The "macromolecular tourist": Universal temperature dependence of thermal diffusion in aqueous colloidal suspensions

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Abstract. By performing measurements on a large class of macromolecular and colloidal systems, we show that thermophoresis (particle drift induced by thermal gradients) in aqueous solvents displays a distinctive universal dependence on temperature. For systems of particles interacting via temperature-independent forces, this behavior is strictly related to the solvent thermal expansivity, while an additional, T-independent term is needed to account for the behavior of "thermophilic" (migrating to the warmth) particles. The former relation between thermophoresis and thermal expansion may be exploited to envisage other fruitful studies of colloidal diffusion in inhomogeneous fluids.

PACS. 82.70.Dd Colloids – 66.10.Cb Diffusion and thermal diffusion

1 Introduction

The admittedly curious title of this paper calls for a preliminary explanation, which is also a good opportunity for stating in a few words the motivations, key results, and main message of this work. Consider a macromolecular solution or a colloidal suspension placed in a weak, stationary temperature gradient: under the influence of this "thermal field", the dispersed particles migrate, focusing either at the cold or the hot side. This effect is known as thermophoresis, and is the counterpart in disperse systems of thermal diffusion (Soret effect) in simple fluid mixtures [1]. While thermal diffusion in simple mixtures is rather weak, macromolecular thermophoresis is a much stronger effect, which can be exploited to engineer efficient separation methods like thermal field-flow fractionation [2] or may lead in concert with thermal convection to a huge enhancement of the local macromolecular concentration, as recently shown in brilliant experiments on DNA solutions [3]. Yet, *in which specific direction* the particles drift seems to be rather unpredictable: in most cases they migrate towards the cold, displaying what we shall call "thermophobic" behavior, but examples of "thermophilic" motion (along the temperature gradient) have been often reported [4–6].

In this paper we show that, at least for aqueous dispersions, both the magnitude and the *direction* of thermophoretic motion can easily be tuned by changing the average temperature of the system: for each system, there exists a well-defined temperature T^*, so that above T^*

particles drift to the cold, while the reverse happens below T^*. In other words, dispersed particles behave as the average vacationer (or any sensible person) would: when it is hot, they drift to colder regions, while, when it is cold, they look for warmer places. In addition, the observed temperature trend is rather universal, showing the same functional behavior for a wide class of systems, including proteins, synthetic polyelectrolytes, charged and nonionic micelles, latex particles, DNA. As we shall see, regardless of the specific value for T^*, the main contribution to the temperature dependence of thermophoresis can be traced back to the thermal expansivity of the solvent.

To be more quantitative, let us give some preliminary definitions. In dilute suspensions (particle weight fraction $w \ll 1$), the mass flow J can be written (considering the temperature gradient directed along the z axis) as:

$$J = -D\frac{dc}{dz} - cD_{\mathrm{T}}\frac{dT}{dz}, \qquad (1)$$

where c is the particle concentration in mass per unit volume, 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 to a steady-state concentration gradient given by

$$\frac{dc}{dz} = -cS_{\mathrm{T}}\frac{dT}{dz}, \qquad (2)$$

where $S_{\mathrm{T}} = D_{\mathrm{T}}/D$ is called the Soret coefficient. With the present definition, S_{T} is therefore positive for thermophobic particle motion.

Up to now there is a limited number of established facts about particle or macromolecular thermophoresis in

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liquids. For instance: for polymers solutions in good solvent, D_T does not depend on molecular weight [7,8]; electrostatic effects have a huge influence on the single-particle Soret coefficient of charged colloids, with interparticle interactions also playing a crucial role [9]; sign-reversal of S_T can be induced by changing the solvent composition [6].

The temperature dependence of thermophoresis has been investigated for polymer blends approaching the critical point [10] or in mixed solvents [11], and in recent experiments by our group [5,12] on globular protein solutions. For the purpose of what follows, we start by considering these latter results. By measuring the Soret coefficient of hen egg-white lysozyme, Iacopini and Piazza [5] have shown that particle motion can be tuned from thermophobic to thermophilic by decreasing the average sample temperature, and that in a wide pH and ionic strength range the temperature dependence of S_T is very well described by the empirical fitting function:

$$S_\mathrm{T}(T) = S_\mathrm{T}^\infty \left[1 - \exp\left(\frac{T^* - T}{T_0} \right) \right], \qquad (3)$$

where S_T^∞ represents a high-T thermophobic limit, T^* is the temperature where S_T switches sign, and the rate T_0 of exponential growth embodies the strength of temperature effects. Both T^* and T_0 are poorly sensitive to salt addition and lysozyme charge.

The observed data have been tentatively interpreted by assuming, as originally made for charged micellar solutions [9], that the particle thermophoretic drift arises from unbalanced interfacial stresses close to the particle surface, originating from the temperature inhomogeneity and pulling particles against the interfacial tension gradient. Later [13], this phenomenological *ansatz* has been given firmer bases by a microscopic hydrodynamic model, yielding a Soret coefficient of the general form:

$$S_\mathrm{T} = \frac{4\pi a}{k_\mathrm{B} T} \frac{\partial(\ell\gamma)}{\partial T}, \qquad (4)$$

where a is the particle radius, γ the particle/solvent interfacial tension, and ℓ is a microscopic length scale set by the range of the particle/solvent interactions, which is assumed to be small compared to a. In reference [11], the temperature dependence of the interfacial free energy of lysozyme was tentatively attributed to specific temperature hydrophobic particle-solvent interactions, which are known to be T-dependent. Yet, as we show in the present paper, the temperature behavior described by equation (3) turns out to be much more universal, embodying therefore more basic features of particle thermophoresis in aqueous solvents.

