Soft Matter

PAPER

Giant thermophoresis of poly(*N*-isopropylacrylamide) microgel particles

Simon Wongsuwarn,[a] **Daniele Vigolo,**[b] **Roberto Cerbino,**[c] **Andrew M. Howe,**†[d] **Alberto Vailati,**[e] **Roberto Piazza**[b] **and Pietro Cicuta***[a]

Thermophoresis is the rectification of Brownian motion induced by the presence of a thermal gradient ∇T, yielding a net drift of colloidal particles along or against the direction of ∇T. The effect is known to depend on the specific interactions between solute and solvent, and quantitative theoretical models are lacking except in a few simple experimental cases. Both the order of magnitude and the temperature dependence of the thermophoretic mobility D_T are known to be very similar for a wide class of aqueous colloidal systems, ranging from latex colloids to polymers, surfactant micelles, proteins, and DNA. Here we show that thermoresponsive microgel particles made of poly(*N*-isopropylacrylamide) (PNIPAM) do *not* share, in the temperature range around the ϑ-point, these common features. Instead, D_T displays an unusually strong temperature dependence, maintaining a linear growth across the collapse transition. This behaviour is not shared by linear PNIPAM chains, for which existing data show D_T falling at the transition, with similar values between the expanded coil and collapsed globule states away from the transition point. A possible connection of the observed giant temperature dependence of D_T to microgel hydration is suggested.

1 Introduction

Thermophoresis is the drift of colloidal particles of macromolecular solutes along a thermal gradient ∇T, amounting to a partial rectification of Brownian motion induced by coupling between heat and mass transport.[1,2] The particle drift velocity can be written as

$$\mathbf{u} = -D_T \nabla T, \qquad (1)$$

where D_T, which plays the role of a thermophoretic mobility, is usually called the "thermal diffusion coefficient" because of the very tight relation between thermophoresis and thermal diffusion (the Ludwig–Soret effect) in simple fluid mixtures.[3–5] If ∇T is constant in time and convection is absent, the balance between thermophoresis and osmotic diffusion leads to a steady state concentration gradient given, for a dilute suspension, by:

$$\nabla c = -c S_T \nabla T \qquad (2)$$

where c is the average weight fraction of particles, $S_T = D_T/D$ is known as the Soret coefficient and D is the usual Brownian diffusion coefficient. In the past decade, the refinement of available experimental methods together with the development of novel and sensitive optical techniques has allowed for the investigation of thermophoresis in a wide class of disperse systems, ranging from simple latex colloids to polymers, micelles, microemulsions, and biomolecular solutions.[6–12] These studies provide a phenomenological insight into the general features of this effect, which can be very helpful in well-established separation methods such as Thermal Field-Flow Fractionation (ThFFF[13]), as well as more recent microscale applications and devices.[14–17]

A dilute suspension of Brownian particles in a moderately weak thermal gradient is one of the simplest examples of a non-equilibrium system, however, understanding the physical origin of thermophoresis remains a theoretical challenge. Strenuous efforts to obtain S_T from the temperature dependence of transport coefficients,[18] or more generally by considering consistent modifications of the Smoluchowski equation in thermally inhomogeneous media,[19] yield Soret coefficients that are only of order $1/T$. More promising is the relation with other "phoretic" kinds of motion driven by applied external fields, such as electro-, dielectro-, and magnetophoresis,[20,21] where particle motion is attributed to a field-induced breaking of the no-slip hydrodynamic boundary condition. A sound explanation of the thermophoresis of rigid particles based on this analogy, which stresses the key role played by particle/solvent interfacial

[a] *Biological and Soft Systems Sector, Cavendish Laboratory, University of Cambridge, CB3 0HE, U.K. E-mail: slw46@cam.ac.uk*
[b] *Dipartimento di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano, 20133 Milano, Italy. E-mail: roberto.piazza@polimi.it*
[c] *Dipartimento di Chimica, Biochimica e Biotecnologie per la Medicina, Università degli Studi di Milano, via F.lli Cervi 93, 20090 Segrate, Italy*
[d] *BPI, University of Cambridge, Madingly Rise, Cambridge, CB3 0EZ, U.K*
[e] *Dipartimento di Fisica, Università degli Studi di Milano, 20133 Milano, Italy*
† Present address: Schlumberger Cambridge Research Centre, High Cross, Madingley Road, Cambridge, CB3 0EL, U.K.

