colloidal particles are carefully standardized by adsorbing a surfactant layer on the particle surface. Even more, all investigated systems show values of D_T which are very close to those measured for simple micellar solutions of the adsorbed surfactant. Our findings could be of relevance for downsizing microfluidics to the nanometric range.

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Thermophoresis, akin to thermal diffusion in simple fluid mixtures, is particle drift induced by temperature gradients [1]. In a thermal gradient, a colloidal particle attains a drift velocity $v_T = -D_T \nabla T$, where the thermophoretic mobility D_T is usually dubbed “thermal diffusion coefficient.” Depending on the sign of D_T , the particles then focus either at the cold or the hot side, leading to a steady-state concentration gradient given, for low particle concentration c , by $\nabla c = -c S_T \nabla T$, where $S_T = D_T/D$ is called the Soret coefficient.

Exploiting thermophoresis to manipulate colloids or macromolecules is an alluring perspective. In fact, careful control by thermal gradients of colloidal crystal growth has already been proved to be fully feasible [2]. Thermophoresis is also currently plied in effective separation methods such as thermal field-flow fractionation (ThFFF, [3]). Another intriguing technique, where thermophoresis is likely to play an important (but still not fully acknowledged) role is Temperature Gradient Focusing (TGF, [4]) where the electrophoretic flux of charged solutes is spatially modulated not by pH gradients, as in common isoelectric focusing of proteins, but by rather strong (typically of the order of 10^4 K/m) temperature gradients. Novel fascinating applications of “thermal forces,” such as the manufacturing of “thermophoretic swimmers” (particles which self-propel by anisotropic heating of the surrounding fluid), have also been recently proposed [5]. Since scaling down the device size is a current mainstream in ThFFF [6], it is also natural wondering whether thermophoretic effects may be exploited in microfluidics. As we shall see, the Soret coefficient of a suspension of 100 nm particles is of the order of 0.5 K^{-1} . This means that a temperature difference of 1°C , applied across a microfluidic channel with section $d = 20 \mu\text{m}$, eventually leads to a fractional separation $\Delta c/c \approx 20\%$: not at all a small effect. As a matter of fact, microfluidic particle separators based on thermophoresis have recently been built and successfully tested [7]. Moreover, TGF is *already* performed in a microfluidic geometry.

Yet, the practical design of separation or manipulation devices requires clear understanding of the microscopic

mechanisms driving particle thermophoresis in liquids, in particular, for what concerns their selectivity to the solute size. A crucial advantage for quantifying the efficiency of ThFFF in fractionating solutions of polymers with sufficiently large molecular weight M_w , is indeed the well-grounded observation that D_T does not depend on M_w [8]. For colloidal suspensions, however, the situation is much more controversial. While a size-independent thermophoretic mobility has been recently found for water-in-oil microemulsions [9], no general consensus on this basic question has so far been reached for suspensions of spherical latex particles. At constant and sufficiently high ionic strength (so that the Debye-Hückel screening length does not play the role of an additional variable length scale), Duhr and Braun [10] found that D_T scales linearly (and therefore S_T quadratically) with the particle size R . This conclusion has however been recently questioned by Putnam *et al.* [11], who found an approximately *linear* dependence of S_T on R : a strikingly divergent claim for a system generally regarded as the simplest “proving ground” for colloid physics!

To solve this riddle, some preliminary caveats are mandatory. First of all, all recent experiments point out the crucial role of the particle-solvent interface, and therefore of specific surface chemistry, in tuning thermophoretic effects. To this end, latex particles are not for sure the best choice: controlling crucial parameters such as the particle charge, the degree of surface ionization, or the amount of residual surfactant used in emulsion polymerization is not easy. Moreover, as originally pointed out by Iacopini and Piazza [12], and later confirmed by many experiments including those reported in Ref. [11], thermophoresis in aqueous solvents strongly depends on temperature. Therefore, care should be taken when considering measurements performed by applying relatively large temperature jumps. A final warning concerns the possible occurrence of spurious effects due to gravity, since thermophoretic measurements on large colloids often require time scales over which particle sedimentation cannot be neglected. This Letter aims at giving a substantial contribution to this debate by performing experiments on colloids

dal latex particles with well-defined surface properties and fully density matched with the solvent. Our main findings can be summarized by stating that, provided that the particle-solvent interface is carefully standardized, the whole temperature dependence of D_T is insensitive to particle size, and depends only on the nature of the particle-solvent interface.

