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Dynamics of core-shell particles in concentrated suspensions

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The dynamics of soft colloidal particles in a concentrated suspension was studied by two color dynamic light scattering. The short-time diffusion coefficient, $D_s(q)$, revealed a weak slowing down around the peak of $S(q)$ in contrast to the much stronger dependence observed in hard sphere systems, and the absence of any slowing down in ultrasoft diblock micelles. The low-q limit of the diffusion coefficient, $D_s(q=0)$, reflecting the cooperative nature of the dynamics was found to decrease from its dilute limit value in contrast to the weak increase observed in hard sphere systems. The behavior of $D_s(q)$ reflects distinct polymer-layer-induced hydrodynamic effects present in concentrated suspensions of core-shell particles.

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A considerable amount of experimental and theoretical work has been done in an effort to understand the physics of concentrated colloidal suspensions and more specifically the interrelation between the structure and the dynamics [1]. For hard sphere systems extensive experiments support to a large extent the theoretical predictions for the static structure factor and the hydrodynamic interactions (HI) which affect the short and long time dynamics of Brownian particles [1]. It is well verified by now that in concentrated colloidal suspensions (of hard and charged spheres) the relaxation of the intermediate scattering function, $f(q,t)$, deduced from the normalized intensity correlation function, $g^{(2)}(q,t) = \langle I(q,t)I(q,0)\rangle / \langle I(q)\rangle^2 = 1+\beta|f(q,t)|^2$, which is measured in a dynamic light scattering experiment, slows down near the peak of the structure factor, $S(q)$ [1–4]. This effect is reminiscent of the so-called ''de Gennes narrowing'' of the quasi-elastic energy spectrum in neutron scattering by simple fluids in the region of the peak of $S(q)$ [5] and was also observed in ordered diblock copolymers [6]. It essentially reflects the fact that the strong fluctuations for values of q corresponding to the peak of $S(q)$ will take longer to decay than the weaker fluctuations away from the peak.

For soft spheres, however—especially for core shell particles with a soft polymer coat—the question whether there is such a slowing down of the dynamics around the peak and how interparticle interactions affect it still remains. Studies in suspensions of charged colloidal particles [1,7–10], which are effectively described by a soft repulsive interparticle potential, have shown that there is a slowing down of the dynamics near the peak that compare reasonably well with theoretical predictions [9]. More recently, the role of a polymeric layer on the dynamics has been addressed [11] in concentrated suspensions of ultrasoft diblock micelles. There, the polymeric layer is affecting the hydrodynamics in such a way that $D(q)$ becomes q independent. However, other studies in a similar system of ultrasoft particles by x-ray photon correlation spectroscopy (XPCS) have suggested that there is a slowing down of the short time diffusion near the peak of $S(q)$ [12,13].

In an effort to shed some light on the role of the polymer-mediated interparticle interactions we study here a concentrated suspension of core-shell particles with a hard silica core and a tethered poly-(dimethylsiloxane) (PDMS) soft polymeric shell. More specifically we study the q dependence of $D(q)$ in the regime around the peak of $S(q)$ and thus investigate the interplay between thermodynamic and hydrodynamic interactions governing the relaxation of concentration fluctuations in concentrated suspensions. In a suspension of hydrodynamically interacting colloidal particles the effective short-time diffusion coefficient D_s, determined from the initial decay of $f(q,t)$ according to $D_s(q) = (1/q^2)\lim_{t\to 0}[(d/dt)\ln|f(q,t)|]$ is given by [1,14]

$$D_s(q) = D_0 H(q)/S(q). \tag{1}$$

Here $H(q)$ is the hydrodynamic factor and D_0 $(=k_BT/f)$ the average ''free particle'' diffusion coefficient with f the friction coefficient.