properties was suggested by Ruckenstein[1] and applied by Piazza and Guarino to quantitatively account for the Soret effect of charged micelles.[6] A number of different hydrodynamic models developed along these lines for the specific case of screened electrostatic particle/solvent interactions[22–24] basically agree in their conclusions. Yet, although very general hydrodynamic models of particle thermophoresis can be developed,[23] deriving from them explicit results is non-trivial, except for the screened Coulomb case we just mentioned and a few other simple kinds of particle/solvent interactions. Nonetheless, a general conclusion from hydrodynamic models is that D_T is a "local" quantity, which should not depend on particle size.‡ We point out that this feature is shared by flexible polymers, where a general scaling argument put forward by Brochard and De Gennes[27] leads, together with careful hydrodynamic analysis, to the requirement that D_T should not depend on the molecular weight (MW). Experimental results[8] have supported this conclusion in the high MW limit (greater than 4.7 kg mol^{-1}). Assuming a local character of D_T, which does not depend on long-range correlations, also allows for the prediction of the observed power-law divergence of S_T close to the critical point of a simple liquid mixture, with the same exponents of the system correlation length.[28]

Aqueous colloids exhibit thermophoretic behaviour that is particularly surprising and unaccounted for by any present model. Not only are the values of thermophoretic mobility very close (of order 10^{-7}–10^{-8} cm^2 s^{-1} K^{-1}), but they also show a strikingly similar temperature dependence. For almost all aqueous particle suspensions and polymer solutions, D_T has a weak linear dependence on T of the form

$$D_T(T) = A(T - T^*), \tag{3}$$

where the temperature T^* where D_T switches sign§ is system-dependent, but the amplitude $A = dD_T/dT$ is always of the order of 10^{-9}–10^{-10} cm^2 s^{-1} K^{-2} for a wide range of systems from small micelles to micron-sized latex colloids.[10,29] Since this feature is common to aqueous systems, we may expect that it is related to the temperature dependence of hydrogen bonding and hydrophobic effects. Hydrogen bonds are broken with increasing thermal agitation whereas the hydrophobic interaction becomes stronger. These forces have been shown to set the behavior of many solution properties including, recently, protein solubility.[30,31]

A strong and system-specific temperature dependence of D_T could be helpful for devising separation methods based on thermophoresis. The main purpose of this paper is to show that the uniformity in thermophoretic behaviour shown by aqueous colloids is apparently broken by the specific system we have investigated, namely an aqueous suspension of poly(N-isopropylacrylamide) (PNIPAM) microgel particles. This system shows much stronger temperature effects on D_T yielding, when compared to suspensions of particles of comparable size, giant values of the Soret coefficient in the vicinity of the microgel

volume transition temperature. By comparing to former thermophoretic experiments,[32] we shall show that this behavior is specific to the microgel form of PNIPAM, being not apparently shared by linear PNIPAM chains.

2   Physical properties of PNIPAM and PNIPAM microgels

PNIPAM is a neutral polymer displaying a distinctive amphiphilic character due to the combination of hydrophilic and hydrophobic groups in its monomer structure (see Fig. 1).[33] At sufficiently low temperature, water molecules bind very effectively to the central amide groups via hydrogen bonds and the chain adopts the random coil structure. The hydrophobic isopropyl side groups are exposed in this expanded coil state, leading to the formation of so-called water "clathrate" structures. On increasing the temperature, the hydrogen-bonds are disrupted and the entropic penalty associated with the clathrate structures increases. PNIPAM displays a ϑ-temperature $T_\vartheta \simeq$ 31 °C, marking the transition from good to bad solvent and corresponding to a value of the Flory parameter $\chi = 1/2$.¶ By further raising the temperature to $T_{cg} \simeq 32.5$ °C, PNIPAM undergoes a coil-to-globule transition known as collapse. In the compact globular structure formed, the hydrophobic regions are better screened from contact with water.[34]

As the coil-to-globule transition plays a key role in many processes involving biological molecules, the solution properties of PNIPAM have been studied in detail.[35,36] An important outcome of these studies is that the globule conformation does not correspond to a compact uniform particle, but rather displays an internal structure with a denser core surrounded by a softer corona.[37] The tendency to screen the hydrophobic groups
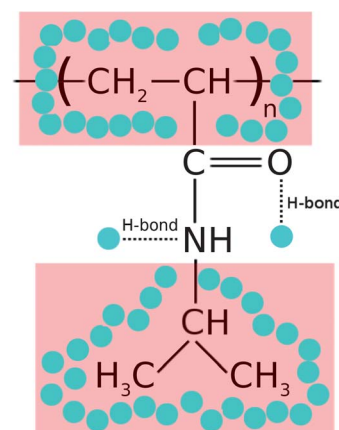

Fig. 1 Chemical structure of a PNIPAM monomer. Solubility in water is promoted, through hydrogen-bonding, by the central amide group, which competes with the hydrophobic character of the chain backbone and side group (shaded in red). Below the ϑ-point, cage ("clathrate") structures of water molecules (cyan) are believed to be coordinated around the hydrophobic parts. The structural properties of bound and coordinated water are discussed in Aseyev et al.[42]

---

‡ This conclusion is not compatible with those by models relying on "local equilibrium" concepts,[25,26] which predict a linear dependence of D_T with particle size.

§ For $T > T^*$, particles migrate to the cold whereas the opposite takes place for $T < T^*$.

