

## Thermophoresis of thermoresponsive polystyrene–poly(*N*-isopropylacrylamide) core–shell particles

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We have investigated diffusion and thermodiffusion of thermo-sensitive core–shell particles (PS–PNIPAM) that consist of a poly(styrene) (PS) core and a poly(*N*-isopropyl acrylamide) (PNIPAM) shell by means of an optical beam deflection technique. The results are compared to recent literature values for linear PNIPAM chains and cross-linked PNIPAM microgel particles. The temperature dependence of the thermodiffusion coefficient of the core–shell colloids resembles that of the linear polymer and a number of other aqueous systems. It is significantly different from one of the crosslinked microgels.

Thermodiffusion, also known as the Soret effect, describes a diffusion flow in a multicomponent liquid which is driven not by a concentration but rather by a temperature gradient. In the case of isolated colloidal particles or polymer molecules the effect is sometimes termed thermophoresis. The time evolution of a binary mixture with  $c$  being the weight fraction of the independent component, usually the solute, is determined by the Fickian diffusion current density  $\vec{j}_D = -\rho D \nabla c$  and the thermodiffusion current density  $\vec{j}_T = -\rho c(1-c)D_T \nabla T$ .  $D$  and  $D_T$  are the isothermal and the thermodiffusion coefficient, respectively. The stationary state is characterized by a vanishing total current,  $\vec{j}_D + \vec{j}_T = 0$ , and the corresponding concentration gradient is  $\nabla c = -c(1-c)S_T \nabla T$ . The ratio  $S_T = D_T/D$  is termed Soret coefficient and is a measure for the susceptibility of the composition of a binary system to temperature gradients.<sup>1</sup>

When compared to non-polar organic mixtures, aqueous systems show a number of peculiarities, like a sign change of  $S_T$  as a function of temperature<sup>2</sup> or composition.<sup>3–5</sup> Frequently, this behavior is discussed in terms of properties of the hydrogen bonds.

In a recent publication Wongsuwarn *et al.*<sup>6</sup> have investigated a very special aqueous system, namely dilute suspensions of

crosslinked microgel networks of the thermoresponsive polymer poly(*N*-isopropyl acrylamide) (PNIPAM). PNIPAM chains undergo a coil-to-globule transition when heated above  $T_{cg} \approx 32.5$  °C, where the solvent quality changes from good to poor.<sup>6</sup> Similar to other colloidal suspensions, these authors observed a giant linear increase of  $D_T$  with temperature, however with an unusually large slope that continues across the collapse region. What made this finding even more surprising are literature data for similar experiments on the linear polymer,<sup>7</sup> which showed only a moderate increase of  $D_T$ , comparable to a number of other aqueous suspensions. As a consequence of the strong increase of  $D_T$ , the Soret coefficient also increases almost by a factor of three between 20 and 30 °C, despite the slight increase of  $D$  in this temperature range.

A linear increase of  $D_T$  with temperature appears to be characteristic for aqueous colloidal suspensions and polymer solutions, but small molecules may behave very differently. Dilute solutions of ethanol in water show the opposite behaviour and both  $S_T$  and  $D_T$  decrease with increasing temperature. For solutions of poly(styrene) (PS) in the organic solvent toluene,<sup>8</sup> a polymer solution without hydrogen bonds, the temperature dependence is completely different from the aqueous polymeric and colloidal systems, and the Soret coefficient decreases like  $S_T \propto T^{-2.4}$ . Away from the dilute limit, at finite concentrations, the temperature dependence of  $S_T$  can be more diverse and even temperature-independent fix points have been observed.<sup>9</sup>

The smooth linear continuation of  $D_T$  across the chain collapse region for both the linear PNIPAM polymer and the crosslinked microgels parallels the insensitivity of  $D_T$  on approaching a critical point observed for poly(dimethyl siloxane)–poly(ethyl methyl siloxane) blends.<sup>10</sup> Such critical mixtures are also systems with huge Soret coefficients, but these are owed to the critical slowing down of the isothermal diffusion coefficient  $D$ . The large Soret coefficients of the PNIPAM microgels are, however, due to the very unique steep increase of  $D_T$ . The difference between the linear polymer and the microgels is particularly surprising, since  $D_T$  is believed to be a local property and loose crosslinking should not change the short-ranged polymer–solvent interaction. In agreement with these arguments, the thermodiffusion coefficient of

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crosslinked PS microgels in toluene has been found to be identical to one of the linear polymer.<sup>11</sup>

To add a new piece of information to these puzzling PNIPAM systems, we report on measurements on core-shell particles, which one would expect to be even farther away from the linear polymer than the microgel. The particles consist of a PS core, which is – other than the microgels – completely impermeable for the solvent water. The outer shell is a crosslinked PNIPAM network similar to the microgel network in ref. 6, however with a somewhat higher crosslink density (molar ratio of *N,N'*-methylene bisacrylamide cross-linker to NIPAM equal to 0.05 vs. 0.014 in ref. 6).

