

Structural Relaxation of Dense Suspensions of Soft Giant Micelles

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The dynamics of liquid-like ordered giant colloidal micelles in the wave vector range around the peak of the structure factor is explored using photon correlation spectroscopy. No thermodynamic slowing down of the collective density fluctuations is found, whereas the long-time diffusion coefficient follows the concentration dependence of the suspension viscosity. Polymer-layer mediated effects are proposed to govern the physics of this unexpected behavior.

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In recent years it has become evident that rational combination of common and distinct hallmarks of different classes of soft materials holds the key to the design of new systems with desired (intermediate) properties [1]. Spherical micelles formed by diblock copolymers in a selective solvent for one of the blocks can display both polymer and colloid behavior [2,3]. Because of the core of nanoscopic size (R_c) formed by the insoluble chains, these systems exhibit liquidlike order at relatively low number densities, much like hard-sphere colloids. The solvated chains forming the corona of tethered arms are in the disordered semidilute state and stabilize the hard core suspension via steric repulsions. Until now attention has been focused on the ordering of soft (micelles and multiarm homopolymers stars) [2,3] and hard sphere colloids [2a], whereas the crucial collective structural relaxation dynamics have been reported only for the latter [4,5]. Yet, as in hard colloids, access to the dynamic structure factor $S(q, t)$ requires sufficiently large dimensions, i.e., $qR = O(1)$ with q being the light scattering wave vector. The anticipated rich dynamics of these systems has not been explored yet.

In this Letter we provide complete experimental assessment of $S(q, t)$ of soft hairy spheres, using giant spherical micelles at the test system. These unique materials are obtained by solubilizing specially synthesized ultrahigh molecular weight styrene-isoprene (SI) diblock copolymers in decane and dimethylacetamide (DMA), preferential solvents for I block and S block, respectively. Thus, the structural relaxation of the polystyrene (PS) or polyisoprene (PI) core density fluctuations, and the collective motion of the tethered PI or PS chains, can be accessed using photon correlation spectroscopy. The absence of thermodynamic slowing down of the long-time diffusion, which follows the suspension viscosity, and its decoupling from the tethered chain dynamics are the main new findings.

Asymmetric monodisperse SI with average molecular weight 1.9×10^6 and 1.7×10^6 g/mol and almost mirror weight fractions $\varphi_s = 0.26$ and 0.85 , respectively, were obtained by anionic polymerization. The giant micelles SI and IS with insoluble glassy PS and rubbery PI cores, respectively, were characterized in dilute solution

(no interactions) by dynamic and static light scattering. The free-micelle translation diffusion D_0 obtained from the normalized intermediate scattering function $C(q, t) = \exp(-D_0 q^2 t)$ yields 400 and 370 nm for the hydrodynamic radius $R_h = kT/6\pi\eta_0 D_0$ (η_0 is the solvent viscosity) of SI and IS, respectively; this material property is a measure of the overall micelle radius, R [2]. The experimental intensity distribution $I(q)$ (inset of Fig. 1) was represented by a theoretical form factor [6] taking into account the starlike structure of the particle with an inhomogeneous density and hence refractive index profile. The sizes $R_c = 58$ and 80 nm, $R = 353$ and 332 nm, for SI and IS, respectively, are compatible with the $I(q)$. From the $I(q \rightarrow 0)$ limits and the dn/dc (0.105 and 0.152 ml/g for SI and IS, respectively) we estimate the aggregation numbers $f_{SI} = 1470$ and $f_{IS} = 1350$ chains/micelle.

Figure 1 shows scattering profiles of concentrated SI micelle solutions in the fluid phase. The development of liquidlike (short-ranged) ordering is evident from the existence of broad secondary peaks in the absence of long-range crystalline order [7]. For the ordered liquid phase at $c \approx 2\%$, the experimental $I(q)$ resembles the structure

