

Brush-Sheathed Particles Diffusing at Brush-Coated Surfaces in the Thermally Responsive PNIPAAm System

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Phase-contrast microscopy and particle tracking algorithms are used to study the near-surface diffusion of poly(*N*-isopropylacrylamide) (PNIPAAm) brush functionalized micron-sized silica microspheres after sedimentation from aqueous suspension onto planar substrates coated with a similar polymer brush above and below the lower critical solution temperature (LCST) of PNIPAAm, 32 °C. A small negative charge on the wall and the particles (ζ potential = -6 mV) prevents adhesion above and below the LCST. The near-surface translational diffusion coefficient (D_{surface}) is compared to the bulk-phase translational diffusion coefficient (D_{bulk}), which was measured by dynamic light scattering. We find that $D_{\text{surface}}/D_{\text{bulk}} \approx 0.6$ at temperatures $T < 32$ °C but rises abruptly to ~ 0.8 – 0.9 at $T > 32$ °C. Near-surface diffusion is expected to be slower than bulk diffusion owing to hydrodynamic coupling to the wall, implying reduced hydrodynamic coupling at the higher temperatures, perhaps mediated by enhanced electrostatic repulsion above the LCST transition.

Poly(*N*-isopropylacrylamide) (PNIPAAm) is a well-known thermally responsive polymer that, for free chains in aqueous solution, shows a lower critical solution temperature (LCST) phase transition around 32 °C.¹ End-grafted PNIPAAm brushes also undergo a LCST transition but over a broader temperature range.² Since the first work on atom transfer radical polymerization (ATRP) of PNIPAAm brushes, the thermal response of PNIPAAm chains tethered onto various substrates has attracted considerable research interest,^{2–6} due to the excellent control offered over the brush homogeneity and length. Here, we focus on hybrid particles consisting of a hard spherical silica core and a soft PNIPAAm brush shell, which is tethered onto the core via surface-initiated ATRP. This hybrid system presents an advantageous model system for physical studies, because the grafting density of the PNIPAAm brush remains constant upon heating or cooling, in contrast to PNIPAAm brushes grafted onto microgel particles.

Prior reports of silica–PNIPAAm core–shell microspheres focused on synthesis, the LCST-induced volume change, colloidal stability, and rheological behavior.^{7–12} What about diffusion dynamics? In the bulk, for dilute systems, the diffusion coefficient is dominated by the particle diameter, a function of the temperature-dependent thickness of the brush coating. What if the diffusion occurs close to a similarly functionalized surface?

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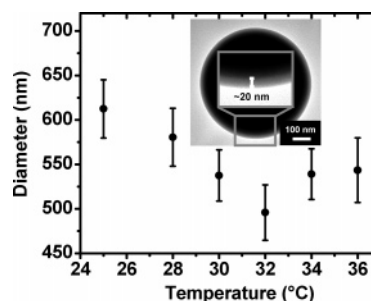


Figure 1. Hydrodynamic diameter of the PNIPAAm-tethered silica microspheres at different temperatures as determined by dynamic light scattering in dilute suspension. A representative TEM image of a microsphere and higher magnification TEM image of the surface, showing the thickness of the polymer brush, is presented in the inset. The contrast of the TEM images is enhanced to show the polymer shell.

Here, on the basis of particle tracking, we have quantified near-surface dynamics in this system, for what is believed to be the first time. Comparison of near-surface diffusion and bulk diffusion shows that a small change of temperature, from a few degrees below the LCST to a few degrees above it, results in a large increase of the ratio of near-surface to bulk diffusion.

PNIPAAm brushes with an average dry thickness of 18 ± 4 nm were grafted onto monodisperse silica spheres (diameter 467 ± 11 nm) using a surface-initiated ATRP procedure we described previously (Figure 1).⁴ A similar procedure was used to graft PNIPAAm brushes on planar substrates, and ellipsometry was used to determine the thicknesses of the planar polymer brushes in dry state, 43 ± 2 nm, and hydrated state, ~ 159 nm, at 25 °C. The ζ potential of the brush-coated particles was determined to be -6 ± 1 mV as measured by electrophoretic mobility (ZetaSizer3000, Malvern Instruments, Ltd.). In comparison, the ζ potential of the bare silica microspheres was -56 ± 1 mV, the negative surface charges being mainly attributed to ionized surface silanol groups. The finite ζ potential of the brush-coated particles is attributed to a small number of residual surface charges, indicating that the surface silanol groups have not been completely consumed during the attachment of surface initiators for ATRP

synthesis. The PNIPAAm brushes on planar substrates were prepared using a similar procedure; we have estimated that the brush-coated substrates also contain a similar density of residual surface charges.