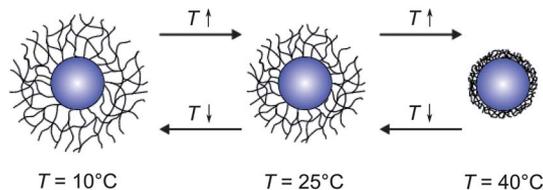
The core-shell particles are prepared by a two-step synthesis which will be summarized in the next lines (for more details see ref. 12 and 13). First the core particles are obtained *via* emulsion copolymerization of styrene and 5 mol% NIPAM, and then purified by ultrafiltration. In the next step the core colloids are used as seeds for the polymerization of the shell with NIPAM and the cross-linker *N,N'*-methylene bisacrylamide (5 mol%) as monomers. After exhaustive serum exchange against pure water to remove free polymer by means of ultra-filtration, the serum is exchanged as well by ultra-filtration to an aqueous 50 mmol l<sup>-1</sup> KCl solution to screen residual charges of the colloids which remained from the synthesis.

The PS-PNIPAM particles are shown in Fig. 1. The PS core has a radius of  $R_{\text{PS}} = 40.6$  nm, a density of  $\rho_{\text{PS}} = 1.054$  g cm<sup>-3</sup> and a mass of  $2.94 \times 10^{-15}$  g. The PNIPAM shell of mass  $2.78 \times 10^{-15}$  g has a temperature dependent thickness. It is swollen by the solvent at low temperature and gradually shrinks in thickness up to approximately 32.5 °C, from this point it starts to collapse within a narrow temperature interval.

All our measurements were carried out with a PS-PNIPAM mass fraction of  $c = 0.005$ . A small amount of KCl (50 mmol l<sup>-1</sup>) was added to screen the electrostatic charges on the PS-core.

The three coefficients  $D$ ,  $D_T$  and  $S_T$  were measured with an optical beam deflection (OBD) technique similar to the one employed in ref. 6. Prior to the measurements the sample was equilibrated for up to ten days. Then, a temperature jump was applied by heating the upper and cooling the lower plate of the Soret cell. Due to the higher density of the PS-PNIPAM and the positive Soret coefficient, this always leads to a stable stratified layering in the cell.

Quite unexpectedly, also the 'isothermal' state needs careful consideration. It turned out that a stable system could only be guaranteed by applying a small stabilizing temperature gradient already during the initial equilibration period. Even the small uncertainty of 10 mK in the temperature measurement and control of the upper and the lower plate can, under unfavorable conditions,



**Fig. 1** Thermoreversible shrinking and expansion of the PNIPAM shell around the PS core of the PS-PNIPAM core-shell colloids.

already be sufficient to cause convective instabilities in the case of a slightly higher temperature of the lower plate. For solute convection the Rayleigh number has to exceed the critical value<sup>14,15</sup>

$$\text{Ra} = \frac{g \beta d^3 \Delta T c (1 - c) S_T}{\nu D} = 720, \quad (1)$$

where  $d$  is the distance between the upper and the lower plate,  $g$  the acceleration of gravity,  $\beta$  the osmotic expansion coefficient, and  $\nu$  the kinematic viscosity. For our diffusion cell and the material parameters of the core-shell suspension (Table 1), eqn (1) leads to a tiny critical temperature difference of only 0.1 mK.

The refractive index derivatives  $(\partial n / \partial T)_{p,c}$  and  $(\partial n / \partial c)_{p,T}$ , which are necessary quantities to determine the thermodiffusion and Soret coefficients, are calculated on the basis of a parametrization of the refractive index:

$$n(T, c) = 1.3341 - 3.343 \times 10^{-5} \frac{T}{^\circ\text{C}} - 1.563 \times 10^{-6} \frac{T^2}{^\circ\text{C}^2} + c \left( 0.2126 + 1.096 \times 10^{-4} \frac{T}{^\circ\text{C}} - 8.910 \times 10^{-6} \frac{T^2}{^\circ\text{C}^2} \right). \quad (2)$$

The parametrization contains both the temperature dependence of a 50 mmol KCl solution and refractive indices of the colloidal suspension. The refractive indices were measured at 633 nm wavelength by means of a high resolution refractometer (Abbemat, Anton Paar).