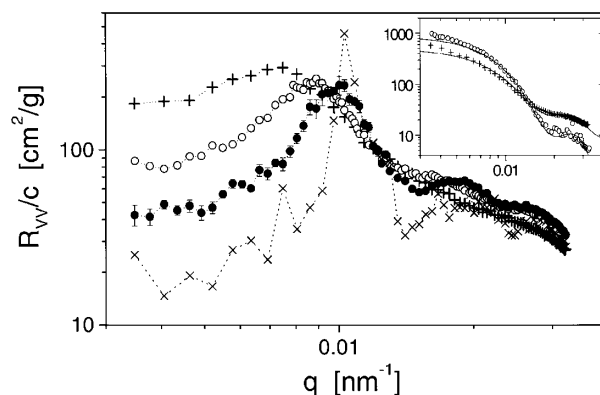


FIG. 1. Experimental scattering intensity distributions $I(q)$ (expressed as Rayleigh ratio R_{vv} divided by c) at different concentrations of the SI suspensions at 20 °C (+: 0.79 wt%; O: 1.33 wt%; ●: 1.91 wt%; x: 2.30 wt%). Inset: The form factors of SI [$c = 2.5 \times 10^{-3}$ wt% (+)] and IS [$c = 7.6 \times 10^{-4}$ wt% (O)] along with their theoretical representation (see text).

factor of dense hard-sphere fluids [4]; in particular, the distance between main and first secondary peaks exhibits the same characteristic q ratio of about 2, suggesting the same liquid structure. Because of the large particle dimension, the structural peak falls within the light scattering q range, a prerequisite to explore the $S(q, t)$ over a broad time range and relevant length scales [8].

The intermediate light scattering function $C(q, t) = \{[G(q, t) - 1]/f^*\}^{1/2} [\propto S(q, t)/I(q)]$ with $G(q, t)$ the normalized light scattering intensity autocorrelation function and $f^*(\leq 1)$ the coherence factor was measured for different scattering vectors q (0.003 – 0.034 nm^{-1}), spanning the position q^* ($\approx 0.01 \text{ nm}^{-1}$) of the main peak in $I(q)$ (Fig. 1) by an ALV-5000 fast multi-tau digital correlator in the time range of 10^7 – 10^3 s , using a Nd:YAG laser ($\lambda = 532 \text{ nm}$), at 20°C [3,9,10]. Figure 2 presents semilogarithmic plots of $C(q^*, t)$ vs the reduced time $D_0 q^{*2} t$ for different concentrations. These are the first measurements of structural relaxation of concentrated soft colloidal suspensions in the fluid state [11]. At low concentrations ($c < 1.3\%$), $C(q^*, t)$ is a single exponential decay (linear behavior in Fig. 2), whereas in denser suspensions a deviation is observed, conforming to the increase of viscosity with concentration. At $c > 1.3\%$, two distinct decays with significantly slower rates are observed. In analogy to hard-sphere suspensions [4], the initial (low amplitude) decay is assigned to particle diffusion within a “cage” of surrounding particles, which is responsible for the main peak in $I(q)$ [12]. The larger-amplitude long-time diffusion relates to the (structural) rearrangements of the cages, since it follows the viscosity and exhibits strong slowing down when the cages become

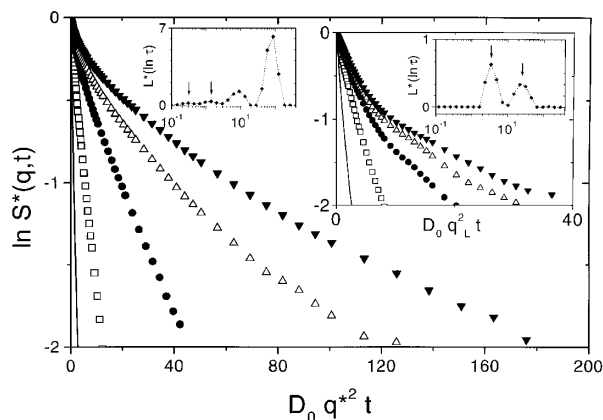


FIG. 2. Normalized intermediate scattering functions $C(q, t)$ for different concentrations (\square : 1.08 wt%; \bullet : 1.5 wt%; \triangle : 1.8 wt%; \blacktriangledown : 1.9 wt%) of SI suspensions in decane plotted against $D_0 q^2 t$ for $q = q^*$ [$\approx 0.01 \text{ nm}^{-1}$, at the peak of $I(q)$ in Fig. 1] and $q = q_L$ ($= 0.034 \text{ nm}^{-1}$, the largest value) (inset). The solid lines in the two plots are for the free particle diffusion D_0 (dilute samples, SI: $c = 2.5 \times 10^{-3} \text{ wt}\%$; IS: $c = 7.6 \times 10^{-4} \text{ wt}\%$). The corresponding normalized distribution of relaxation functions $L^*(\ln \tau)$ obtained from inversion of $C(q, t)$ is also shown for $c = 1.9 \text{ wt}\%$. The arrows denote the two fast processes with q -independent rates.

stronger with concentration, as reflected in the width of the main peak in $I(q)$ (Fig. 1). However, besides these similarities, the structural relaxation of the present soft colloidal system is clearly distinguished from that of hard spheres by the observed strong variation of $C(q, t)$ with reduced time $D_0 q^2 t$ and the presence of additional collective motions of the “grafted” chains [9] at high q 's, as discussed below.

