

Particle dynamics within a wetting layer in a colloid-polymer mixture

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(Received 29 December 2007; published 6 May 2008)

The near-wall dynamics at the top and bottom phases of a phase-separated colloid-polymer mixture were measured by evanescent-wave dynamic light scattering. The short-time dynamics near the wall were found to be liquidlike in both phases, confirming the presence of a liquid wetting layer. The short-time diffusion within the wetting layer was slower than in the bulk liquid phase. Similarly, the near-wall dynamics in both phases of the colloid-polymer mixture were also slower compared to the near-wall colloidal dynamics in a pure concentrated suspension at the same volume fraction. These effects highlight the role of interparticle attractions and specific wall-induced hydrodynamic interactions in slowing down the colloidal motion in confinement.

DOI: [10.1103/PhysRevE.77.051402](https://doi.org/10.1103/PhysRevE.77.051402)

PACS number(s): 82.70.Dd, 05.40.Jc, 68.35.Ja, 78.35.+c

Functioning as “giant atoms” [1,2] with tunable interactions, colloidal systems provide model systems to study fundamental phenomena of condensed matter and statistical physics such as phase equilibrium [3], crystallization [4], and interfacial phenomena [5] with experimental accessibility of their structure and dynamics via microscopy and dynamic light scattering [2,6]. In the last decade or so, colloid-polymer mixtures have attracted significant attention due to their rich phase diagram, much modified compared to the pure components. At an appropriate size ratio the polymer-induced depletion attraction between nearly hard-sphere colloids may lead to phase separation between two fluids, of very different composition, a colloid-rich (“liquid”) and colloid-poor (“gas”) phase [7,8]. Both theoretical predictions [9] and experiments [10,11] suggest that the “liquid” phase wets the wall as a result of the effective wall-colloid depletion attraction. This constitutes an especially simple, entropically driven case of wetting phenomena in phase-separated systems, otherwise observed widely [12].

The structure and the kinetics of formation of the wetting layer have been studied using microscopy [10,13]; however, their dynamics remain largely unexplored. Here we focused on the “microscopic” dynamics—i.e., the dynamics on a length scale comparable to the radius R of the colloids—in the vicinity of a solid wall. To specifically resolve the dynamics near the solid-liquid interface, we utilized evanescent-wave dynamic light scattering (EWDLS) which combines dynamic light scattering with the short penetration depth of evanescent waves produced at total internal reflection [14]. It has been used to study various systems such as polymer brushes [15], rodlike polymers [16], and dilute colloids near hard [17,18] or polymer-coated walls [19]. However, the near-wall dynamics in phase-separated systems with interparticle attractions or in wetting layers have not been studied yet. Here we present the colloidal dynamics in a wetting layer and the wall-fluid interface [called two dimensional (2D)] of a colloid-polymer mixture at a gas-liquid coexistence and compare with the dynamics of the corresponding bulk phases (3D).

Suspensions of nearly hard-sphere poly(methylmethacrylate) (PMMA) particles ($R=118$ nm) sterically stabilized by a thin poly(hydrostearic) acid (PHSA) layer were prepared in a refractive index matching tetralin-decalin mixture to avoid multiple scattering. A colloid-polymer mixture was prepared using polystyrene (PS) with $M_w=5.8 \times 10^6$ g/mol ($R_g=90$ nm the measured radius of gyration) at colloid volume fraction $\phi_c=0.3$ and a PS concentration $c_p=1.14$ mg/cm³. The latter corresponds to $c_p/c_p^*=0.362$ with $c_p^* (=3.15$ mg/cm³) the overlap concentration.

In agreement with previous studies [8], at this point of the phase diagram a long-range depletion attraction (size ratio $\xi=0.76$) leads to phase separation into a “gas” top phase with $\phi_c=0.0013$ and $c_p/c_p^*=0.97$ and a “liquid” bottom phase with $\phi_c=0.42$ and $c_p/c_p^*=0.093$.