We have studied aqueous suspensions of polystyrene (PS) spheres (Duke Scientific Corp., calibration standards) with a radius R varying between 11 and 253 nm in the temperature range $5^\circ\text{C} \leq T \leq 45^\circ\text{C}$. The original particles were fully carboxylated so that pH control is mandatory to fix the particle surface charge. Consequently, we have performed experiments in 1 mM Tris-HCl buffer at pH = 7.8 (corresponding to the same conditions used in Ref. [10]), which moderately screens electrostatic interparticle interactions. Although PS has a density $\rho = 1.053 \text{ g cm}^{-3}$, which is close to water, particle settling is a problem: in water at room temperature (viscosity $\eta \approx 1 \text{ cP}$), PS particles with $R = 250 \text{ nm}$ have a gravitational length $\ell_g = k_B T / mg \approx 120 \mu\text{m}$, where m is the buoyant mass, and a Stokes sedimentation velocity $v_S = 2\Delta\rho g R^2 / 9\eta \approx 7.5 \times 10^{-3} \mu\text{m/s}$. Since it is easy to show that $v_T / v_S = \ell_g / \ell_T$, where $\ell_T = D / v_T = (S_T \nabla T)^{-1}$ is a characteristic ‘‘thermophoretic length,’’ this value corresponds (taking $S_T \sim 1 \text{ K}^{-1}$) to the thermophoretic velocity attained by the particle in a temperature gradient $\nabla T > 8^\circ\text{C/mm}$. To minimize sedimentation effects, samples were prepared in a buffered 1:1 mixture of $\text{H}_2\text{O} + \text{D}_2\text{O}$ (which has a negligible Soret coefficient, $S_T < 10^{-4} \text{ K}^{-1}$), corresponding to a solvent density $\rho = 1.051 \text{ g cm}^{-3}$ at $T = 20^\circ\text{C}$. To rule out possible interparticle interaction effects, we worked at very low particle volume fraction, ranging from $\Phi = 4 \times 10^{-5}$ for the largest particles to $\Phi = 3.5 \times 10^{-3}$ for the smallest.

Measurements were performed using a ‘‘beam deflection’’ (BD) setup, which exploits the deflection of a laser beam due to the concentration (and, therefore, refractive index) gradient induced by the imposed temperature field. This method allows to obtain at the same time S_T and D , respectively, from the steady-state and time-dependence of the signal. A full description of the method can be found in Ref. [13]. Here, we only recall that the key advantage of BD is to be an intrinsically *differential* method, which requires only to compare the laser deflection for the suspension, knowing its refractive index increment (for PS colloids, $dn/dc = 0.26 \text{ ml g}^{-1}$), to the deflection observed for a calibration solvent at a fixed temperature, due to the T -dependence of the refractive index (for water at 25°C , $dn/dT = -1.03 \times 10^{-4} \text{ K}^{-1}$). To deal with large colloidal particles, we have designed and built a BD microcell, allowing to reduce the separation between the hot and cold plate down to $h \approx 400\text{--}500 \mu\text{m}$ over a 20 mm optical path. We first carefully checked whether residual sedimentation effects were detectable over the experimental time scale by

monitoring the beam position in the absence of any applied thermal gradient. For particles with $R \leq 125 \text{ nm}$, no appreciable BD effects were observed over all the investigated temperature range. Conversely, due to the different thermal expansivity between particles and solvent, a progressive deflection of the beam can still be detected for the largest PS particles for $T > 40^\circ\text{C}$. For the latter system, measurements were therefore limited to $T \leq 40^\circ\text{C}$.