¶ Because of the strong temperature dependence of hydrogen-bonding, this is the opposite of what happens for simple polymers in organic solvent, where χ increases by lowering T.

from contact with water competes with the presence of severe conformational constraints, making PNIPAM globules strongly frustrated systems. In this sense, they may be regarded as a simplified model of globular proteins, whose tertiary structure is mainly dictated by a similar kind of frustration.[38] This analogy has been exploited to get useful hints about the complicated problem of protein denaturation.[39–41]

As well as affecting the single-chain conformation, the transition from good to bad solvent also affects inter-particle interactions. The second osmotic coefficient vanishes at T_ϑ, marking the onset of attractive effective interactions between the chains that rapidly lead to a liquid–liquid (L–L) phase separation, with a lower critical solution temperature (LCST) of about 34 °C. According to mean-field Flory–Huggins theory, the L–L critical point corresponds to a Flory parameter $\chi \simeq 1/2 + N^{-1/2}$, and to a critical polymer volume fraction $\Phi_c \simeq N^{-1/2}$, where N is the number of monomers in a chain. This means that the polymer apparently "aggregates" even at very low concentration for temperatures that almost coincide with T_{cg}. For PNIPAM then, single chain and collective effects are intrinsically combined, complicating the experimental analysis of the coil-to-globule transition. As pointed out by Rička and coworkers,[43,44] however, the addition of a small amount of ionic surfactant adsorbing on the chain raises the LCST, without appreciably modifying T_{cg}. In other words, adding slight repulsive interchain interactions results in PNIPAM solutions that are stable well beyond the coil-to-globule transition.

PNIPAM can then be regarded as a useful model of thermosensitive polymers such as polypeptide chains; but its distinctive thermal properties can be further exploited by synthesising *connected* networks of PNIPAM chains known as microgels, which constitute a novel class of colloidal particles. When $T \lesssim T_\vartheta$, these microgel particles appreciably swell in water,[45] while maintaining a chain network structure because due to the crosslinks. Temperature effects on the single PNIPAM chain conformation strongly influence the microgel particle size, which undergoes a sharp contraction at the volume phase transition temperature (VPTT), defined as the temperature where the contraction rate $|dR_H/dT|$ is maximal. The volume of the collapsed particles may be smaller than in the swollen state by a factor that can range between 5 and 20, depending on the cross-link density.[37,46]

An important difference between PNIPAM microgels and linear chain PNIPAM is that the stability of the suspension against aggregation is considerably improved. The particle synthesis is performed as an emulsion polymerisation, with anionic surfactants as stabilisers, in the presence of a negatively charged persulfate initiator. Even after extensive dialysis, a negative charge remains from the initiator and, possibly, from residual bound surfactant molecules too. This residual charge provides electrostatic stabilisation, raising the L–L phase separation temperature with respect to the VPTT.[47]

3 Experimental

3.1 PNIPAM microgels

The PNIPAM microgel particles we used, obtained by emulsion polymerisation with sodium dodecyl sulfate (SDS) and kindly supplied by Kodak European Research, have been formerly characterised by Howe *et al.*,[47] to which we refer for more details. Additives and aggregates were removed from the mother batch by dialysis, following the standard recipe described by the group of Pelton.[48] The molar ratio of the methylene bisacrylamide crosslinker to NIPAM used in the synthesis was 0.014. The particle translational diffusion coefficient D was measured by dynamic light scattering (DLS) using a Malvern Zetasizer Nano instrument (Malvern Instruments, U.K.), and their hydrodynamic radius R_H *versus* T was obtained as $R_H(T) = k_B T / 6\pi\eta D(T)$, where η is the solvent viscosity.

3.2 Soret measurements

All measurements of the Soret coefficient were performed using a standard optical probing technique known as Beam-Deflection (BD).[49–51] We proceed with a brief overview, however, a full description of the setup may be found in ref. 51. BD consists of sensitively detecting the deflection that a laser beam suffers by propagating though a thin cell containing the sample, to which a moderate thermal gradient (of the order of 0.1–1 K mm^{-1}) is imposed. After a fast initial deflection $\Delta\vartheta_{th}$, due to the temperature dependence of the refractive index, the beam undergoes a further bending due to the progressive buildup of the Soret-induced concentration gradient. This leads to a further steady-state deflection $\Delta\vartheta_s$, which can be easily distinguished from the former because it takes place on the much longer time scale of particle diffusion. The Soret coefficient can then be evaluated from the ratio $\Delta\vartheta_s/\Delta\vartheta_{th}$ at steady-state as:

$$S_T = -\frac{1}{c}\frac{\partial n/\partial T}{\partial n/\partial c}\frac{(\Delta\vartheta)_s}{(\Delta\vartheta)_{th}}, \tag{4}$$

where $\partial n/\partial T$ and $\partial n/\partial c$ are respectively the temperature and concentration dependence of the refractive index. BD is therefore an intrinsically differential method, which compares the laser deflection for the suspension, to the deflection observed for a calibration solvent at a fixed temperature difference, due to the T-dependence of the refractive index.