Suspensions were held between the flat surface of a semi-cylindrical lens with high refractive index ($n=1.61$) and a microscope slide separated by a Viton O-ring, forming a tight container (Fig. 1). The vertical axis of the cell was placed in the rotation axis of a θ -2 θ goniometer, allowing an independent variation of the scattering wave vector, $q \approx (4\pi n/\lambda)\sin(\theta/2)$, and the evanescent-wave penetration depth, $\kappa^{-1}=(\lambda/2\pi n)(\sin^2 \theta_i - \sin^2 \theta_c)^{-1/2}$, with θ the scattering angle, θ_i the incident angle, θ_c the critical angle of total reflection, n the dispersion refractive index, and λ the wave-

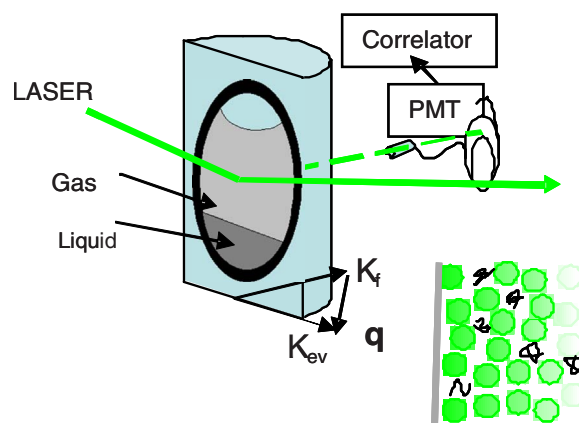


FIG. 1. (Color online) Schematic of the EWDLS setup and representation of the colloid-polymer mixture near the surface.

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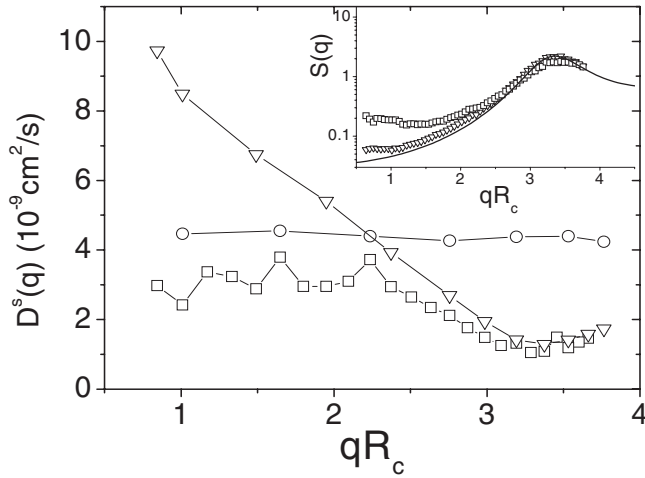


FIG. 2. q dependence on the diffusivities $D^s(q)$ and the structure factors $S(q)$ (inset) in bulk (3D): (○) gas phase, (□) liquid phase, and (▽) concentrated suspension. The line in the inset depicts the PY prediction at $\varphi_c=0.42$.

length of light. A focused vertically polarized laser beam (532 nm) was totally reflected at the glass-suspension interface. The interface scattered intensity was collected on a photomultiplier tube via an optical fiber, and the correlation function was computed with a digital correlator. The absence of multiple-scattering effects even at high volume fractions was verified by the high transmission values ($>90\%$). The presence of static scattering from the glass surface added a static intensity component that partially heterodyned the signal. The field correlation function $g^{(1)}(t)$ was determined from the measured intensity autocorrelation function $g^{(2)}(t)$ under mixed homodyne-heterodyne conditions using a generalized Siegert relation (see, e.g., [18])

$$g^{(2)}(t) = 1 + \frac{1}{(1+\alpha)^2} |g^{(1)}(t)|^2 + \frac{2\alpha}{(1+\alpha)^2} g^{(1)}(t),$$

with $\alpha=I_0/I_s$ the ratio of the unscattered to scattered intensity determined at the intercept $g^{(2)}(t=0)$. The available q range is $1 < qR < 4$, and the penetration depth range is $1 < \kappa R < 0.2$; i.e., the EWDLs scattering volume extends to few-particle diameters from the surface. The effective short-time diffusion coefficient is determined from the initial decay rate of $g^{(1)}(t)$ according to [2]

$$D^s(q) = \frac{\Gamma}{q^2} = \left(\frac{1}{q^2} \right) \lim_{t \rightarrow 0} \left(\frac{d[\ln g^{(1)}(t)]}{dt} \right).$$