A Nicomp 380 ZLS instrument ($\lambda_{\text{incident}} = 633 \text{ nm}$) was used to collect dynamic light scattering (DLS) data from a dilute dispersion of the PNIPAAm-coated microspheres ($\sim 5 \times 10^{-5}$ in volume fraction). Nicomp software was used to analyze the number-average particle size. The hydrodynamic diameters of the PNIPAAm-tethered silica microspheres over the temperature range 25–36 °C, as determined by DLS, are presented in Figure 1, confirming the expected collapse of the PNIPAAm brush as the temperature increases through the LCST. At 25 °C, the number-average diameter is 613 nm; it continuously decreases as the temperature increases from 25 to 32 °C. The particle diameter reaches a minimum of 496 nm at 32 °C and then increases to 544 nm as the temperature increases to 36 °C. The reason for the minimum at 32 °C is not understood at this time; however, similar effects were seen for PNIPAAm brushes on planar substrates.⁴ A key advantage of using microspheres containing a solid silica core is that the grafting density of the PNIPAAm brush stays constant upon heating or cooling, in contrast to PNIPAAm brushes grafted on microgel particles used in a prior study.¹³ At 25 °C, the relative change in thickness of the dry and hydrated brushes on the planar substrate and the microspheres is about the same, 3.7 and 4.0 times, respectively, indicating that the physical properties of the two brushes are similar. Since the surface of the PNIPAAm-coated microsphere contains residual charges, leading to an electric double layer, the electroviscous effect,¹⁴ which increases the apparent viscosity and thus an overestimation of particle diameter as determined by DLS may need to be considered. However, because of the small ζ potential of the brush-coated microspheres, the electroviscous effect on the apparent viscosity is less than 0.1% and is thus negligible under our experimental conditions.

Near-surface diffusion studies were performed using phase-contrast microscopy (Zeiss Axiovert 200) equipped with a back-illuminated electron multiplying CCD camera (Andor iXon DV-887 BI) and a programmable heat stage. Sequential images were collected using an LD Achromplan Ph2 63 \times objective (NA = 0.75) with 1.6 \times postmagnification at the speed of 10 frames/s (except that, at 34 and 36 °C, 20 frames/s were acquired), and 400 frames were collected continuously. In these studies, the brush-coated particles were allowed to sediment onto the planar PNIPAAm brush functionalized substrates that comprised the bottom of our sample cell. The surface packing fraction of the microspheres was only $\sim 9 \times 10^{-4}$. Therefore, hydrodynamic interactions between microspheres were negligible, and diffusion was dominated by temperature and microsphere–surface interactions. The upper wall of the sample cell was located 1 mm above the bottom and thus did not influence particle diffusion either. All of the tracked microspheres were observed to remain within the depth of field, $\sim 2.3 \mu\text{m}$, throughout the tracking time, as indicated by the fact that the brightness of the particles did not change over the tracking time. A small number of microspheres were observed not to move, presumably reflecting some defects on the planar surface to which these microspheres adsorbed; these microspheres were ignored in the analysis.

Surprisingly, the microspheres were not observed to stick to the planar PNIPAAm brush at any of the studied temperatures. Below the LCST, this is to be expected, as the hydrated PNIPAAm