The PDMS-grafted silica particles were prepared by grafting hydroxy-terminated PDMS onto Stoeber silica from a suspension in diethylketone according to [15]. The particles were dispersed in a 50-50 mixture of toluene and heptane to attain close to refractive index matching conditions. The hydrodynamic radius, measured by TCDLS in dilute suspensions was $R_H = 196$ nm with a size polydispersity of about 8% as determined by the variation of the measured diffusion coefficient in the region of the first minimum of the form factor [16]. The grafted PDMS chains had a molecular weight, $M_w = 110$ kg/mol and surface coverage $\Gamma = 1.5$ mg/m^2 creating a polymer coat with thickness of about 20 nm (equal to the end to end distance of the polymer chain according to the rotational isomeric state model for the PDMS chain). Thus, such particles are of intermediate softness between hard spheres (such as the sterically stabilized PMMA particles) [1] and the ultrasoft diblock micelles [11]. Here we present measurements from a 40% by weight concentrated suspension which corresponds to a volume fraction

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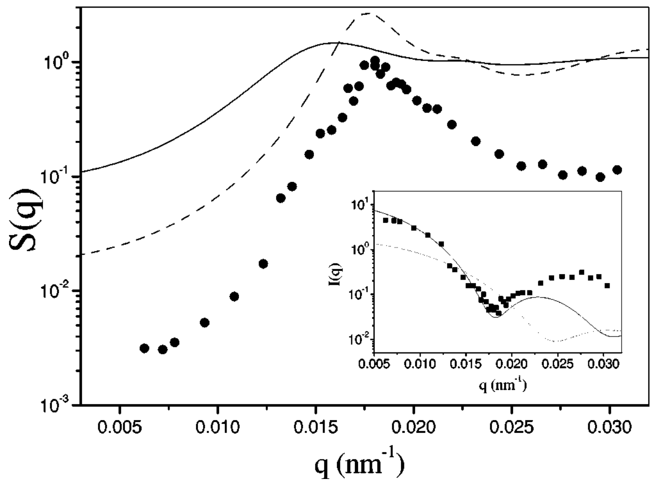

FIG. 1. Structure factor $S(q)$ for a suspension with $\phi = 0.3$ as a function of q measured by TCDLS. The lines correspond to the Percus-Yevick prediction for hard spheres; the solid line corresponds to $\phi = 0.494$ and the dashed line to $\phi = 0.3$. Inset: Form factor $F(q)$ as a function of q, measured at a dilute suspension (with $\varphi = 0.0005$). Predictions for polydisperse core-shell particles with refractive indices $n_c = 1.46$ (core), $n_{\text{shell}} = 1.425$ (shell), $n_s = 1.44$ (solvent) for (a) core radius $R_c = 250$ nm, shell thickness $\Delta = 20$ nm (solid line) and (b) $R_c = 180$ nm, $\Delta = 20$ nm (dotted line).

of $\varphi = 0.302 \pm 0.005$ (the error corresponds to an error of ± 10 nm in the size of the core and ± 5 nm in the shell thickness).

In order to eliminate multiple scattering effects which could not be avoided at high concentrations by refractive index matching we have used the technique of two color dynamic light scattering (TCDLS) which utilizing a two-color cross-correlation technique is able to suppress multiple scattering both in dynamic [17] and static light scattering measurements [18]. The measurements were contacted at the TCDLS setup of the University of Edinburgh.

The inset of Fig. 1 shows the q dependence of the scattered intensity $I(q)$ (in arbitrary units) for a 0.1 wt. % ($\varphi = 5.5 \times 10^{-4}$) sample together with representations of the form factor according to the core-shell sphere model for two different sizes (see the figure caption). The experimental $I(q)$ cannot be fitted well in the total q range by the form factor of solid or core shell particles with reasonable values of refractive indices and dimensions. The fitting discrepancies are mainly observed in the high q regime where there is an excess of scattered intensity. The form and the minimum of $F(q)$ of a core shell particle are very sensitive to the refractive indices of the core, shell and solvent; hence the hydrodynamic radius R_H is a safer estimate of the overall size of the particle.

Figure 1 shows the q dependence of the structure factor, $S(q)$, in the concentrated ($\varphi = 0.3$) sample. It was calculated from the measured intensity in the TCDLS set up according to [18]:

$$S(q) = \frac{\phi_D}{\phi_C} \beta_{MS} \sqrt{\frac{1}{T_B T_G}} \sqrt{\frac{I_B I_G}{I_{B,D} I_{G,D}}} \tag{2}$$

Here I_B, I_G and $I_{B,D}$, $I_{G,D}$ are the measured average scattered intensities from the concentrated and dilute sample for the blue (B) and green (G) laser beams, respectively. T_B and T_G are the corresponding—in blue and green—transmissions from the concentrated sample and ϕ_C, ϕ_D are the volume fractions of the dilute and concentrated samples respectively. Finally, β_{MS} is the ratio of the single to the total scattered intensity which is determined from the zero time value of the correlation function $g^{(2)}(q, t = 0)$ [18].