Good quality 2D data allow a precise evaluation of the initial decay time. Despite index matching, colloid scattering still dominates in the measured static and dynamic structure factors. In bulk suspensions of interacting colloids, $D^s(q)$ is affected by direct colloid-colloid and hydrodynamic interactions (HIs), so that $D^s(q) = D_0 H(q) / S(q)$ with D_0 the single-particle diffusion coefficient at $\varphi \rightarrow 0$, $H(q)$ the hydrodynamic factor, and $S(q)$ the structure factor of the suspension [2].

To date, reports of structure and dynamics in phase-separated colloid-polymer mixtures remain somewhat lim-

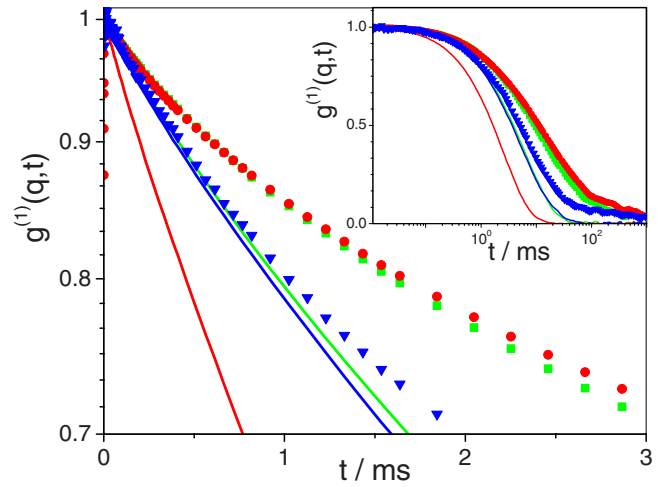


FIG. 3. (Color online) Normalized surface (2D) correlation functions $g^{(1)}(t)$ at $qR=2.95$ and $\kappa^{-1}=321$ nm in the wetting layer (○), the liquid phase (□), and the concentrated suspension (▽). The lines correspond to the bulk (3D) correlation functions at the same q . Inset: the same data in a log-log plot.

ited [20]; therefore, we first provide results obtained in the bulk fluids—i.e., far from the wall. The static structure factors $S(q)$ at the bottom “liquid” phase and the pure concentrated suspension at the same colloid volume fraction are shown in the inset of Fig. 2. They both show a strong peak at $qR \sim 3.5$, a bit less marked in the liquid phase. $S(q)$ in the concentrated suspension is well represented by the Percus-Yevick (PY) prediction for hard spheres [2] with a slight deviation at low q . More importantly, though, at low q the liquid phase $S(q)$ exhibits an upturn, revealing significant long-range concentration fluctuations. This enhanced osmotic compressibility, similar in character but weaker than those observed in nonergodic gel states [20,21], is caused by depletion attraction.

Short-time $D^s(q)$ measured in the gas and liquid phases are reported in Fig. 2. A q -independent $D^s=4.5 \times 10^{-9}$ cm²/s measured in the former, although smaller than the single-particle diffusion ($D^s/D_0=0.69$), suggests that short-time motion is only weakly affected by the increased viscosity of the polymer matrix (around 10 times the solvent viscosity at $c_p/c_p^*=0.97$). This is probably due to polymer-induced hydrodynamics [22] related to the large polymer-depleted volume around the particle (size ratio $\xi=0.76$). $D^s(q)$ in both the liquid phase and concentrated suspension exhibits the expected dip at qR around the $S(q)$ maximum, typical of interacting colloids [2]. However, the long-range (low- q) short-time dynamics in the liquid phase is significantly slower, essentially reflecting the departure of $S(q)$ from the one measured in the concentrated suspension.