The inset of Fig. 2 depicts the $\ln C(q_L, t)$ at the highest $q_L = 0.034 \text{ nm}^{-1}$ vs $D_0 q_L^2 t$, at various concentrations. Whereas at $c < 1.3\%$ one diffusive mechanism is reflected in $C(q, t)$, at high concentrations $C(q_L, t)$ exhibits two-step decays which are faster (on the reduced time scale) than at $q = q^*$. This speedup of dynamics at high q 's should not be confused with (weaker) thermodynamic effects in hard-sphere colloids [4] and diblock copolymers near the ordering transition [10], since the corresponding speedup at $q < q^*$ was not found [invariant long-time limiting slope of $\ln C(q, t)$ in the reduced time scale]. This suggests that at length scales ($2\pi/q_L$) shorter than interparticle distance, core/shell (colloid/polymer) correlations become important.

In the presence of multiple relaxation processes, $C(q, t)$ can be best analyzed via inverse Laplace transformation to yield the characteristic decay rates and amplitudes from the normalized distribution of relaxation times $L^*(\ln \tau) = I(q)L(\ln \tau)$ (Fig. 2). Based on this analysis, $C(q, t)$ is represented by a number of contributing processes which is increasing systematically with concentration up to four distinct modes for $c > 1.3\%$, where the secondary intensity peak is clearly resolved in $I(q)$ (Fig. 1). The two slow modes in $L^*(\ln \tau)$ at q^* (Fig. 2), being the main contributions to the $C(q, t)$, have diffusive rates in the range $0.3 \leq q/q^* \leq 2$, and the slower is assigned to long-time collective diffusion (see Fig. 3 below). For the two faster modes, which dominate the scattering pattern at $q/q^* > 2$ and are distinguished at q_L (inset of Fig. 2), the rates are q independent, as expected for local (polymeric) relaxation [13]; the apparent shift by $(q_L/q^*)^2$ of the two fast peaks (denoted by arrows in Fig. 2) is caused by the different reduced time scales. The mechanisms for these processes should relate to the dynamics of densely grafted deformable interacting chains, as the amplitude of relaxation clearly increases with q . Dynamic shear measurements performed with a Rheometric Scientific ARES 100FRTN1 rheometer in the Couette geometry support this assignment, exhibiting dispersion at frequencies similar to the rates of the fast modes in $C(q, t)$ (Fig. 4 below). These might reflect arm relaxation and shape fluctuations of the micelles.

A virtually q -independent long-time effective diffusion coefficient D is observed in Fig. 3 for both micellar systems with an associated intensity almost 90% of the static $I(q)$ in the peak (q^*) region [14]. At $c > 1.3\%$ $I(q^*)$ is enhanced (Fig. 1), yet there is no evidence of thermodynamic slowing down, i.e., D^{-1} following $I(q)$.

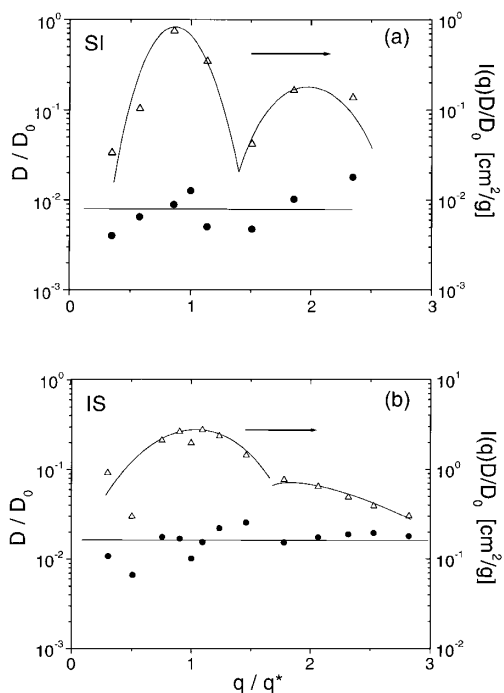


FIG. 3. Normalized long-time diffusion D/D_0 (●) and mobility (Onsager) coefficient $DI(q)$ (Δ , right hand axis) for SI in decane (1.9 wt %) (a) and IS in DMA (2.7 wt %) (b) versus the normalized (to the peak value) scattering wave vector q/q^* . Lines are drawn to guide the eye.