The peak of $S(q)$ occurs at much higher qR values (with $R_H = 196$ nm) compared to the Percus-Yevick (PY) approximation [1] for hard spheres at $\phi = 0.3$ (dashed line in Fig. 1). It actually corresponds to $qR = 3.55$ which is very similar to the PY prediction at $\phi = 0.494$ (solid line in Fig. 1). Although the shape is reminiscent of that for high ϕ's in a hard sphere suspension the amplitude of the peak is significantly lower and similar to that at $\phi = 0.3$. Moreover, the high q values seem to reach a plateau which is much lower than that expected, due to negligible positional correlations at very local length scales, value of 1. Such a discrepancy could be related with the large scattered intensity at high q's measured in the dilute sample. Finally, the low q value of $S(q)$, related to the osmotic compressibility $[S(0) = k_B T(\partial\rho/\partial\Pi)_T$, with Π the osmotic pressure and ρ the number density], is very small implying a high degree of homogeneity at large length scales. Although such homogeneity would be expected at large effective φ's (>0.64) due to significant overlapping of the polymer shells it is very difficult to envisage at volume fractions of around 0.3. Another cause of such homogeneity could be the presence of repulsive interactions due to the positive second virial coefficient A_2 of the PDMS shell in the solvent used. However, such an effect cannot lead to so low values of $S(0)$. More importantly one could reasonably suspect that the form factor $F(q)$ changes with increasing φ due to alterations in the shape and/or refractive index of the polymeric coat. Another complication arises from the fact that the measured $S_M(q)$ and $H_M(q)$ from particles with internal optical structures are in general different from the ideal purely statistical mechanical properties $S(q)$ and $H(q)$ of optically homogeneous spheres [19] and depend on both the size and internal optical structure of the particles. The above complications render a quantitative assessment of the measured $S(q)$ ambiguous. The matter could be resolved by a combination of TCDLS or XPCS with small angle x-ray scattering where scattering from the polymeric layer would be negligible compared to that from the silica core and thus $S(q)$ would be unaffected by possible changes of the polymeric coat.

In contrast to the static structure factor the dynamics are unaffected by changes in $F(q)$ or in the scattering conditions. Hence, they directly reflect the relaxation of concentration fluctuations through the cooperative or self-diffusion mechanisms. In Fig. 2 we show the intermediate scattering function $f(q,t)$ as a function of $q^2 t$, for the concentrated suspension ($\phi = 0.3$) at several q's and for the dilute suspension at $q = 0.026\ \text{nm}^{-1}$ (dashed line). Figure 2 reveals the overall effect that the hydrodynamic and thermodynamic interactions have on the dynamics of $f(q,t)$ as concentration

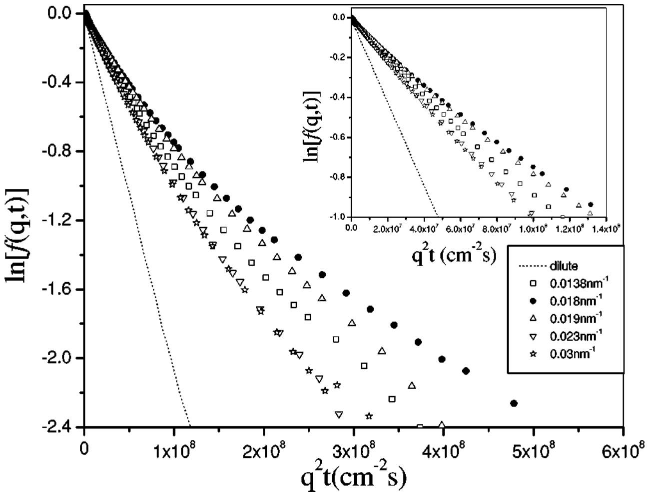

FIG. 2. Intermediate scattering function $f(q,t)$ measured by TCDLS for a suspension with $\phi = 0.3$ for several scattering wave vectors: $q = 0.0138\ \mathrm{nm}^{-1}$ (□), $0.018\ \mathrm{nm}^{-1}$ at the peak of $S(q)$ (●), $0.019\ \mathrm{nm}^{-1}$ (△), $0.023\ \mathrm{nm}^{-1}$ (▽), and $0.03\ \mathrm{nm}^{-1}$, (⋆). Inset: $f(q,t)$ at short times for the same q to show the initial decay better. The dotted line shows the experimental correlation function for the dilute solution.