For the present measurements, we have used a custom-designed micro-cell with a separation between the hot and cold plate of $h \simeq 400$ μm over a 20 mm optical path. As discussed in ref. 6,11,12, the laser beam is mildly focused to a beam-spot size within the cell of about 50 μm, which is sufficient to avoid reflections from the gilded plates. Moreover, the temperature difference is chosen to be small enough to avoid the deflected beam impinging on either the top or bottom plates during propagation in the cell. The position of the deflected beam is measured by a calibrated position-sensitive detector (Hamamatsu, Japan) with an accuracy of ±5 μm, placed along the beam path 60 cm from the cell.

The diffusion coefficient of the particles, D, found *via* DLS, was used to calculate the thermophoretic mobility $D_T = S_T D$. The refractive index increment of PNIPAM microgel suspensions, needed for obtaining S_T from eqn (4), was measured using a high-resolution Kernchen ABBEMAT (Anton Paar GmbH, Austria). The refractive index temperature dependence is found to be well described by $dn/dc(T) = (0.43 \pm 0.01) - (0.0008 \pm 0.0001)T$ in the range 20 °C to 40 °C.

4 Results

4.1 Volume phase transition and Soret coefficient

Fig. 2(a) shows the temperature dependence of the translational diffusion coefficient, D, and the corresponding hydrodynamic radius, R_H, of a dilute ($c = 1$ g l^{-1}) PNIPAM microgel suspension. The sharp decrease in particle size observed on heating through the VPTT (approximately 33.5 °C) is fully consistent with literature data.[37] In particular, the values of $R_H(T)$ almost coincide with the N70 sample data in Varga et al.[46] (open circles), prepared at a very similar cross-link density, and we refer the reader there for a more detailed light scattering characterisation. Over the investigated T-range, the microgel size decreases by a factor 2.4, from $R_H \simeq 140$ nm at 20 °C, corresponding to an expanded, fully hydrated network, to $R_H \simeq 60$ nm at 40 °C, which corresponds to a much more compact globule. The change in size is non-linear and most rapid between 32–34 °C.

Fig. 2(b) shows the Soret coefficient of the PNIPAM microgel suspension in the same T-range. S_T is observed to increase up to a maximum at the $T = 32$ °C before decreasing to a plateau beyond the VPTT. A first striking feature of this data between 20 °C and 31 °C is the growth itself of S_T, in a region in which the diameter is shrinking (weakly). A second striking feature is the overall change of S_T, in this narrow temperature window, to which we comment further below when discussing D_T. For

comparison, while the value of S_T at 20 °C is comparable to that found for polystyrene latex particles of similar radius, its value in the globular state beyond the VPTT is about 5 times larger.[12]

In the same figure, the results of an investigation on single PNIPAM chains with MW $\simeq 3 \times 10^6$ by Kita and Wiegand[32] are shown for comparison. The data for linear chain PNIPAM show a maximum at T_θ, close to the peak for the microgel data. However, S_T below the transition reaches a value 5 times larger than the globular state, in direct contrast to the behaviour found for the microgel. When the two sets of data are rescaled to their respective value at 38 °C, corresponding to the "compact", globular state for both systems, the Soret coefficient for the linear chain shows a more pronounced peak than for microgels (Fig. 2, inset).

The absolute value of S_T in the globular state of linear chain PNIPAM, where $R_H \simeq 21$ nm, is about a factor of 20 less than for the microgel globular state (that has a hydrodynamic radius 3 times larger, at the same temperature). The observed difference in S_T is therefore very much greater than would be expected by assuming that S_T is proportional to the particle size, as predicted by hydrodynamic theories of the Soret effect for solid, compact particles,[12,24] and at least twice what is predicted by "local equilibrium" models.[26] However, the models mentioned assume homogeneous colloids, interacting with the solvent only via interfacial forces confined to a thin layer close the particle surface. As already stated, this description does not strictly hold for PNIPAM globules or PNIPAM microgels.

4.2 Thermophoretic mobility

More hints about this huge thermophoretic effect for PNIPAM microgels can be obtained by analyzing the temperature dependence of the thermophoretic mobility (thermal diffusion coefficient) D_T, which can be found from the data in Fig. 2 as $D_T = S_T D$. The results, plotted in Fig. 3, show some key features.

1. The microgel $D_T(T)$ (solid circles) shows an approximately linear growth over the whole investigated T-range, and is almost insensitive to the abrupt collapse in size taking place around the VPTT.[||] This is consistent with a view of the thermal diffusion coefficient as a local quantity, which is not affected by overall, large-scale changes of the particle structure. Rather, D_T seems to be linked to changes of PNIPAM hydration taking place in this temperature range that, albeit inducing a dramatic structural change close to the ϑ-temperature of PNIPAM, are expected to be continuous. Note also that D_T strongly increases even if R_H considerably decreases, a feature which seems to contradict all "equilibrium" models of thermophoresis, that predict a linear increase of D_T with particle size.