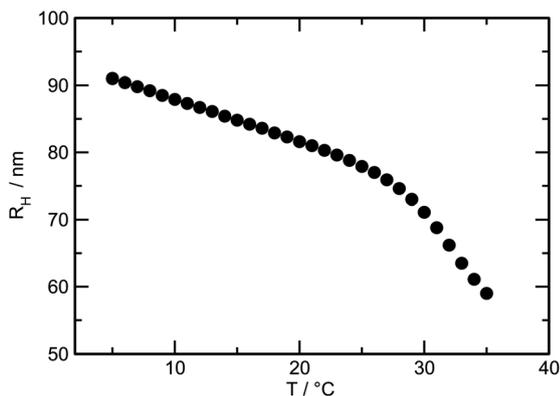
The measured diffusion and Soret coefficients are plotted in Fig. 3. The values above  $T = 30$  °C are considered as not reliable. In this temperature range the second virial coefficient changes sign, with the consequence of a collapsing PNIPAM shell and aggregation and sedimentation of the colloids. The upper part of the figure shows the diffusion coefficient together with predicted values based on a hard-sphere potential between the colloids that goes back to the work of Batchelor:<sup>16</sup>

$$D = \frac{k_B T}{6\pi\eta R_H} (1 + 1.45\phi) = \frac{k_B T}{6\pi\eta R_H} \left( 1 + 1.45 \left( \frac{R_H}{R_{\text{PS}}} \right)^3 c \frac{\rho_{\text{tot}} m_{\text{PS}}}{\rho_{\text{PS}} m_{\text{tot}}} \right). \quad (3)$$

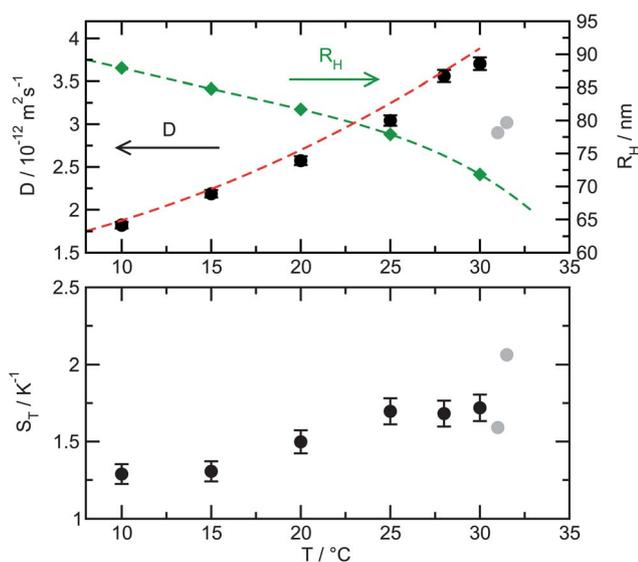
The hydrodynamic radius  $R_H$  of the particles has been taken from dynamic light scattering experiments (Fig. 2).  $\phi$  is the colloid volume fraction. The simple model coincides with the measured data within a few percent and the agreement between dynamic light scattering and OBD for the isothermal part of the diffusive transport is excellent. The lower part of the figure contains the Soret

**Table 1** Hydrodynamic system parameters of the PS-PNIPAM suspension and the diffusion cell

quantity	Value	Units
$g$	9.81	m <sup>2</sup> s <sup>-1</sup>
$\beta$	$9.17 \times 10^{-2}$	1
$d$	$1.43 \times 10^{-3}$	m
$\nu$	$1 \times 10^{-6}$	m <sup>2</sup> s <sup>-1</sup>
$S_T$	1.70	K <sup>-1</sup>
$D$	$3.04 \times 10^{-12}$	m s <sup>-2</sup>



**Fig. 2** Hydrodynamic radius of the particles measured by dynamic light scattering for a dilute ( $c \rightarrow 0$ ) suspension of PS-PNIPAM.