increases. First one notes that the dynamics is slowing down as the volume fraction increases. Then, comparing $f(q,t)$ at different q's one observes an additional slowing down around the peak of $S(q)$. Moreover, the shape of $f(q,t)$ departs from that of a single exponential; a weak slow mode appears if the data are treated as a sum of exponentials. At high q's the decay of $f(q,t)$ scales with q^2 reflecting a q-independent $D_s(q)$. As the peak of $S(q)$ is approached the scaled (by q^2) decay of the correlation function becomes slower with its slowest relaxation at the peak, $q_{\max}$ of $S(q)$ ($q = 0.018\ \mathrm{nm}^{-1}$). For q's below $q_{\max}$ the decay of the correlation function speeds up again. As shown in the inset of Fig. 2 the decay of $\ln f(q,t)$ is linear with t at short times and is related with the short-time diffusion coefficient D_s.

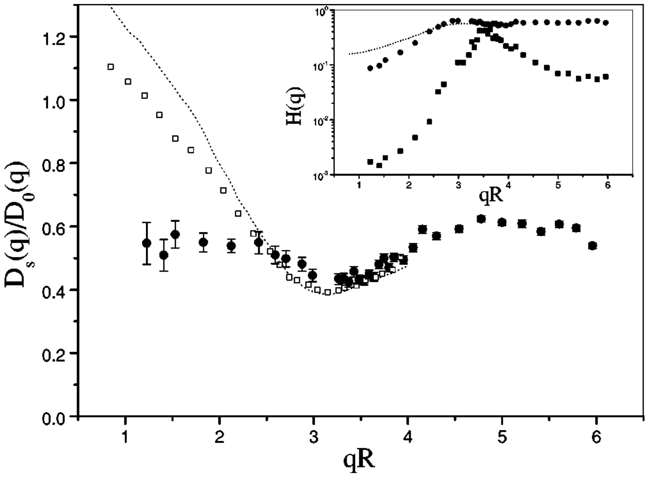

FIG. 3. Data of the normalized short-time diffusion coefficient, $D_s(q)/D_0(q)$ (●) together with data for a hard sphere suspension at $\varphi = 0.3$ (□) reproduced from Ref. [3] and theoretical prediction (dotted line) according to Beenakker and Mazur [20]. The error in our experimental data originates from the calculation of the initial decay rate of $f(q,t)$. Inset: $H(q)$ data calculated according to Eq. (1) using (a) the experimental $S(q)$ (■) and (b) the theoretical PY prediction for $\varphi = 0.3$ (●). The dotted line corresponds to the theoretical prediction according to Beenakker and Mazur [20].