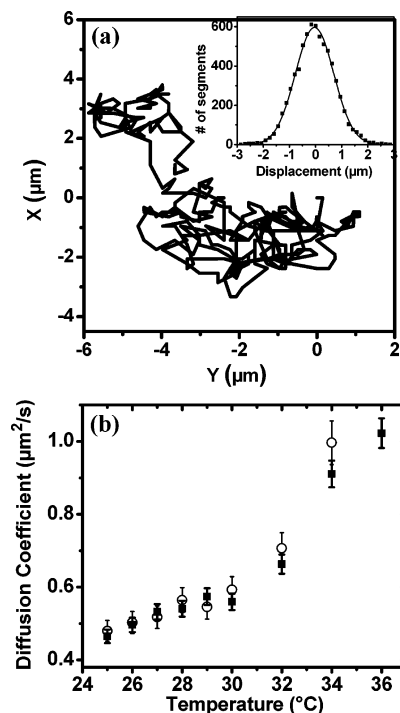


Figure 2. (a) A typical trajectory of a PNIPAAm-tethered microsphere diffusing near the planar PNIPAAm brush at 25 °C. The inset shows the histogram of displacement steps and the Gaussian fit to this histogram. (b) Near-surface diffusion coefficient plotted against temperature, obtained from raw data of the kind shown in panel (a). Reversibility is demonstrated from the comparison of data obtained upon heating (filled squares) and cooling (open circles).

brush has stabilized the microspheres, presumably through the high osmotic pressure within the swollen brush.¹⁵ We believe the lack of adhesion above the LCST can be attributed to the small residual surface charge and ensuing electrostatic repulsion. This is also believed to be the reason that particle–particle aggregation was never observed, not even above the LCST. Experiments were performed where only the microspheres or substrate was coated with the PNIPAAm brush. In both cases, the particles irreversibly stick to the surface above and below the LCST.

From the captured sequential images, the trajectories of the microspheres were analyzed following a procedure described previously by this laboratory to analyze single-molecule trajectories,¹⁶ which is a modification of standard particle tracking methods in the literature.¹⁷ Gaussian fittings to histograms of particle displacements were then applied to yield diffusion coefficients of the microspheres. A typical trajectory of one microsphere tracked at 25 °C and the corresponding histogram with its Gaussian fit are presented in Figure 2a. This method combines both time-averaged and ensemble-averaged statistics, and thus offers a fast and accurate statistical analysis of particle motion.

The diffusion coefficients, D_{surface} , of the microspheres as a function of temperature are summarized in Figure 2b. Below 32 °C, D_{surface} increases slowly with increasing temperature. Then at 32 °C, an abrupt increase in D_{surface} is observed, corresponding to the LCST transition of PNIPAAm. Similar behavior is observed upon cooling. There is minimal hysteresis in the diffusion coefficients obtained from the heating and cooling traces.

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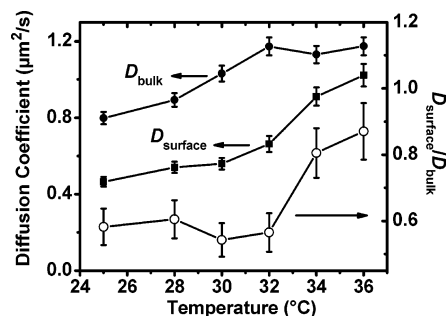


Figure 3. Left ordinate axis: near-surface diffusion coefficient D_{surface} and bulk diffusion coefficient D_{bulk} (data acquired during heating) are plotted against temperature. Right ordinate axis: the ratio $D_{\text{surface}}/D_{\text{bulk}}$ is plotted against temperature.

On the basis of the radius as determined by DLS, the bulk diffusion coefficient, D_{bulk} , is calculated using the Stokes–Einstein relationship $D = kT/6\pi\eta r$, where η is the viscosity of water and r is the radius of the microsphere. Direct comparison of the diffusion coefficients of the microspheres near the surface and in the bulk during heating is presented in Figure 3. D_{surface} is smaller than D_{bulk} at all temperatures; however, while both D_{surface} and D_{bulk} increase as temperature rises, the difference between them becomes significantly smaller above the LCST of PNIPAAm. The ratio of the surface diffusion coefficient to the mean bulk diffusion coefficient, $D_{\text{surface}}/D_{\text{bulk}}$, is also presented in Figure 3. This ratio remains almost constant, 0.54–0.6, up to 32 °C. It then increases quite abruptly to 0.80 when the temperature is raised to 34 °C and continues to increase to 0.87 at 36 °C. Clearly, the conformation of the PNIPAAm brushes on both the spherical and planar silica surfaces significantly modulates microsphere motion.