We now turn to the colloidal dynamics close to the wall. Figure 3 shows the normalized correlation functions $g^{(1)}(t)$ at $qR=2.95$ measured near the surface (2D) ($\kappa^{-1}=321$ nm) and in bulk (3D). The 2D dynamics are clearly slower than the 3D ones, both at early times, but even more so at slow times, where all 2D $g^{(1)}(t)$ exhibit a strong long-time tail (inset of Fig. 3), more pronounced in the gas and liquid phases rather than in the concentrated suspension. Remarkably, the short-

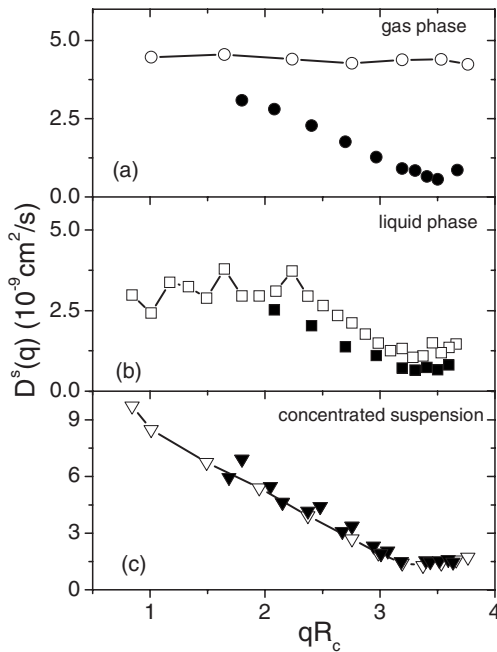


FIG. 4. q dependence of the 3D (open symbols) and the 2D (solid symbols) diffusion coefficients $D^s(q)$ for all phases: (a) gas phase and wetting layer (O), (b) liquid phase (□), and (c) concentrated suspension (▽).

time 2D dynamics, measured at the top and bottom parts of the cell, superimpose, despite their very different dynamics in 3D (gas and liquid phase in Fig. 2).

Comparing the 2D and 3D $D^s(q)$ (Fig. 4) we first note the clear differences in particle dynamics in the gas phase [Fig. 4(a)]. The 2D $D^s(q)$ presents the typical liquidlike dip at $qR \sim 3.5$ that resembles that found in 2D and 3D dynamics in both the liquid and concentrated suspensions [Figs. 4(b) and 4(c)]. A quantitative comparison of the 2D $D^s(q)$ (Fig. 5) in the gas and liquid phases verifies their similarity regardless of the 3D dynamics. The liquidlike surface dynamics throughout the sample provides clear evidence of the existence of a “liquid” layer close to the wall, not only at the bottom dense phase, but also at the top dilute one. Therefore the measured dynamics offers an alternative signature of the wetting layer related to particle diffusion within it.

It should be noted that no significant penetration depth dependence of $D^s(q, \kappa^{-1})$ was observed within the explored range. The insensitivity to penetration depth variation up to $\kappa^{-1} = 1 \mu\text{m}$ indicates a layer thickness larger than $1\text{--}2 \mu\text{m}$. A wetting layer thicker than several particle diameters is consistent with confocal microscopy observations [23].

Furthermore, we note that in the concentrated suspension the 2D and 3D [Fig. 4(c)] dynamics are virtually indistinguishable. This finding will be further discussed elsewhere [24]. A similar effect has already been noticed in colloidal suspensions confined between two plates [25].

On the other hand, in the liquid phase the 2D short-time dynamics is clearly slower than in 3D [Fig. 4(b)]. In view of the results in concentrated suspensions, such a slowing down is not expected to originate from HIs with the wall and may therefore be attributed to polymer-induced effects such as a depletion-induced increase of the near-wall particle concentration [26].