2. We show for comparison the results obtained in a number of other aqueous colloidal and polymer systems, ranging from other hydrophilic polymers, to polystyrene latex particles of comparable size, nonionic surfactant micelles, and a globular protein. In all these systems, the slope of the linear fits to $D_T(T)$ are very similar, ranging from 0.5–1.2 × 10^{-9} cm^2 s^{-1} K^{-2}. For PNIPAM
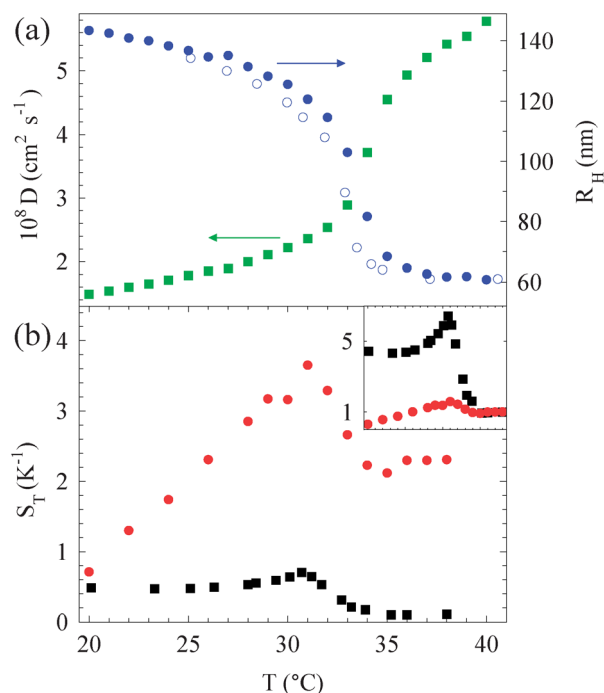

Fig. 2 (a) Temperature dependence of the diffusion coefficient (■, left axis) and of the hydrodynamic radius (●, right axis) of PNIPAM microgel particles, for suspensions at $c = 0.1$ g l^{-1}. Open circles show, for comparison, the values of R_H obtained by Varga et al.[46] for particles of N70, having an almost identical cross-link density. (b) The Soret coefficient obtained by BD in the same temperature range (●), compared to the results obtained for single PNIPAM chains by Kita and Wiegand[32] (■). The two sets of measurements are rescaled in the inset to their respective values at $T = 38$ °C.

[||] The small "kink" around the VPTT still visible in the figure would vanish by assuming a mismatch of about 0.5 °C between the temperature values used in BD versus DLS measurements.
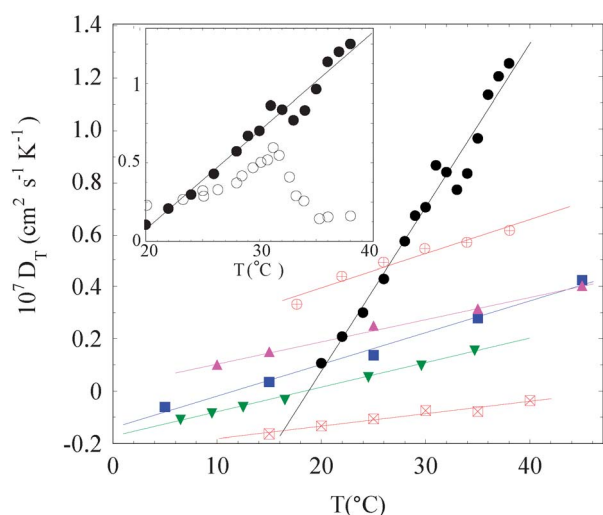
Fig. 3 Thermophoretic mobility D_T of PNIPAM microgels (●), fitted with a linear temperature dependence, and compared to the data obtained for polystyrene latex particles[12] with a radius $R = 125$ nm (■), polyoxyethylene[52] (⊕), dextran[53] (⊠), Triton X100 nonionic micelles[12] (▲), and β-lactoglobulin[10] (▼). A comparison with the results for linear chain PNIPAM[32] is shown in the inset.

microgels the gradient is much greater: $dD_T/dT \simeq 6.3 \times 10^{-9}$ cm² s⁻¹ K⁻². This means that, while at $T = 20$ °C the thermophoretic effects in an aqueous PNIPAM microgel almost vanish, on raising the temperature above the VPTT D_T reaches values that are larger than those of polyethylene oxide (PEO). PEO has the largest reported values of D_T for an aqueous system.

3. The peculiar huge dependence of D_T on T we found for microgels does not seem to be shared by linear PNIPAM chains.[32] The inset in Fig. 3 shows that the thermophoretic mobility of the linear chain retains the "peak" observed for S_T, and that the value of D_T is actually *smaller* in globule than in the expanded coil state.