Figure 1 shows the full temperature dependence of the Soret coefficient for different particle radii. Notice first of all that, as already pointed out in [11], S_T has a very strong temperature dependence: In particular, around $T = 20^\circ\text{C}$, S_T can vary by as much as 50% in a 5°C temperature range. All curves are very well fitted by using the empirical expression proposed in [12]:

$$S_T(T) = S_T^\infty \left[1 - \exp\left(\frac{T^* - T}{T_0}\right) \right]. \quad (1)$$

Figure 2, where values at fixed temperatures are plotted versus R , strongly suggests a *linear* (definitely, not a quadratic) dependence of the Soret coefficient on particle radius, not only for what concerns S_T^∞ , as pointed out in Ref. [11], but over the whole temperature range. This conclusion is further supported by carefully considering the contribution of the thermal expansivity α of the $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixture, which we accurately measured using a Paar oscillating-capillary densimeter. As already found for many colloidal and macromolecular systems [14], S_T/α turns out to be, within about 10%, a temperature-independent quantity for all values of the particle size. The

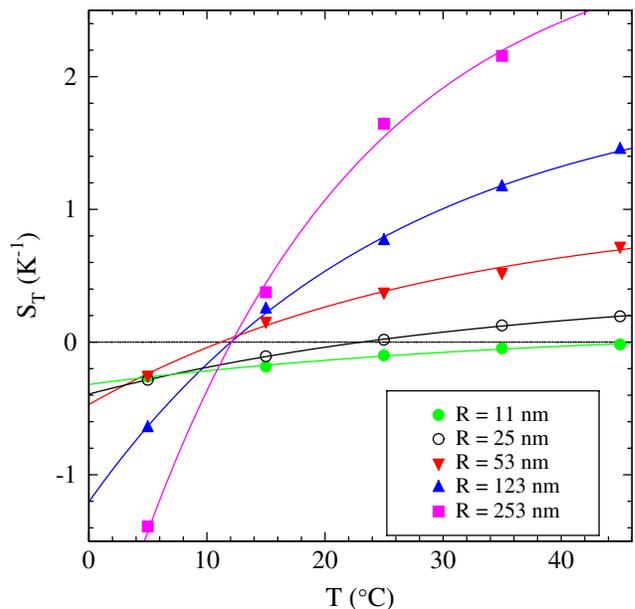


FIG. 1 (color online). Temperature dependence of the Soret coefficient for PS particle suspensions. The particle hydrodynamic radii, measured by dynamic light scattering, as shown in the legend. Each curve is fitted using Eq. (1).

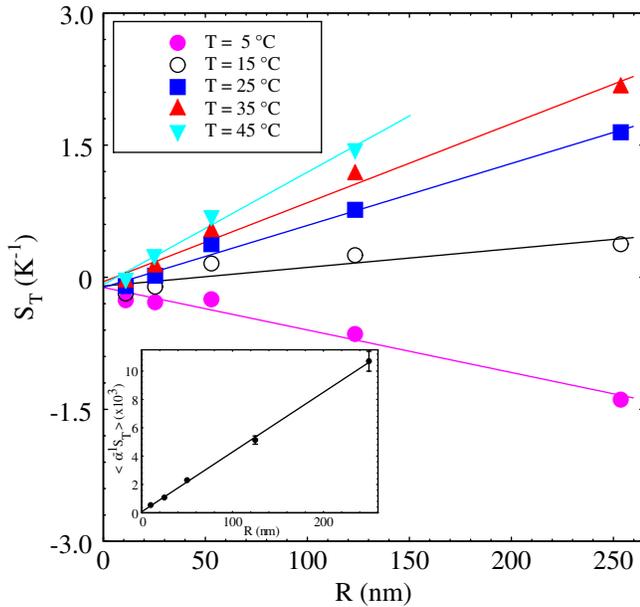


FIG. 2 (color online). Soret coefficient versus particle radius at some fixed temperatures shown in the legend, with linear fits to the data. Inset: Size dependence of the average ratios $\langle S_T/\alpha \rangle$ for the data in Fig. 1. Error bars are the standard deviations of S_T/α over the measured temperature range.

inset in Fig. 2 shows that the average value of S_T/α is again pretty linear in R .