In Fig. 3 we show the ratio $D_s(q)/D_0(q)$, where $D_s(q)$ is the q-dependent short time diffusion coefficient at $\varphi = 0.3$ and $D_0(q)$ the q-dependent diffusion coefficient measured at a very dilute sample. The weak slowing down near the peak of $S(q)$ is revealed by the shallow dip of $D_s(q)/D_0(q)$ (by a factor of about 20%). Although not large, such a change is experimentally detectable due to the use of the TCDLS technique. In Fig. 3 we also show the experimental results for a hard sphere suspension at $\varphi = 0.3$ measured by Segre *et al.* [3] together with the theoretical prediction of Beenakker and Mazur [20]. Compared to the case of suspensions of hard [1–4] as well as charged spheres [7–10] the q dependence of $D_s(q)/D_0(q)$ is much weaker in the present system while it was totally absent in suspensions of ultrasoft diblock micelles [11]. The dynamics near the peak of the structure factor is very similar in the core-shell and hard sphere suspensions. However, the suspension of the soft core-shell particles reveal significantly different dynamics compared to its hard sphere counterpart at the region away from the peak. The cooperative diffusion coefficient at the low q limit, responsible for relaxing the long wavelength concentration fluctuations, is almost half of its dilute limit value D_0. Such a decrease with φ contrasts the weak increase observed in hard spheres systems [1,3] due to the increase of the thermodynamic force (or the osmotic modulus, $[\partial\Pi/\partial\rho]_T$) associated with concentration fluctuations. A similar effect was also observed in concentrated suspensions of ultrasoft diblock micelles (see Figs. 3 and 4 of Ref. [13]) where both the short time and the long time structural relaxation were found to slow down with φ (the latter twice as strong compared to hard sphere suspensions). In principal, size polydispersity may lead to a decrease of $D_s(q \to 0)$ due to hydrodynamic effects or to incoherent scattering leading to an additional mode in $f(q,t)$ with dynamics relaxing through the self-diffusion mechanism (which slows down with increasing φ [1]). However, for a polydispersity of about 8% both these effects have a minimal effect; the former gives a rather low decrease of D_s and the latter a low amplitude of the polydispersity mode. Hence, the decrease of $D_s(q=0)$ reflects the distinct, polymer-mediated, interactions among core-shell particles at concentrated suspensions. Such interactions are evidently affecting predominantly the cooperative diffusion dynamics probed in the low q limit rather than the dynamics related with the structural diffusion measured at the peak of the structure factor. In other words collective motions of groups of neighboring particles towards one direction become more severely slowed down than the motion of two particles against each other related with the structural relaxation of concentration fluctuations at the peak of $S(q)$.

The inset of Fig. 3 depicts the hydrodynamic factor $H(q)$ deduced from Eq. (1) using the measured $D(q)$ and either the experimental $S(q)$, shown in Fig. 1, or the PY approximation for a hard sphere suspension with $\varphi = 0.3$. While the former deviates markedly from the theoretical prediction of Beenakker and Mazur [20] for a hard sphere system in the entire q range, the latter is in significant disagreement only at the low q region. This fact further strengthens our assertion that the measured $S(q)$ does not correspond to the real $S(q)$ of the system due to an alteration of the form factor compared to its dilute solution measurement. Hence, if we assume that the true $S(q)$ of the suspension resembles that of hard spheres the calculated $H(q)$ deviates from the theoretical hard sphere one mainly in the low q region in agreement with the $D_s(q)/D_0(q)$ data (Fig. 3). Both our data and those of Ref. [11] imply that for particles with a soft polymeric shell the decrease of the short-time collective diffusion coefficient D_s^c with volume fraction is a direct consequence of a stronger decrease of $H(0)$ with the volume fraction than that of $S(0)$. Figures 2 and 3 suggest that modifications of the hydrodynamic interactions due to the polymeric shell of the particle are stronger in the low q limit (and secondly at high q's) rather than at the peak of $S(q)$. The lower the value of $H(q)$ the higher is the hydrodynamic resistance. This means that the hydrodynamic resistance of collective motions of neighboring polymer-layered particles towards the same direction is larger that in the case of hard spheres. On the contrary, since the $H(q)$ near the peak (the inset of Fig. 3) is similar to the values observed in a hard sphere system the hydrodynamic resistance related to the structural relaxation of concentration fluctuations (i.e. for motions of particles in different directions) is not affected by the presence of the polymeric coat. Hence, the weak q dependence of $D_s(q)$ is due to its decrease at low and high q values rather than to changes at the peak. The hydrodynamic interactions are such that all diffusion mechanisms (collective, structural and self-diffusion) slow down with increasing volume fraction in contrast to hard or charged spheres where the collective diffusion exhibits a weak speed up due to cancellation effects of $H(0)$ and $S(0)$. For charged particles hydrodynamic interactions tend to speed up the structural relaxation near the peak of $S(q)$ $[H(q_m)>1]$ increasingly with increasing φ contrary to hard spheres where $H(q)$ never exceeds one and decreases with increasing φ. Furthermore, both theory and experiments suggest that HI in the limit of low q's are more pronounced in charged particles than in hard spheres at the same volume fraction. Still they are such that $D_s^c/D_0>1$ but decreasing towards 1 at $\varphi\approx0.08$ [9]. In this sense the polymer-grafted colloids resemble qualitatively the charged spheres, however, with even stronger HI at low q's that lead to a decrease of D_s^c below D_0. In contrary, at the peak of $S(q)$ the polymer-grafted colloids exhibit similar HI with the hard sphere suspensions.

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