5 Discussion

The most striking feature of PNIPAM microgel thermophoresis is the much stronger temperature dependence of the thermal diffusion coefficient D_T compared to any other investigated aqueous system. The linear temperature dependence of D_T, in a system where the temperature dependence of the size is non-linear, suggests that the behaviour is dominated by local micro-scopic interactions between the microgel and the solvent, and not by the particle size. As we mentioned, the origin of the temper-ature dependence of D_T for aqueous systems is very probably associated with hydrophobic effects. Unlike other contributions to the particle solvation energy, such as those due to electrostatic interactions, that are weakly dependent on temperature T^{**}, hydrophobic effects are strongly temperature dependent. Furthermore, these effects are very different for large, partially

---

** Screened Coulomb forces directly depend on T only through the negligible temperature dependence of the Debye–Hückel screening length. Additional electrostatic contributions to thermophoresis may however derive from the temperature dependence of the water dielectric constant, which is itself related, *via* the Fröhlich–Kirkwood equation, to temperature effects on the hydrogen bonds.[54]

hydrophobic particles, compared to those for small hydrophobic solutes. For instance, the excess chemical potential per particle $\Delta\mu$ due to that solvation of large non-polar particles (that strongly perturb the hydrogen-bond network of water) decreases linearly with T. By contrast, the temperature dependence is found to be non-monotonic for small hydrocarbons.[30] A direct relation between thermophoresis and the temperature depen-dence of the particle/solvent interfacial tension γ was heuristi-cally suggested by Ruckenstein,[1] and later put on a firmer basis by Parola and Piazza. More precisely, the Soret coefficient for spherical particles of radius R is found to be:

$$S_T = \frac{4\pi R}{k_B T}\frac{\partial(\ell\gamma)}{\partial T},\qquad(5)$$

where the microscopic length scale $\ell \ll R$ is a measure of the range of the colloid–solvent interactions. It is also useful to recall that, in the Gibbs framework, $\partial\gamma/\partial T$ is equal to the isothermal and isobaric increase of the interfacial entropy $(\partial S/\partial A)_{p,T}$ with surface area.[55] Eqn (5) assumes a solid particle, and thus a fixed interface with the solvent given by the particle surface. In the case of PNIPAM microgel, however, the interfacial area exposed to the solvent changes drastically across the VPTT, introducing an additional mechanism for the temperature dependence of D_T. Furthermore, it has been shown that a significant amount of bound water is restructured from exposed sites *within* the microgel as well as on its surface,[56,57] across the VPTT, sug-gesting a further element of complexity in the change in solvent-exposed area. In other words, not only do the specific monomer interactions with the solvent depend on T, but also total number of involved interactions and the balance between hydrophobic and hydrophilic contributions too. Together, these changes modify the overall "thermophoretic force" felt by the particle. Given the current poor status of understanding of thermophoretic effects in general, it is challenging to go beyond a qualitative justification of the peculiar behaviour of PNIPAM microgels, which does not explain, for instance, why a similar effect is apparently absent for linear chain PNIPAM.

With regards to the Soret coefficient, it remains to inquire why S_T shows a pronounced growth at the temperatures leading to the VPTT. It is useful to examine first the behaviour of the linear polymer, which displays an even more pronounced peak in S_T close to T_{cg}. A possible explanation of the latter is related to the onset of critical effects that lead to L–L phase separation of PNIPAM solution at $T \simeq 34$ °C (we stress again that, since the critical concentration almost vanishes, the latter takes places even at polymer concentrations as low as a few micrograms per liter[43]). Unlike D_T, the Soret coefficient is expected to depend on inter-particle interactions because of its inverse proportionality with the (concentration-dependent) diffusion coefficient. On approaching the critical point, D is expected to show a critical slowing-down, and therefore (assuming a regular D_T) S_T should diverge as $(T_c - T)^\nu$, where ν is the exponent of the correlation length.[28] In fact, the data for the Soret coefficient of linear PNIPAM[32] up to the peak, when plotted as a function of the reduced temperature $\epsilon = (T_c - T)/T_c$ on a double-log scale assuming $T_c = 34$ °C, can be reasonably fitted by a power-law with an exponent which is slightly smaller than the mean-field value $\nu = 0.5$. Although the presence of charges in the PNIPAM microgels is expected to shift up, or even hinder completely the

L–L transition, the residual growth in S_T demonstrated in the present experiments may still be due to the presence of an attractive contribution to inter-particle interactions.