2 Experimental methods

The results presented in this paper have been obtained using two complementary optical methods, which we shall refer to as *beam-deflection* (BD) and *thermal-lensing* (TL). BD [4] exploits the deflection of a laser beam due to the concentration, and therefore refractive index gradient, induced by the imposed temperature field. A weak vertical temperature gradient is rapidly imposed between two metal plates enclosing the sample, and the deflection of a horizontally-propagating laser beam passing through the cell is monitored by a position sensitive detector (a detailed description of the apparatus can be found in [12]). Since the plates cannot be set closer than about 1 mm, BD measurements, whose duration is set by diffusion over the plate spacing, are however time consuming even for small colloids, and essentially precluded for suspensions of big latex particles.

TL [14] is an alternative, all-optical method, which exploits the self-effect on beam propagation taking place when a focused laser beam heats up a partially absorbing medium. This generates a locally inhomogeneous refractive index profile acting as a negative lens, which in turn increases the divergence of the transmitted beam. In fluid mixtures or solutions, the laser-induced temperature profile also drives Soret motion, which leads to the progressive buildup of a concentration gradient within the heated region, acting as an additional lenslike element [15]. We have recently developed a TL setup making use of a near-infrared laser, tuned to match a small vibrational overtone peak of water [16]. Since the focused beam has a spot of few tens of μm, measurement time scales are considerably shorter than in BD experiments. There is however a specific feature of the TL method requiring careful consideration. At variance with BD, a radially-symmetric laser beam unavoidably sets *horizontal* temperature gradients: this means that convection effects are inescapable. The basic strategy to limit their effects is reducing the focused spot so that on its spatial scale diffusion is much faster than convection. A detailed description of our experimental apparatus and an extensive analysis of convective effects can be found in reference [16]. Both methods have two common advantages. First, the Soret coefficient can be extracted using an internal calibration method with no reference to the apparatus geometry, once the increment with temperature and concentration of the solution refractive index are known. Second, the dynamics of the effect can be monitored, allowing for a simultaneous measurement of the Soret coefficient and of the diffusion coefficient D.

3 Temperature dependence of the Soret coefficient

3.1 Polypeptide solutions

We first show that the temperature dependence of S_T on T observed in [5,12], and described by equation (3), is shared by other protein and polypeptide solutions. Figure 1 compares the behavior of lysozyme ($M_\mathrm{W} \simeq 14$ kDa) with that of β-lactoglobulin-A (BLGA), a 36 kDa globular protein, and of poly-L-lysine, the homopolymer of the charged amino acid lysine, having a molecular weight $M_\mathrm{W} \simeq 50$ kDa. To investigate whether hydrophobic interactions are essential in order to get a sign reversal of S_T,
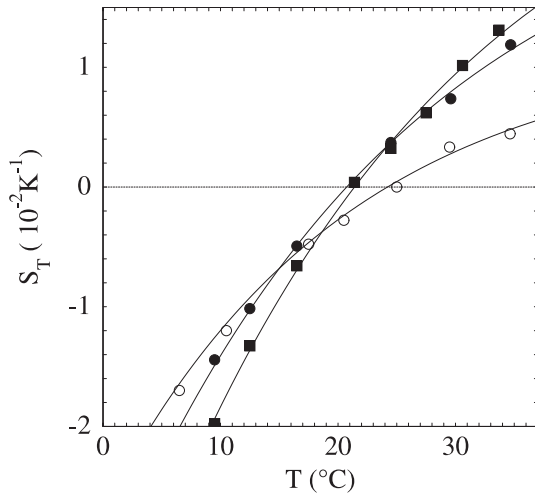
Fig. 1. Temperature dependence of the Soret coefficient S_T for BLGA ($\bullet$, $c = 13$ g/l, pH = 7.0, NaCl 50 mM) and for 50 kDa poly-L-lysine solutions ($\blacksquare$, $c = 5.4$ g/l, pH = 7.0, NaCl 100 mM), compared to the results obtained in reference [12] for lysozyme ($\circ$). Full lines are obtained from equation (3) using the fit parameters listed in Table 1.

Table 1. Values of the parameters obtained by fitting equation (3) to the experimental $S_T(T)$ for different polypeptides. Fits (here and in the other Tables) were performed using a Kelvin temperature scale, although in the text T^* is generally expressed for easier comparison in Celsius (obviously, fit values for T_0 do not depend on the choice of K or °C).

sample	$S_T^\infty (\text{K}^{-1})$	$T^*(\text{K})$	$T_0(\text{K})$
lysozyme	0.0111 ± 0.0015	297.5 ± 0.3	20 ± 2
BLGA	0.0275 ± 0.0035	293.9 ± 0.3	26 ± 3
poly-L-lysyne	0.034 ± 0.006	294.6 ± 0.3	26 ± 4

we specifically chose poly-L-lysyne as a model polypeptide with the lowest possible hydrophobic character [17]. Yet, the temperature dependence of the Soret coefficient for poly-L-lysine fully conforms to equation (3), ruling therefore out any crucial role of hydrophobic interactions.