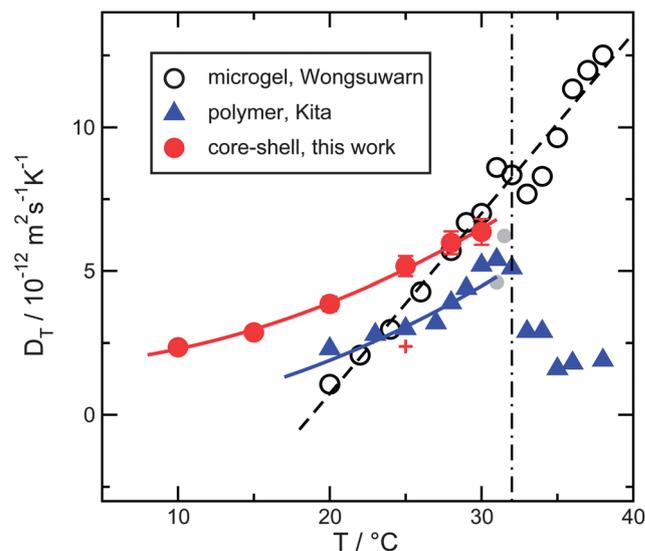
**Fig. 3** Diffusion (top) and Soret (bottom) coefficients of the PS-PNIPAM microgels in water. The red curve shows calculated values of the diffusion coefficient based on a hard-sphere potential according to eqn (3).

coefficient. Contrary to the strong linear increase reported for the crosslinked PNIPAM microgels in ref. 6,  $S_T$  shows only a negligible variation in this temperature range.

Fig. 4 shows the thermodiffusion coefficients of PS-PNIPAM in comparison to the data presented in Fig. 3 of ref. 6. The latter comprises the PNIPAM microgels measured by Wongsuwarn *et al.*<sup>6</sup> and linear PNIPAM chains measured by Kita and Wiegand.<sup>7</sup> The additional literature data for a number of aqueous polymeric and colloidal systems plotted in ref. 6 have been omitted for clarity.

As already discussed, our PS-PNIPAM colloids could not be measured above the transition temperature due to aggregation and sedimentation problems. Below  $T = 30$  °C, under good solvent conditions, the sign of  $D_T$  is always positive and the magnitude of  $D_T$  is comparable for all three PNIPAM systems.

Surprisingly, the temperature dependence of  $D_T$  of the core-shell particles is practically identical to that of the linear PNIPAM



**Fig. 4** Thermal diffusion coefficient of PS-PNIPAM core-shell particles in comparison to literature data for the linear PNIPAM polymer<sup>7</sup> and for PNIPAM microgels<sup>6</sup> in water. The red plus has been measured by Winkel *et al.* for the same PS-PNIPAM system at a much higher concentration ( $c = 0.087$ ,  $\phi = 0.32$ ).<sup>17</sup>

polymer. There is only a temperature-independent vertical shift of approximately  $2 \times 10^{-12} \text{ m}^2 \text{ s}^{-1} \text{ K}^{-1}$ . Within experimental resolution, both curves even show a comparable slight positive curvature. Despite the similarity of the microgels and the crosslinked PNIPAM shell of the core-shell particles, both systems behave distinctly different. The increase of  $D_T$  with temperature is much steeper in the case of the microgels. The PS-PNIPAM core-shell particles show more similarity to the linear PNIPAM polymer and also to the other polymeric and colloidal systems discussed for comparison in ref. 6.

Also shown in Fig. 4 is a single data point measured for the same PS-PNIPAM core-shell system at a much higher concentration of  $c = 0.087$ .<sup>17</sup> The smaller  $D_T$  is in agreement with the already significantly increased viscosity of this more concentrated suspension.

In the light of the new results for the core-shell system, the giant temperature dependence reported by Wongsuwarn *et al.* appears even more outstanding and peculiar. The similarity of  $D_T$  of the core-shell particles and of the linear polymer seems to be more compatible with the experience that  $D_T$  is usually rather insensitive to certain modifications and parameter changes. Examples are the independence of  $D_T$  on the chain length of high polymers,<sup>18</sup> the absence of critical scaling near a consolute critical point,<sup>10</sup> or, of particular importance for the present case, the identical value of  $D_T$  for dilute solutions of PS in toluene<sup>19</sup> and for crosslinked PS microgels in the same solvent.<sup>11</sup>

It has been stressed by the authors of ref. 6 that the Soret effect of the PNIPAM systems is most likely dominated by a delicate balance between hydrophobic and hydrophilic interactions and that the current status of understanding is still poor. Although our new results cannot answer the open questions, it adds a valuable piece of information to the puzzle and a quantitative theory will have to answer the question as to why the microgel behaves so differently from the linear polymer and the core-shell colloids.

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