An alternative explanation, which does not rely on inter-particle interactions, but rather on single-particle effects may also be considered. Provided that the interfacial tension and the length ℓ depend on temperature mainly through the local density of the liquid $\rho(T)$, eqn (5) predicts the Soret coefficient to be roughly proportional to the thermal expansion coefficient $\alpha = \rho^{-1}(\partial\rho/\partial T)_p$ of the solvent, a feature observed for many colloidal systems.[10] Since the PNIPAM microgel size is not fixed, but instead varies dramatically with T in the vicinity of the VPTT, we may expect $\partial\gamma/\partial T$ to depend on the *particle* compressibility too. It is then intriguing that the thermal expansivity of PNIPAM displays a strong peak just around the coil-to-globule transition.[58] Correlations between the thermal expansion of PNIPAM microgels and their response to thermal gradients may then exist.

6 Conclusion

Our results show that PNIPAM microgels display a very peculiar thermophoretic behaviour. The thermophoretic mobility D_T shows a T-dependence that is at least five times greater than reported for any other aqueous system, increasing by more than an order of magnitude over a temperature range of 20 °C. In addition, the T-dependence of D_T for PNIPAM is different in its two forms (linear chain and microgel). This suggests that further investigation of PNIPAM in its linear chain and weakly cross-linked microgel particles forms may lead to insights into the physical mechanism underlying thermophoresis.

The Soret coefficient S_T is shown to grow strongly, up to the θ-temperature of the polymer. Beyond the volume phase transition temperature of the microgel, values of S_T are found to be much larger than both rigid particles of comparable size and a number of common polymers. We present qualitative discussion of potential physical mechanisms consistent with the observed trends in D_T and S_T.

A giant thermophoretic effect may have utility in the study of the related phenomenon of Soret driven colloidal convection. In general, a thermophoretic concentration gradient can be used to produce a single, continuous and top-heavy fluid layer between two horizontal plates held at different temperatures T_1 and T_2. Since

$$\frac{\mathrm{d}c}{\mathrm{d}z} = -cS_T(T)\frac{\mathrm{d}T}{\mathrm{d}z},$$

where z is along the vertical direction, the concentration ratio between plates is given by:

$$\frac{c_2}{c_1} = \exp\left(-\int_{T_1}^{T_2} S_T \mathrm{d}T\right).$$

Therefore, when S_T is very large, a large concentration gradient can be produced even for small temperature differences $T_1 - T_2$. Together with the already well-known temperature dependence of the viscosity near the VPTT,[47] a study of colloidal convection in this system may be of interest to understand and exploit interplay of these independent effects on the density stress. Winkel and co-workers,[59] for example, have recently

shown the existence of transient oscillations, at high solutal Rayleigh number, in a suspension of core–shell PNIPAM particles.

Acknowledgements

References

1 E. Ruckenstein, *J. Colloid Interface Sci.*, 1981, **83**, 77.
2 R. Piazza, *Soft Matter*, 2008, **4**, 1740.
3 C. Ludwig, *Sitzber. Akad. Wiss. Wien, Math.-naturw. Kl*, 1856, 539.
4 C. Soret, *Arch. Sci. Phys. Nat.*, 1879, **2**, 48.
5 J. V. Tyrrell, *Diffusion and Heat Flow in Liquids*, Buttherworths, London, 1961.
6 R. Piazza and A. Guarino, *Phys. Rev. Lett.*, 2002, **88**, 208302.
7 D. Braun and A. Libchaber, *Phys. Rev. Lett.*, 2002, **89**, 188103.
8 J. Rauch and W. Köhler, *J. Chem. Phys.*, 2003, **119**, 11977.
9 S. Duhr and D. Braun, *Phys. Rev. Lett.*, 2006, **96**, 168301.
10 S. Iacopini, R. Rusconi and R. Piazza, *Eur. Phys. J. E*, 2006, **19**, 59.
11 D. Vigolo, G. Brambilla and R. Piazza, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2007, **75**, 040401.
12 M. Braibanti, D. Vigolo and R. Piazza, *Phys. Rev. Lett.*, 2008, **100**, 108303.
13 J. Giddings, *Science*, 1993, **260**, 1456.
14 J. Janca, J. Berneron and R. Boutin, *J. Colloid Interface Sci.*, 2003, **260**, 317.
15 P. Geelhoed, R. Lindken and J. WesterweelL, *Chem. Eng. Res. Des.*, 2006, **84**, 370.
16 R. Golestanian, T. B. Liverpool and A. Ajdari, *New J. Phys.*, 2007, **9**, 126.
17 R. Rusconi, L. Isa and R. Piazza, *J. Opt. Soc. Am. B*, 2004, **21**, 605.
18 S. Chapman, *Proc. R. Soc. London, Ser. A*, 1928, **119**, 34.
19 N. G. van Kampen, *J. Phys. Chem. Solids*, 1988, **49**, 673.
20 B. V. Derjaguin and G. P. Sidorenkov, *Dokl. Acad. Nauk SSSR*, 1941, **32**, 622.
21 J. Anderson, *Annu. Rev. Fluid Mech.*, 1989, **21**, 61.
22 K. I. Morozov, *J. Exp. Theor. Phys.*, 1999, **88**, 944.
23 A. Parola and R. Piazza, *Eur. Phys. J. E*, 2004, **15**, 255.
24 S. Fayolle, T. Bickel and A. Würger, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2008, **77**, 041404.
25 J. K. G. Dhont, *J. Chem. Phys.*, 2004, **120**, 1632.
26 S. Duhr and D. Braun, *Phys. Rev. Lett.*, 2006, **96**, 168301.
27 F. Brochard and P. De Gennes, *C. R. Acad. Sci., Paris II*, 1981, **293**, 1025.
28 L. Mistura, *Il Nuovo Cimento B (1971–1996)*, 1972, **12**, 35.
29 Y. Kishikawa, S. Wiegand and R. Kita, *Biomacromolecules*, 2010, **11**, 740.
30 K. Lum, D. Chandler and J. D. Weeks, *J. Phys. Chem. B*, 1999, **103**, 4570.
31 M. Carpineti and R. Piazza, *Phys. Chem. Chem. Phys.*, 2004, **6**, 1506.
32 R. Kita and S. Wiegand, *Macromolecules*, 2005, **38**, 4554.
33 H. G. Schild, *Prog. Polym. Sci.*, 1992, **17**, 163.
34 B. M. Baysal and F. E. Karasz, *Macromol. Theory Simul.*, 2003, **12**, 627.
35 C. Wu and S. Q. Zhou, *Macromolecules*, 1995, **28**, 5388.
36 C. Wu and X. Wang, *Phys. Rev. Lett.*, 1998, **80**, 4092.
37 B. Saunders, *Langmuir*, 2004, **20**, 3925.
38 C. Wu and S. Zhou, *Phys. Rev. Lett.*, 1996, **77**, 3053.
39 G. Graziano, *Int. J. Biol. Macromol.*, 2000, **27**, 89.
40 Y. Zhang, S. Furyk and D. Bergbreiter, *J. Am. Chem. Soc.*, 2005, **127**, 14505.
41 E. I. Tiktopulo, V. E. Bychkova, J. Ricka and O. B. Ptitsyn, *Macromolecules*, 1994, **27**, 2879.
42 V. Aseyev, H. Tenhu and F. Winnik, *Conformation-Dependent Design Of Sequences In Copolymers Ii*, 2006, **196**, 1.