Looking more carefully, however, one may notice that the values obtained in Fig. 2 for $R = 11$ and 25 nm tend to fall slightly below the fits, pushing the intercepts to slightly negative values. The former “anomaly” is emphasized by the behavior of the thermophoretic mobility D_T shown in the inset of Fig. 3. While suspensions of particles with $R > 50$ nm show very close values of D_T over the whole T -range, marked deviations can be observed for the smaller particle sizes. The origin of this discrepancy can be traced to a marked difference in the temperature dependence shown in Fig. 1. Indeed, while particles with $R > 50$ nm show closely matched sign-switching temperatures $T^* \approx 12$ °C, we get $T^* \approx 26$ °C for $R = 25$ nm, and $S_T < 0$ (that is, a “thermophilic” behavior) for $R = 11$ nm at all investigated values of T . Since it has been shown that T^* is very sensitive to the nature of the particle-solvent interface [14], such a different behavior casts doubts on the evenness of the interfacial properties over different size batches.

Where may interfacial disparities come from? Former extensive studies [15] have shown that, for latex colloids, fixing pH and ionic strength may not be sufficient to control the particle surface properties. The bare particle charge of “standard” latices cannot be carefully handled. Moreover, even when the batches are sold as “surfactant-free,” there are often clues of the presence on the particle surface of a residual amount of the surfactant used in the emulsion polymerization of the latices, in particular, for small colloids [11]. The method we have followed to try

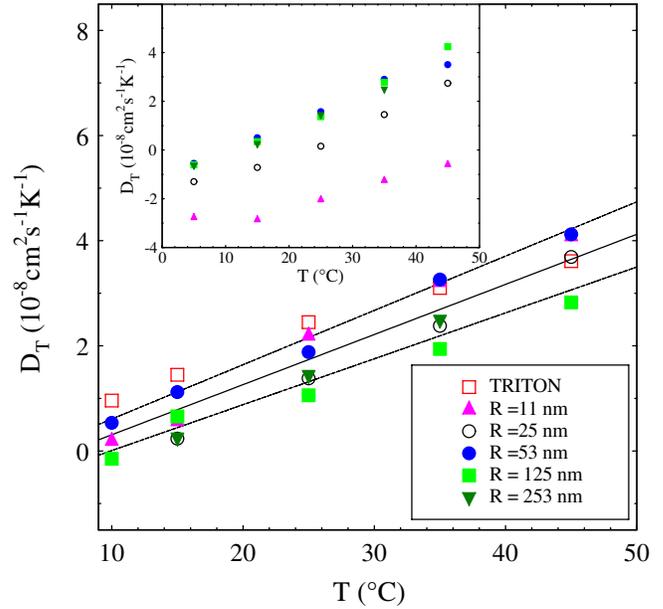


FIG. 3 (color online). Temperature dependence of the thermophoretic mobility for Triton-coated PS particle suspensions (ionic strength $I = 10$ mM), with particle size shown in the legend. Open squares are the data obtained for a 0.5% Triton micellar solution. The full line is a linear fit to the whole data set, while dotted lines correspond to 1 standard deviations for the slope and intercept. Inset: $D_T(T)$ for the same suspensions without Triton in 1 mM buffer.

and avoid these problems consists in adding to the suspensions a small amount of the nonionic surfactant Triton X100. Triton adsorbs on the particle surface forming a monolayer that is fully saturated for a surfactant volume fraction $\phi_s \approx 3(d/R)\Phi$, where $d \approx 2$ nm is the length of a Triton head group [16,17]. Although we do not claim that this protocol yields literally “identical” surface properties for the different batches, it is quite reasonable to assume that the particle-solvent interface (now basically an interface between water and surfactant head groups) should be much better standardized. Besides, Triton stabilizes the particles against coagulation up to high ionic strength, allowing us to add to the suspensions about 10 mM NaCl to quench any residual electrostatic effect.