3.2 "Athermal" systems

Many solution properties witness the strong temperature dependence of protein/water interactions [18]. One may therefore wonder whether relevant temperature effects on thermophoresis are exclusive of "thermal" systems, where the particle solvation entropy plays a major role. To settle this point, we have investigated solutions of simple macroions like ionic micellar and synthetic polyelectrolyte solutions, where particle/solvent and interparticle interactions have a purely electrostatic nature. Figure 2 shows that the $S_T(T)$ curves obtained for sodium dodecyl sulfate (SDS) micellar solutions at two different surfactant (10 and 20 g/l) and added salt (10 and 20 mM
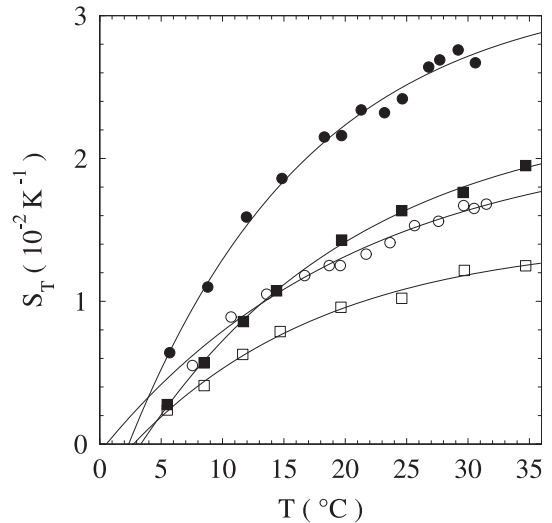

Fig. 2. Temperature dependence of the Soret coefficient S_T for SDS ionic micelles at concentration $c = 10$ g/l (full symbols) and 20 g/l (open symbols), in the presence of 10 mM (squares) and 20 mM (circles) NaCl. Full lines are fits with equation (3) using the parameter values listed in Table 2.

NaCl) concentrations[1] are once again nicely described by equation (3), with fit parameters T^* and T_0 that do not depend on the ionic strength I and SDS concentration c (see Tab. 2). Therefore I and c, which tune the contribution of interparticle interactions to S_T, only influence the overall strength S_T^∞ of the thermophoretic effect, while T^* and T_0 are essentially single-particle properties. According to the model presented in references [9,12], the Soret coefficient for systems of interacting particles is proportional to the osmotic compressibility of the solution. The results shown in Figure 2 support this picture: in the presence of repulsive electrostatic interactions, S_T indeed *decreases* with increasing surfactant concentration. We point out that clear evidence that collective effects on S_T are strictly related to the osmotic compressibility of the solution has also been obtained by Enge et al. in thermal diffusion experiments on polymer blends [19]. Besides, the data in Figure 2 also show that, in dilute conditions, varying the particle/solvent electrostatic interactions does not change the functional dependence of S_T on T. Yet, an important difference emerges for what concerns the sign-reversal temperature, which shifts from $T^* \sim 20$ °C, the value observed for polypeptides, down to $T^* \sim 3$–4 °C, and approximately coincides with the maximum-density temperature of the solvent[2].

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[1] Measurements at higher ionic strength are precluded, since the Krafft temperature where SDS precipitates shifts well above 4 °C.

[2] We point out however, that both for SDS and for other "athermal" systems to be analyzed in what follows, T^* is only an extrapolated value. Experimental problems such as vapour condensation on the cell windows make measurements below $T \simeq 5$ °C hardly feasible, so that we could not collect any direct evidence of sign-reversal for S_T, except for polystyrene latex particles (see below).

Table 2. Values of the parameters obtained by fitting equation (3) to the experimental $S_T(T)$ for SDS samples.

I (mM); c (g/l)	S_T^∞ (K^{-1})	T^* (K)	T_0 (K)
10; 10	0.0235 ± 0.001	276.5 ± 0.3	18 ± 1
10; 20	0.0145 ± 0.001	275.9 ± 0.6	16 ± 3
20; 10	0.0320 ± 0.002	275.6 ± 0.7	15 ± 3
20; 20	0.0220 ± 0.002	274.9 ± 1.2	21 ± 5

Table 3. Values of the parameters obtained by fitting equation (3) to the experimental $S_T(T)$ for NaPSS samples.

sample	S_T^∞ (K^{-1})	T^* (K)	T_0 (K)
$M_W = 15200$	0.047 ± 0.005	276.2 ± 1.0	20 ± 5
$M_W = 32900$	0.055 ± 0.003	276.9 ± 0.5	19 ± 2
$M_W = 74000$	0.072 ± 0.005	277.0 ± 0.4	22 ± 3

Fig. 3. Temperature dependence of the Soret coefficient S_T for NaPSS molecular weight standards $M_W = 15\,200$ (●), $M_W = 32\,900$ (▲), $M_W = 74\,000$ (■) fitted to equation (3) (see Tab. 3). In the inset, $S_T(T)$ for the same curves is rescaled with $M_w^{1/4}$ (full symbols) and $M_w^{1/2}$ (open symbols).

