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 $\mathbf{pH}$ 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 $d = 20 \mu$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 collo-
effects were detectable over the experimental time scale by
We first carefully checked whether residual sedimentation
precipitation, knowing its refractive index increment (for PS
particles, only to compare the laser deflection for the sus-
ceptible particles to
0.0008
. To minimize sedimentation ef-
fications were fully carboxylated so that pH control is manda-
tory 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 inter-
particle 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 gravita-
tional length \( \ell_g = k_B T / m g \approx 120 \mu \text{m} \), 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 \( S_T \approx 1 \text{ K}^{-1} \)) to the ther-
mospheric velocity attained by the particle in a temperature
gradient \( \nabla T > 8 \text{ C/mm} \). To minimize sedimentation ef-
fications, 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,
\( S_T^{\text{exp}}<10^{-4} \text{ K}^{-1} \)), corresponding to a solvent density \( \rho = 1.051 \text{ g cm}^{-3} \) at \( T = 20 \text{ C} \). To rule out possible interpar-
ticle interaction effects, we worked at very low particle
volume fraction, ranging from \( \Phi = 4 \times 10^{-5} \) for the larg-
est particles to \( \Phi = 3.5 \times 10^{-3} \) for the smallest.

Measurements were performed using a “beam deflec-
tion” (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 sus-
pension, 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 \text{ C},
\( dn/dT = -1.03 \times 10^{-4} \text{ K}^{-1} \)). To deal with large collo-
dal particles, we have designed and built a BD microcell,
allowing to reduce the separation between the hot and cold
plate down to \( h \approx 400–500 \mu \text{m} \) 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 ap-
preciable BD effects were observed over all the investig-
ated temperature range. Conversely, due to the different
thermal expansivity between particles and solvent, a pro-
gressive deflection of the beam can still be detected for the
largest PS particles for \( T > 40 \text{ C} \). For the latter system,
measurements were therefore limited to \( T \leq 40 \text{ C} \).

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 \( T = 20 \text{ C} \),
\( S_T \) can vary by as much as 50% in a 5 \text{ C} temperature
range. All curves are very well fitted by using the empirical
expression proposed in [12]:

\[
S_T(T) = S_T^{\text{exp}} \left[ 1 - \exp \left( \frac{T - T_0}{T_0} \right) \right].
\]  

Figure 2, where values at fixed temperatures are plotted
versus \( R \), strongly suggests a linear (definitely, not a qua-
dratic) dependence of the Soret coefficient on particle
radius, not only for what concerns \( S_T^{\text{exp}} \), 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 \( \alpha \) 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],
\( S_T / \alpha \) turns out to be, within about 10%, a temperature-


dependent 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 hydrody-
namic 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 \([S_T/\alpha]\) for the data in Fig. 1. Error bars are the standard deviations of \([S_T/\alpha]\) over the measured temperature range.

inset in Fig. 2 shows that the average value of \([S_T/\alpha]\) 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 \(T^* \approx 12^\circ C\), we get \(T^* \approx 26^\circ C\) 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” lattices 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

and avoid these problems consists in adding to the suspensions a small amount of the nonionic surfactant Triton X100. Triton adsors 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 incertitude in the values of \(\Phi\) 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 $R = 1 \mu$m PS particles in water, with a cell height $h = 10 \mu$m, is about 90 s. Over that time, all particles get confined in a thin layer of thickness comparable to the gravitational length $\ell_g \approx 2 \mu$m. 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 $\ell_T$, 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 $\mu$m$^{-1}$ K. Using the values for $S_T$ plotted in Fig. 5 of Ref. [10], one gets $\ell_T/R \approx 0.3$ for $R = 0.95 \mu$m, while even for $R = 0.55 \mu$m, $\ell_T$ is only about 1.5$R$. Yet, even for $\ell_T \leq R$, the energy $m v_T^2/2$ 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, $D_T \approx R^s$ 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 $\dot{v}$ of the fluid by the reciprocal theorem for low Reynolds-number hydrodynamics [5], it is easy to show that $\dot{v}$ would diverge for a flat ($R \rightarrow \infty$) surface. Evidently $\dot{v}$, and therefore $v_T$, must depend not on $R$, but on a microscopic length scale $\lambda$ 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 underlaying 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 $\lambda/R$, 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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