43 J. Rička, M. Meewes, R. Nyfrenegger and Th. Binkert, *Phys. Rev. Lett.*, 1990, **65**, 657.

44 M. Meewes, J. Rička, M. de Silva, R. Nyffenegger and Th. Binkert, *Macromolecules*, 1991, **24**, 5811.

45 B. R. Saunders, N. Laajam, E. Daly, S. Teow, X. Hu and R. Stepto, *Adv. Colloid Interface Sci.*, 2009, **147–148**, 251.

46 I. Varga, T. Gilányi, R. Mészáros, G. Filipcsei and M. Zrínyi, *J. Phys. Chem. B*, 2001, **105**, 9071.

47 A. M. Howe, S. Desrousseaux, L. S. Lunel, J. Tavacoli, H. N. Yow and A. F. Routh, *Adv. Colloid Interface Sci.*, 2009, **147–148**, 124–131.

48 X. Wu, R. Pelton, A. Hamielec, D. Woods and W. Mcphee, *Colloid Polym. Sci.*, 1994, **272**, 467.

49 M. Giglio and A. Vendramini, *Phys. Rev. Lett.*, 1977, **38**, 26.

50 K. J. Zhang, M. E. Briggs, R. W. Gammon, J. V. Sengers and D.J.F, *J. Chem. Phys.*, 1999, **111**, 2270.

51 R. Piazza, *Philos. Mag.*, 2003, **83**, 2067.

52 R. Kita, S. Wiegand and J. Luettmer-Strathmann, *J. Chem. Phys.*, 2004, **121**, 3874.

53 R. Sugaya, B. A. Wolf and R. Kita, *Biomacromolecules*, 2006, **7**, 435.

54 I. F. Hakem, A. Boussaid, H. Benchouk-Taleb and M. R. Bockstaller, *J. Chem. Phys.*, 2007, **127**, 224106.

55 A. W. Adamson and A. P. Gast, *Physical Chemistry of Surfaces*, 6th Edition, Wiley–Interscience, New York, 1997.

56 K. Tauer, D. Gau, S. Schulze, A. Voelkel and R. Dimova, *Colloid Polym. Sci.*, 2009, **287**, 299.

57 A. Lele, M. Hirve, M. Badiger and R. Mashelkar, *Macromolecules*, 1997, **30**, 157.

58 P. Kujawa and F. M. Winnik, *Macromolecules*, 2001, **34**, 4130.

59 F. Winkel, S. Messlinger, W. Schpf, I. Rehberg, M. Siebenbrger and M. Ballauff, *New J. Phys.*, 2010, **12**, 053003.