The main body of Fig. 3 shows that, for the “standardized” particle batches, D_T is essentially the same for *all* particle sizes over the whole temperature range, the residual differences (poorly related to R) being probably due to the uncertainty in the values of Φ for the original batches. What is really amazing is that even the thermophoretic mobility of Triton *micelles* with a radius $R \approx 3.5$ nm, obtained from BD measurements of $\Phi_s = 1\%$ Triton solutions *without* PS particles, essentially share the same temperature dependence and absolute values for D_T (implicitly validating our surface “standardization” method). These findings then strongly suggest that the thermophoretic mobility of surfactant-stabilized colloidal

particles with controlled interfacial properties is size-independent, and that D_T is mainly fixed by the nature of the interface.

Our results therefore fully support and considerably extend the findings reported in Ref. [11], while they clash with the data presented in [10]. It is worth trying to speculate from where such a pronounced discrepancy may arise. There are actually some puzzling features in the experiments reported in [10]. First of all, although temperature differences $\Delta T \approx 8$ K were applied, data fitting seems to imply a constant (temperature-independent) Soret coefficient. Conversely, both our measurements and those in Ref. [11] show that, around room temperature, S_T can vary by more than 50% within a similar T -range. Even the *sign* of S_T is sometimes opposite: both the present experiments and those in [11] yield $S_T < 0$ for PS particles with $R \approx 20$ nm, while Duhr and Braun found a thermophobic behavior. Sedimentation effects may also have biased the latter measurements (performed in simple water). Although the thermal gradient was applied horizontally, building up of vertically inhomogeneous concentration profiles on the time scale of the experiment (tens of minutes, according to Ref. [10]) can be severe for the largest particles. The Stokes settling time h/v_S for $R = 1$ μm PS particles in water, with a cell height $h = 10$ μm , is about 90 s. Over that time, all particles get confined in a thin layer of thickness comparable to the gravitational length $\ell_g \approx 2$ μm . This means that measurements of the thermophoretic velocity, which for the larger particles were made by direct particle tracking, were probably made in an essentially 2-D geometry. Nonetheless, it is hard stating that accurate consideration of the former effects might drastically change the observed trend. One may then wonder whether the measurement reported in [10] have been performed in a different coupling regime. As formerly discussed, the concentration profile varies over a characteristic length ℓ_T , which also gives the characteristic distance over which the thermophoretic drift eventually “beats” Brownian diffusion. In all our experiments, we have $\ell_T \gg R$. However, the thermal gradients applied in Ref. [10] are, close to the beam center, of the order of 0.1 μm^{-1} K. Using the values for S_T plotted in Fig. 5 of Ref. [10], one gets $\ell_T/R \approx 0.3$ for $R = 0.95$ μm , while even for $R = 0.55$ μm , ℓ_T is only about $1.5R$. Yet, even for $\ell_T \lesssim R$, the energy $mv_T^2/2$ effectively transferred to the particle is still a tiny fraction of the thermal energy $k_B T$, so that linear coupling should fully hold.

Giving a sound explanation of the observed discrepancy is then, at present, rather hard. In any case, a size-dependent thermophoretic mobility, $D_T \propto R^s$ with $s > 0$, would lead to serious theoretical puzzles. Indeed, let us consider the reciprocal effect of thermo-osmosis, i.e., the

flow of a liquid past a surface along which a longitudinal thermal gradient is maintained. Since the thermophoretic velocity acquired by a particle is simply related to the thermo-osmotic velocity \tilde{v} of the fluid by the reciprocal theorem for low Reynolds-number hydrodynamics [5], it is easy to show that \tilde{v} would diverge for a flat ($R \rightarrow \infty$) surface. Evidently \tilde{v} , and therefore v_T , must depend not on R , but on a *microscopic* length scale λ related to the range of the interfacial forces [18]. This is well established for other “phoretic” phenomena such as diffusio-osmosis, and is the basic idea underlying the theoretical approach to thermophoresis developed in Ref. [18]. Actually, in a general model of interfacial transport [19], Ajdari and Bocquet have recently proved that this is true, at order λ/R , for interfacial flows induced by the gradient of *any* thermodynamic quantity (concentration, temperature, charge). A size-independent mobility makes interface-driven transport a robust strategy, compared to motion induced by a body force such as dielectrophoresis or magnetophoresis, for downsizing into the nanometric world, turning thermophoresis into a very interesting tool for the promising field of nanofluidics.

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