The observations made for spherical charged micelles are further supported by the results obtained on solutions of the linear polyelectrolyte sodium polystyrene sulfonate (NaPSS, Polyscience, USA) for three different values of NaPSS molecular weight M_W. In order to limit the effects of interparticle electrostatic interactions, dilute NaPSS ($c = 2$ g/l) solutions were prepared in the presence of 100 mM added NaCl, preliminarily checking that, in these working conditions, S_T does not change on further dilution, with a possible exception for the highest molecular weight ($M_W = 74\,000$), where small residual concentration effects were still detectable. Once again, Figure 3 shows that equation (3) yields the correct trend for the temperature dependence of S_T. Table 3, moreover, shows that T^* and T_0 are weakly affected by NaPSS molecular weight, which mainly fixes the high temperature limit S_T^∞.

Due to the short-range nature of monomer/solvent interactions and to the lack of correlations between different monomers, the Soret coefficient of *neutral* polymer solutions is predicted [20] end experimentally found (see, for instance, [8][3]) to scale as $S_T \propto M_w^{0.5}$. The inset in Figure 3 shows however that the three $S_T(T)$ curves, when rescaled with $M_w^{1/2}$, do not overlap. Conversely, a rather good superposition is found by taking the ratios $S_T(T)/M_w^{1/4}$. This preliminary observation seems to suggest that long range interactions between monomers due to electrostatic repulsion noticeably influence the thermophoretic behavior of polyelectrolytes, even at moderately high ionic strength.

One might still wonder whether micelles or polyelectrolytes undergo slight morphological changes as a function of temperature that may concur to set the temperature dependence of S_T. It is therefore wise to investigate the behavior of suspensions of rigid charged colloids. Since the minimal size of monodisperse

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[3] As recently pointed out by Rauch *et al.* [21], however, scaling arguments should be applied with a bit of care: finite-size effects may be non negligible even for moderately long oligomers, in particular when the end groups display a thermophilic behaviour.
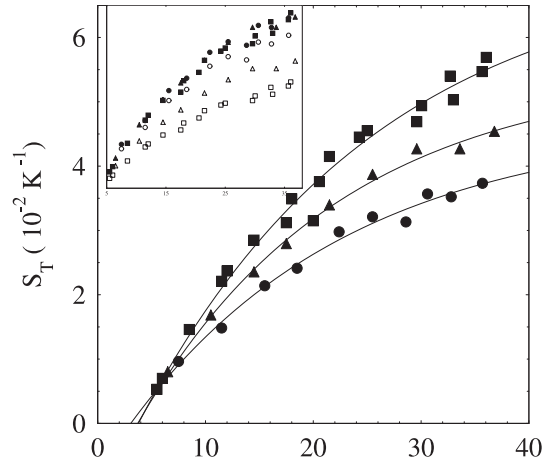
spherical latex particles typically falls in the tens on nanometers size range, thermophoretic measurements have necessarily to be performed using the TL apparatus. We have therefore performed preliminary TL measurements on polystyrene particles (Interfacial Dynamics Corporation, USA) with radius $R = 30$ nm, measured by Dynamic Light Scattering, and surface charge density $\sigma = 0.4$ μC/cm^2 (as stated by the producer), at fixed particle volume fraction $\Phi = 0.005$. In order to screen electrostatic interactions, samples were prepared in the presence of 4 mM NaCl, corresponding to a screening length $\lambda_{DH} \simeq 5$ nm. Figure 4 shows that, for what concerns both the sign-reversal temperature ($T^* = 278.3 \pm 0.7$ K) and the rate of temperature change ($T_0 = 19 \pm 4$ K), $S_T(T)$ is quite similar to what we found for SDS and NaPSS (notice however that, at variance with the former data, a weak thermophilic behavior is already observed at $T = 5$ °C). Conversely, the amplitude of the effect ($S_T^\infty = 0.92 \pm 0.3$ K^{-1}) is about an order of magnitude larger than for SDS micelles, suggesting, for spherical colloids, an approximately linear dependence of the Soret coefficient on the particle size.

3.3 The case of DNA

As a further example of TL measurements, we shall discuss the temperature dependence of the Soret effect in DNA solutions. Thermal diffusion of DNA has recently attracted the attention of the large audience, after Braun and Libchaber [3] proved that the concurrent action of thermophoresis and thermal convection may lead to a huge increase of the local macromolecular concentration around specific "hot spots". In simple words, DNA tends to concentrate in the regions where advective mass transport and thermophoretic motion act in opposite directions. This observation, besides being of practical interest for developing new PCR replication methods [22], lead the
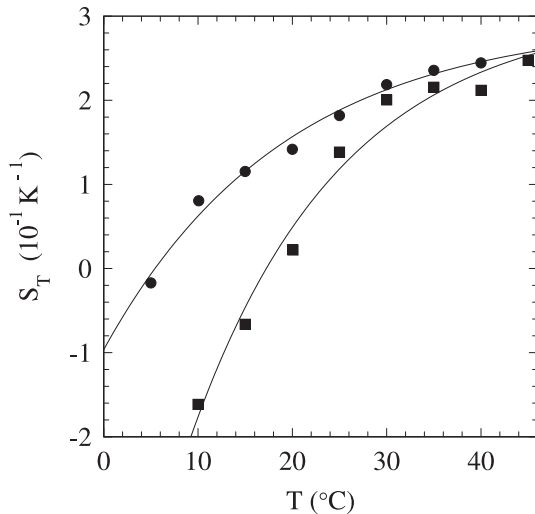
Fig. 4. Thermal-lensing measurements of the Soret coefficient for polystyrene latex spheres (●) and pMD31 plasmid DNA (■). Full lines are again fits to equation (3).
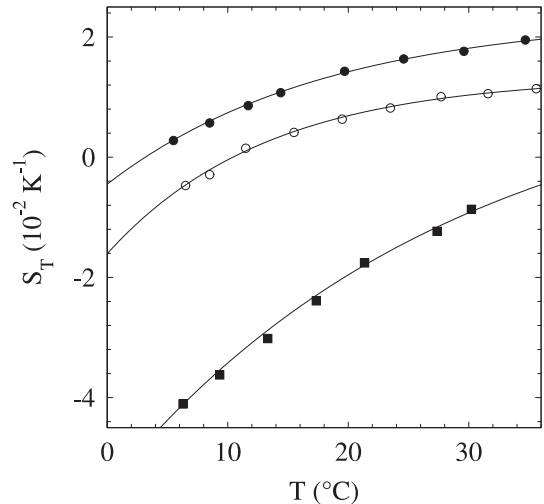