This can be addressed through the formal description of the main structural process:

$$S(q, t) = S(q) \exp(-Dq^2 t) \quad \text{with } D = \Lambda(q)/S(q),$$

where the phenomenological Onsager coefficient $\Lambda(q)$ relates the Fourier components of the chemical potential $[\propto S(q)]$ and density current $[\partial \rho(q, t)/\partial t]$ [15]. Actually, Fig. 3 demonstrates the virtual q independence of D for the two micellar systems at high c [16]. For comparison, the corresponding plots of $DI_L(q) \propto \Lambda(q)$ [$I_L(q) \propto S(q)$ is the associated intensity from $L(\ln \tau)$] are also included in Fig. 3. Changes in $I(q)$ by 1 order of magnitude are not reflected in D [17]; this is in sharp contrast to concentrated hard-sphere suspensions with similar $D(q^*)/D_0$, where even smaller variations in $I(q)$ are revealed in the collective dynamics [4]. Further, for diblock copolymers in common good solvent, a polymeric self-organized system, the rate of composition fluctuations assumes its lowest value at the structural peak q^* near the order-disorder transition [10]. In the present situation, the peak $I(q^*)$ reflects the short-ranged ordering of the cores within an average distance shorter than the effective one of hard spheres [18], and this dense micellar suspension fluctuates in time due to collective particle diffusion. Based on these results (Fig. 3), it is conceivable that the drastic difference between the present soft and the hard-sphere suspensions might arise from the different nonlocal character of $\Lambda(q)$. This can be ratio-

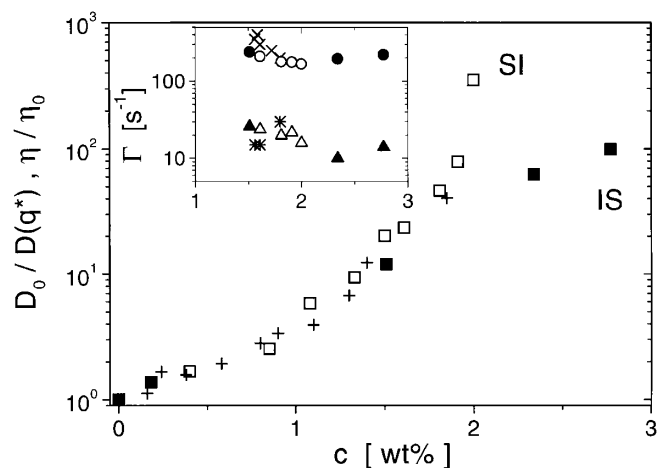


FIG. 4. The normalized long-time diffusion $D_0/D(q^*)$ versus concentration for SI in decane (\square) and IS in DMA (\blacksquare). The normalized (to solvent, η_0) viscosity for SI is also included ($+$). Inset: The relaxation rates for the (two fast) collective motions of the tethered chains for different concentrations of SI (\circ, \triangle) and IS (\bullet, \blacktriangle) (along with mechanical shear relaxation estimates for SI ($\times, *$)).

nalized with polymeric-layer mediated forces [19] over distances $O(R)$, which, in addition to the central forces, include coupling of translation to particle rotation (shearing); these effectively would dissipate the thermodynamic slowing down.

The influence of the polymeric layer on the main diffusion of these soft micelles is reflected differently in the concentration dependence. Increasing the suspension concentration from dilute regime up to crystallization decreases the collective structural relaxation D by a factor of about 400 (Fig. 4), which is twice stronger the respective reduction for hard spheres up to freezing [4]; this might be due to the possible inhibition of crystallization in this system. This dramatic decrease of D follows the increasing suspension (zero-shear) viscosity, in excellent agreement with the respective behavior of hard colloids [4,5]. In contrast, the motions of the tethered chains (inset of Fig. 4), which are decoupled from the core diffusion [14], are rather insensitive to this increase of viscosity, which is dominated by the sluggish core motions. Neglecting grafting density effects, an estimate of the rate of tethered chain configurational motions [9] is $\Gamma \sim kT/\eta_0 R_h^3 \approx 100 \text{ s}^{-1}$.

In summary, the absence of thermodynamic slowing down of the collective diffusion coefficient of dense suspensions of soft polymeric micelles at the structural peak is a result of their nonlocal mobility due to the interacting tethered chains; this effect, however, does not influence the concentration dependence which follows that of the suspension viscosity.

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