The retardation in microsphere diffusion at all temperatures can in part be attributed to hydrodynamic coupling between the microspheres and the bottom wall.^{18–20} Given the large thickness of the fluid layer between the surfaces (> 100 nm) relative to the characteristic pore size in the PNIPAAm brushes (~2 nm), the assumption of no-slip boundary conditions is reasonable. The hydrodynamic effect of a solid no-slip boundary on the diffusion coefficient of a solid Brownian particle in the tangential direction is given by eq 1^{19,20}

$$\frac{D_{\text{surface}}}{D_{\text{bulk}}} = \left(\frac{\eta_{\text{surface}}}{\eta_{\text{bulk}}}\right)^{-1} \approx 1 - \frac{9}{16}\left(\frac{r}{z}\right) + \frac{1}{8}\left(\frac{r}{z}\right)^3 - \frac{45}{256}\left(\frac{r}{z}\right)^4 - \frac{1}{16}\left(\frac{r}{z}\right)^5 \quad (1)$$

where η_{surface} is the effective water viscosity near the bottom wall; r and z are the radius of the particle and the distance between the center of mass of the particle and the surface of the polymer brush, respectively. This predicts that the ratio of $D_{\text{surface}}/D_{\text{bulk}}$ should decrease monotonically as the particle approaches the boundary and eventually drop to ~0.33 if the particle were in physical contact with the wall.¹⁹ In reality, there is always a distribution of z -position of the particle given by a Boltzmann factor. If the energy profile of the particle–wall interaction is known, the distribution in z -position can be computed and the hydrodynamic effect can be rigorously quantified, an approach that has been reported,^{20–22} though not for the brush–brush

interactions characteristic of the present system. The confining wall in our system is not a rigid wall as in several prior studies of confined Brownian motion,^{20,23–27} but is rather a polymer brush that undergoes continuous dynamic fluctuations of thickness. In spite of the differences between the experiment and the assumptions that underlie eq 1, this equation still qualitatively explains the hydrodynamic coupling that slows down the microsphere when it is near the bottom wall.

What causes the large increase in the relative diffusion coefficient upon heating to the LCST? In the context of hydrodynamic coupling, it is reasonable to deduce that the increase in the diffusion coefficient is due to a reduced hydrodynamic coupling effect between the particle and the bottom wall. Initially, this may appear counterintuitive. PNIPAAm surfaces become more hydrophobic above the LCST,² so at first we expected the microspheres to stick to the bottom wall and slow down or stop moving, which is the opposite the observed effect. The total microsphere–wall interaction energy also includes the previously mentioned electrostatic repulsion due to the residual surface charges, which apparently prevents the microspheres from coming into physical contact, even above the LCST. When PNIPAAm brushes collapse upon heating through the LCST, the local dielectric constant of the collapsed PNIPAAm brushes decreases owing to lower water content. For the planar brushes, a dry 43 ± 2 nm thick PNIPAAm brush swells to 159 nm at 25 °C under water, then collapses to 64 nm when heated to 36 °C. Using the effective medium approximation,²⁸ we estimate that the local dielectric permittivity is changed from ~48 at 25 °C to ~12 at 36 °C.

This in turn has the intriguing consequence that counterions to the residual surface charges are effectively expelled from the brush region at 36 °C, since the chemical potential for the counterions, which scales inversely to dielectric constant,²⁹ is too high inside the collapsed brush. This expelling of the counterions increases the electrostatic repulsion between the microspheres and the substrate. Since electrostatic effects operate over a much longer range than van der Waals attraction, it is likely that this enhanced repulsion increases the microsphere–substrate separation above the LCST of the PNIPAAm brush.

Furthermore, even if the position of the microspheres relative to the top surface of the glass does not change, the collapse of PNIPAAm brushes increases the gap between the microsphere and substrate PNIPAAm brush layers, which also decreases the hydrodynamic coupling predicted from eq 1. The increase in the gap distance alone, however, is not sufficient to explain the observed increase in the ratio of the diffusion coefficients; it can explain only an increase of ~25% in this ratio, not the observed change of ~50%, which enhances our confidence that electrostatic interactions are important.

We would like to note that the thermally triggerable acceleration in colloidal diffusion reported here may find application in situations where near-surface particle mobility influences surface functionality, especially bearing in mind that PNIPAAm is considered to be biofriendly and environmentally benign.³⁰

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Supporting Information Available: Experimental details including materials, synthesis and characterization of the PNIPAAm-coated silica microspheres, and planar PNIPAAm brush, and a schematic illustration of the sample geometry and the details of the phase-contrast microscopy experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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