Fig. 5. Temperature dependence of the Soret coefficient S_T for pure SDS (●, 10 mM NaCl) and DM (■, in water) solutions, and for a 1:1 molar mixture of DM and SDS (○, total surfactant concentration $c_{\text{tot}} = 25$ mM, NaCl 10 mM). Full lines are fits using equation (3).

former authors to speculate about the role of Soret effect in prebiotic molecular evolution near hydrothermal vents [23]. Any strong temperature dependence of DNA thermophoresis would however influence, at least quantitatively, the aforementioned evidence. In Figure 4 we report preliminary results for Soret coefficient of 6.7 kbp pMD31 plasmid DNA, kindly prepared for us by Livia Visai (University of Pavia, Italy), obtained for a 0.6 g/l solution in 7.5 mM phosphate buffer (pH = 7.0). Due to the low sample concentration, the data are rather dispersed when compared to the systems we have discussed so far: nonetheless, the general trend of the results is quite similar to what we found for polypeptide solutions. In particular, while at high temperature S_T is still positive, at temperatures around 4 °C, corresponding to marine deep-water temperature, DNA is strongly *thermophilic*. We believe that this sign-reversal of DNA Soret effect coefficient must be taken into due account to perform realistic simulations of DNA convective transport.

3.4 Tuning the sign-reversal temperature

Both the simple approach developed in reference [9] and the general model of thermophoresis presented in reference [13] suggest that the thermophoretic motion arises from unbalanced stresses localized in a thin layer close to the particle surface, and is therefore primarily set by the nature and strength of particle/solvent interactions. To test this basic idea, we have attempted to tune the particle/solvent interfacial properties while keeping constant the particle size. This goal can be achieved by exploiting the aggregation properties of ionic/nonionic surfactant mixtures.

The nonionic surfactant β-dodecyl-maltoside (DM) is a glycolipid having the same $C_{12}H_{25}$ hydrophobic tail

as SDS, but a *nonionic* hydrophilic head group consisting of two glucose rings. DM micellar solutions show a rather peculiar thermophoretic behavior, witnessing a strong "thermophilic nature" (see Fig. 5). Similarly to the systems we have described so far, $S_T(T)$ is still well described by equation (3): yet, the Soret coefficient is negative even at room temperature, T^* being shifted to much higher temperatures ($T^* \sim 43$ °C). Mixtures of DM and SDS self-aggregate into almost ideally-mixed globular micelles [24]. Since the aggregate size weakly depends on the SDS/DM molar ratio f, these micelles bear a "bare" charge that grows almost linearly with f up to $Z \simeq 70$. However, due to counterion condensation [25], the micellar *effective* charge saturates by increasing f to a value $Z_{\text{eff}} \simeq 20$ [24,25]. In particular, SDS/DM mixtures with $f = 1$ form mixed micelles with essentially the same size and effective charge of pure SDS micelles.

Figure 5, which compares the Soret coefficients of the two pure surfactants with the results obtained for SDS/DM mixtures with $f = 1$ and total surfactant concentration $c = 25$ mM, shows that mixed micelles have an intermediate behavior, with a sign reversal temperature $T^* \simeq 10$ °C. The full S_T curve for SDS/DM mixtures can actually be obtained from that of SDS by adding a constant negative value $\Delta S_T = -0.008$ K^{-1}. The insertion of sugar surface groups interacting with the solvent via hydrogen bounds (like many of the amino acids present on a protein surface) leads therefore to a more thermophilic behavior.