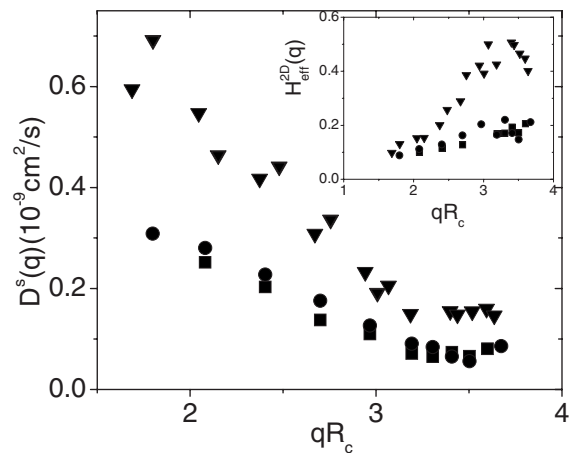


FIG. 5. q dependence of the surface diffusivities $D^s(q)$ for the concentrated suspension (▽), liquid phase (□), and wetting layer (O) at penetration depth $\kappa^{-1} = 320 \text{ nm}$. Inset: corresponding effective $H_{\text{eff}}^{2D}(q)$ deduced from the 2D data using the 3D $S(q)$.

Moreover, the 2D dynamics in the colloid-polymer mixture (both wetting layer and liquid phase) is clearly slower than in the concentrated suspension, despite its similar 3D dynamics near the peak of $S(q)$ (Fig. 2). This further stresses the influence of the polymer-induced depletion on the near-surface colloidal dynamics.

A closer look at the 2D particle dynamics in the liquid phase and wetting layer reveals slightly larger values of $D^s(q)$ in the latter at q 's below the peak of $S(q)$ (Fig. 5). At longer times the reverse trend is observed as the decay of $g^{(1)}(t)$ in the wetting layer is systematically slower (Fig. 3). Although the lack of analysis tools for the long-time tails in EWDLs makes this effect difficult to quantify, we may speculate that the origin of such behavior lies in the double confinement of the particles in the wetting layer.

Finally, although the 2D $S(q)$ could not be obtained with high enough accuracy, we may attempt to calculate an effective $H_{\text{eff}}^{2D}(q)$ using the measured 3D $S(q)$ (Fig. 2) as justified by microscopy findings that the 2D $S(q)$ in a confined HS monolayer is similar to the 3D one [27]. Assuming the 3D relation holds also near the wall, the obtained effective $H_{\text{eff}}^{2D}(q) = D^s(q)S^{3D}(q)/D_0^{3D}$ (inset of Fig. 5) reveals similar long-range HIs (low q) whereas near the peak of $S(q)$, $H_{\text{eff}}^{2D}(q)$ is significantly smaller in the liquid phase and wetting layer compared to the concentrated suspension. This behavior would imply a stronger slowing down due to HI at length scales of the order of the particle-particle separation. To this end we should mention the possibility of anisotropic near-wall particle motion which cannot be unequivocally resolved with the present setup; nonetheless, such effects are not expected to be strong at highly concentrated suspensions due to the dominance of the particle-particle HIs.

The detailed findings presented of the near-wall dynamics disclose the power of EWDLs and call out for a theoretical investigation of the dynamics of colloidal systems in confinement.

In summary, we have utilized EWDLs to look into particle dynamics within a wetting layer near a solid wall in a colloid polymer mixture at a gas-liquid coexistence and com-

pare it with the 2D dynamics in the liquid phase and in a pure concentrated colloidal suspension. In this way we manage to dynamically detect the existence of the liquidlike layer that fully wets the surface and show that while its thickness is more than 5–10 particle diameters, the short-time particle dynamics at low q are slightly faster than in the liquid phase near the wall. Furthermore, the 2D particle dynamics within both the wetting layer and the liquid phase is slower than the

corresponding dynamics in 3D due to an increased depletion attraction near the wall.

We thank Andy Schofield (University of Edinburgh) for providing the PMMA particles. This work was partly funded by the EU through the NoE “SoftComp” (Grant No. NMP3-CT-2004-502235) and the Marie-Curie ToK “Cosines” (Grant No. MTC-D-CT-2005-029944).

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