4 Soret coefficient and thermal expansion

As we have seen in the former Sections, $S_T(T)$ is very conveniently described, for all investigated systems, by

equation (3) that, besides performing quite better than a simple polynomial fit with the same number of free parameters, yields a simple physical interpretation of the quantities T^*, T_0, and S_T^∞. Nonetheless, equation (3) is still an empirical fit function, which is not based on any specific model for the temperature dependence of the Soret effect. In particular, a crucial question that cannot be answered by resorting to empirical fits is why a strong temperature dependence of thermophoresis is observed even for "athermal" systems where the particle/solvent and interparticle interactions are primarily electrostatic. It is therefore useful seeking correlations between $S_T(T)$ and other solution properties that depend on T. A possible hint is that, for "athermal" systems, T^* approximately coincides with the temperature where the solvent density ρ is maximal. More recently [26], Parola and Piazza have shown that the model presented in reference [13], when applied to a suspensions of particles interacting with a hard-sphere solvent solely as a hard wall, yields a Soret coefficient that is rigorously proportional to the solvent thermal expansivity $\alpha \equiv -1/\rho\,(\mathrm{d}\rho/\mathrm{d}T)$. The upper graph in Figure 6 shows that, for the systems discussed in Section 3.2, the dimensionless quantity $\widetilde{S_T}$, which is obtained by taking the ratio of $S_T(T)$ to the accurate expression for water thermal expansivity given in reference [27], turns out to be very weakly dependent on temperature. We can therefore conclude that the dominant contribution to the temperature dependence of the Soret coefficient of athermal systems is simply the solvent thermal expansivity[4]. Notice that, in terms of $\widetilde{S_T}$, equation (2) can be written as:

$$\frac{1}{c}\frac{\mathrm{d}c}{\mathrm{d}z} = \widetilde{S_T}\frac{1}{\rho}\frac{\mathrm{d}\rho}{\mathrm{d}z},$$

which, once integrated, yields a simple relation between the local solute concentration and solvent density:

$$\frac{c(z)}{c_0} = \left[\frac{\rho(z)}{\rho_0}\right]^{\widetilde{S_T}}, \qquad (5)$$

where c_0 and ρ_0 are, for instance, the initial uniform particle concentration and solvent density.

Such a simple rescaling does not obviously hold for systems like polypeptides, nonionic micelles, or DNA, where T^* is considerably larger than 4 °C. We recall, however, that "thermal" and "athermal" systems share the *same* functional dependence of $S_T(T)$. This means that, for instance, if we vertically translate each $S_T(T)$ curve so that the sign-reversal temperature is shifted to 4 °C (which means, if we add to the amplitude S_T^∞ a negative "excess" contribution S_T^{exc}), the ratio $(S_T - S_T^{exc})/\alpha$ is again found to be temperature independent. This is shown in the lower graph of Figure 6. Although we shall not attribute any deep physical meaning to this observation, it is anyway curious that the Soret coefficient of "thermal" systems can be formally thought to differ from "athermal" systems just by a *temperature-independent* contribution.

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[4] We neglect here possible additional slowly-varying terms, *i.e.* factors of O(T).
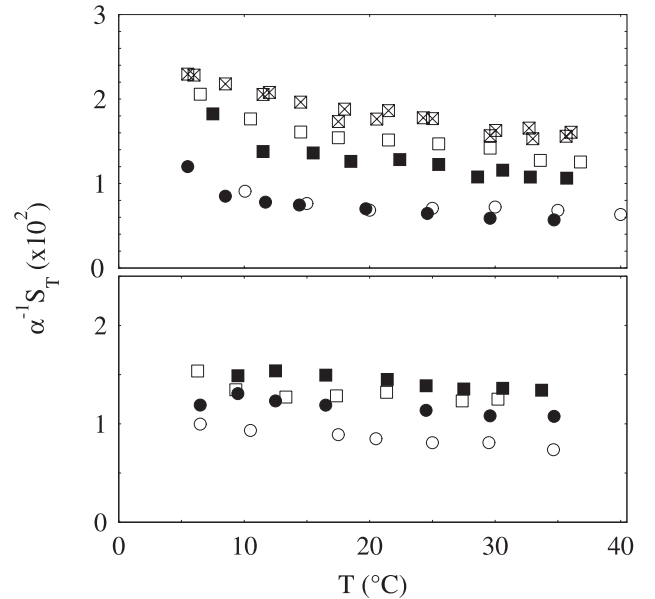

Fig. 6. Upper graph: dimensionless Soret coefficient $\widetilde{S_T} = S_T/\alpha$ for SDS (●, 10 g/l, 10 mM NaCl), NaPSS 15.4 kDa(■), 32.9 kDa (□), 74 kDa (⊠), and Polystyrene latex particles (○, scaled down by a factor of 10). Lower graph: $\widetilde{S_T}$ for lysozyme (○, $S_T^{exc} = -0.021$ K^{-1}), BLGA (●, $S_T^{exc} = -0.025$ K^{-1}), Poly-l-lysine (■, $S_T^{exc} = -0.032$ K^{-1}), and β-dodecyl-maltoside (□, $S_T^{exc} = -0.047$ K^{-1}).

5 Thermal diffusion coefficient

The time dependence of both BD and TL signals also allows extracting the particle Brownian diffusion coefficient D [16,28][5], so that the thermal diffusion coefficient can be directly obtained as $D_T = S_T D$.

D_T is a rather complex transport coefficient[6], embodying cross-correlations between heat and mass flow [30]: its physical meaning is therefore rather obscure when compared to S_T, which is simply related to the steady-state inhomogeneous concentration profile through equation (2). Yet, measurements on lysozyme solutions have shown that D_T displays a simple linear dependence on T [12]. Figure 7, which summarizes the results for D_T obtained on the systems discussed in the former Sections, shows that this linear behavior is strikingly universal, so that we can write:

$$D_T = A(T - T^*), \qquad (6)$$

where T^* has the same meaning as in equation (3) and A is a system-dependent amplitude, but the sign-switching temperature does not depend on interparticle interactions or, for polyelectrolytes, on the molecular weight. Notice also that the amplitude A has the same order of magnitude for PS colloids and SDS or NaPSS, despite the large

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[5] Obtaining D from thermophoretic transients is particularly useful for polyelectrolytes at low ionic strength, which display very low light scattering signals. In general, thermophoretic measurements may profitably complement dynamic light scattering analysis of poorly scattering samples [4].

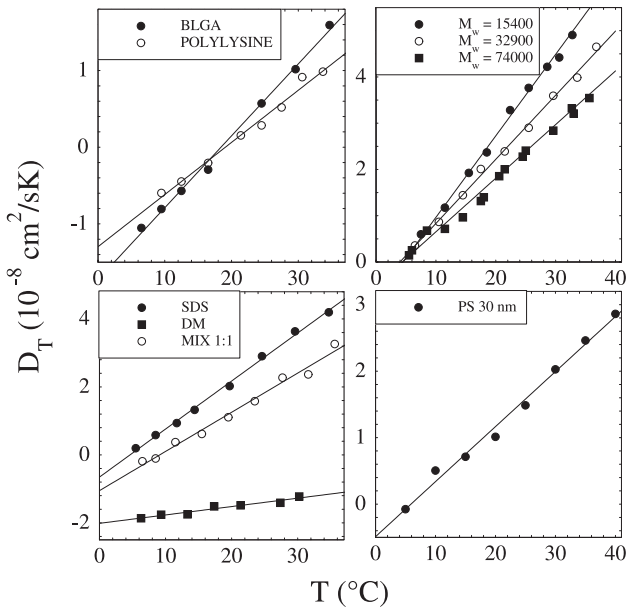[6] Notice that, dimensionally, D_T is *not* a diffusion coefficient.

Fig. 7. Temperature dependence of the thermal diffusion coefficient D_T for polypeptides (upper left graph), NaPPS (upper right), mixed SDS/DM micelles (lower left) and polystyrene latex particles (lower right). Full lines are linear fits to the data.

difference in particle size. This evidence is fully consistent with the linear dependence of S_T on particle size suggested in Section 3.2 that, due to the inverse scaling of D on the particle size, yields a size-independent thermal diffusion coefficient, similar to what has been found for polymer random coils. According to the model presented in reference [13], insensitivity of D_T to the particle size should hold whenever the range of particle/solvent interactions is short compared to the particle size (in other words, in a quasi-planar approximation, D_T depends only on "local" interfacial properties).

Since $D_T = S_T D$, where D is inversely proportional to the temperature-dependent solvent viscosity η, scaling the thermal diffusion coefficient to the thermal expansivity, as we made for S_T in the former section, still yields a rather substantial temperature dependence of the quantity D_T/α even for "athermal" systems. Yet, scaling by α still considerably reduces the temperature dependence of D_T. Indeed, the temperature dependence of water viscosity (which changes by a factor of 2.4 between 4 and 40 °C) is rather weak compared to the strong variation of α.

One of the key aspects of thermal transport in fluids is that *no pressure gradient is associated to the temperature gradient*. This result, which was already known for gases from kinetic theory [29], has been rigorously extended to liquids in reference [26] using the general linear response approach to thermal transport coefficients developed by Mori [30]. Therefore, gradients in the solvent density $\rho(T,P)$ are only due to temperature inhomogeneities[7].

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[7] Notice that, even in the presence of pressure gradients, $(\partial\rho/\partial P)_T$ would be negligible compared to $(\partial\rho/\partial T)_P$, due to the very low compressibility of a liquid.

Thus, equation (1) for the mass flux can be written as:

$$J = -D\frac{\mathrm{d}c}{\mathrm{d}z} + \widetilde{D}\frac{\mathrm{d}\rho}{\mathrm{d}z} \qquad (7)$$

with

$$\widetilde{D} = \left[(\rho_{\mathrm{p}}/\rho)\Phi\widetilde{S_T}\right]D, \qquad (8)$$

where ρ_{p} and Φ are the particle material density and volume fraction. Notice that, at variance with D_T, $\widetilde{D}$ has the usual dimensions $[\ell]^2/[t]$ of a diffusion coefficient. A key feature of equation (7) is that *no reference to the presence of a thermal gradient is anymore present* (this is why we have omitted placing a "T" subscript in $\widetilde{D}$). The second term only means that, for positive $\widetilde{D}$, particles drift toward regions where the solvent density is higher, so that $\widetilde{D}$ may be more generally envisaged as *the particle diffusion coefficient due to an artificially imposed solvent density profile*. The latter may well be due to a thermal gradient, but it is not necessarily so. For instance, the drift of neutrally-buoyant particles in an effective solvent made inhomogeneous by gravity or centrifuge sedimentation (like salt-gradient separation of biological macromolecules), where density gradients are due to pressure instead of thermal gradients, presents strong analogies with the present case. Although we do not presently have a physical picture of the (T-independent) dimensionless quantity $\widetilde{S_T}$, it might likely be expressed in terms of basic particle and solvent properties, so that the pre-factor in $\widetilde{D}$ depends only on general equilibrium quantities. It would be therefore interesting to scrutinize whether other diffusion processes driven by solvent density gradients share with thermophoresis the same value for the diffusion coefficient associated to $\nabla\rho$.

6 Discussion and conclusions

Main aim of this paper has been solving an old and rather debated riddle [4–6], namely the occurrence of negative Soret coefficients for a small, but non negligible number of macromolecular and colloidal systems. In addition, we have tried to address the more general problem of the temperature dependence of thermophoretic effects.

First of all, we have shown that the experimental trend for $S_T(T)$ originally observed for lysozyme solutions [5], is shared by a wide class of aqueous systems. According to the value of the parameter T^* in equation (3) (which turns out to be a single-particle property and, for polyelectrolytes, does not depend on the molecular weight), disperse systems can be roughly split into two classes. For those we called "athermal systems", encompassing for instance suspensions of particles interacting via screened Coulomb forces, the temperature dependence of S_T is basically due to the thermal expansivity α of the solvent. Particles of this kind are therefore always thermophobic at room temperature, eventually switching their thermophoretic motion only for $T \lesssim 4$ °C. Other systems like proteins, surfactant micelles with sugar head

groups, and DNA have conversely a much more pronounced thermophilic behavior. Yet, their behavior can be reconciled with the former one provided that a negative, T-independent contribution to the Soret coefficient is added. As we anticipated, direct proportionality of the Soret coefficient to α is rigorously predicted in the limiting case of a particle acting as a hard-wall (no specific particle/solvent interactions) dispersed in a hard-sphere solvent [26]. The experimental observation of a T-independent $\widetilde{S_{\mathrm{T}}}$ for more complex systems like charged colloidal suspensions suggests that the primary role of α in setting the temperature dependence of S_{T} may be a general feature of thermophoresis.

At variance with the rather complex trend for S_{T} embodied in equation (3), the temperature dependence of D_{T} is found to be strictly linear for all investigated systems. This result is rather surprising and poses a subtle question. Apparently, the nonlinear temperature behavior of $S_{\mathrm{T}}(T)$ is indeed traced out by simply taking its ratio to the solvent viscosity (which is also nonlinear in the investigated temperature range). At a first inspection, one would therefore conclude that S_{T} is proportional to η, while D_{T} is not. Yet, S_{T}, being the *ratio* of two transport coefficients describing the steady-state concentration profile, may be rather expected to be independent from hydrodynamic quantities, while the contrary may be guessed for D_{T}. Indeed, general models of particle thermophoresis in liquids (see, for instance [13,31,32]), predict S_{T} to be dependent only on *equilibrium* properties. This theoretical suggestion is for instance supported by the results obtained by Rauch *et al.* [33] for thermal diffusion close to a polymer glass: while approaching the glass transition leads of course to a sharp decay of both D and D_{T}, S_{T} is essentially constant, mirroring the insensitivity of the solution structural properties to the kinetic arrest. The linear behavior of D_{T} we have observed may however be partly incidental. Indeed, in the investigated temperature range, the viscosity of water itself turns out to decrease almost linearly with α, *i.e.* $\eta \simeq \eta_0 - C\alpha$: taking the ratio of $S_{\mathrm{T}} = \alpha \widetilde{S_{\mathrm{T}}}$ with η leads to a sensible reduction of the quadratic temperature term. Further analysis is anyway needed to settle this point.

It would be very useful to test the *ansatz* we made about the scaling of the Soret coefficient with α using *non-aqueous* systems. One of the peculiarities of water is indeed the change of sign for α below 4 °C. For "athermal" systems in non polar solvent, where the density is usually a monotonically decreasing function of T, no sign-reversal of S_{T} should therefore be observed. Unfortunately, as we already pointed out, we are aware of very few experimental results for the temperature dependence of thermophoresis. Temperature data for poly-ethylene oxide in mixed water/ethanol solvents, where both D_{T} and S_{T} are also found to decrease with T, have been presented in reference [11]. Interestingly, while the results for D_{T} in pure water seem to extrapolate to zero at about 4–5°C, the sign-switching temperature seems to *increase* by adding ethanol. At variance with all the systems discussed in the present paper, however, more recent results for semidilute solutions of poly(N-isopropylacrylamide) in ethanol [34] show a Soret coefficient that *decreases* with T. Neither these systems can be assumed to be "athermal" suspensions of rigid colloidal particles (such as those considered in Ref. [13]) and, in addition, ethanol is a solvent rather akin to water. Obviously, ideal systems would be suspensions of sterically stabilized particles in a non-polar fluid, like for instance poly-methylmetacrylate latices in decalin, whose colloidal properties have already been thoroughly investigated. Unfortunately, our present experimental setups do not easily allow performing similar studies. It is indeed rather difficult to synthesize very small latex particles suitable to be investigate using BD, while the TL apparatus has been specifically designed to deal with aqueous suspensions. An alternative approach, which we are currently following, would be investigating water-in-oil microemulsions with well-known structural properties.

Finally,we stress again that the introduction of the dimensionless quantity $\widetilde{S_{\mathrm{T}}}$ and of the diffusion coefficient $\widetilde{D}$ allows "tracing out" the actual causative agent of the solvent density profile (the thermal gradient) and may help to extend our analysis to other effects of colloidal diffusion in inhomogeneous solvents.

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