Long-Time Dynamics of Concentrated Charge-Stabilized Colloids

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Dynamic light scattering was used to study the dynamic structure factor, $S(q, t)$, of suspensions of charged colloidal silica spheres over the full colloidal time range. We show that a dynamic scaling relation for $S(q, t)$ found by Segrè and Pusey [Phys. Rev. Lett. **77**, 771 (1996)] for hard spheres, relating long-time and short-time dynamics, and collective and self-diffusion, also applies to charged colloids up to the freezing concentration. The universality of this scaling is analyzed theoretically. Our experimental data confirm dynamic freezing criteria proposed for the long-time self- and cage-diffusion coefficients, along with a theoretical prediction for the self-diffusion coefficient.

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The dynamics in suspension of charged colloidal particles is of fundamental interest and the subject of ongoing research [1–4]. A rich variety of charge-stabilized colloids are encountered in chemical industry, biology, and food science. While static properties of colloids resemble that of atomic liquids, their dynamics is diffusive rather than ballistic. This poses a challenging many-body problem where both electrosteric and solvent-mediated hydrodynamic interactions (HIs) need to be considered.

Information on the dynamics of colloidal particles is embodied in the dynamic structure factor, $S(q, t)$, which describes the dynamics of Fourier components of fluctuations in number density as function of correlation time t and wave number q. It can be determined by dynamic light scattering (DLS) [1,5] and x-ray photon correlation spectroscopy (XPCS) [4]. From the knowledge of $S(q, t)$, a deeper insight can be obtained into transport properties such as diffusion coefficients, viscoelastic quantities [6], and crystallization lines [7]. Short-time properties of charged colloids are now rather well understood thanks to detailed scattering experiments [8] and simulations [9]. In contrast to this, a lot remains to be learned about long-time dynamics.

A comprehensive study on the dynamics of suspensions of neutral hard spheres was made by Segrè and Pusey using two-color DLS [10]. They measured the $S(q, t)$ of hard spheres in the whole fluid concentration regime. The key finding of their study is that the normalized dynamic structure factor, $f(q, t) = S(q, t)/S(q)$, of hard spheres of radius a is well approximated for $q > 2.5/a$ including the principal peak of $S(q)$, by the scaling relation [10]

$$f(q, t) \approx \exp\left\{-q^2 \frac{D_S(q)}{d_S} W(t)\right\}. \tag{1}$$

Here $W(t) = \langle \Delta r^2(t) \rangle /6$ is the mean-square displacement of a particle with initial and long-time slopes equal to, respectively, the short- and long-time self-diffusion coefficients d_S and d_L. Furthermore, $D_S(q) = d_0 H(q)/S(q)$ is the short-time diffusion function proportional to the hydrodynamic function, $H(q)$, which reflects the influence of HIs. The single-particle diffusion coefficient is d_0. The Segrè-Pusey factorization suggests that density relaxations at nonsmall wave numbers are controlled by self-diffusion.

Equation (1) assumes that the q and t dependence of $\log f(q, t)$ can be factorized. It reproduces the small- and large-q behavior of $f(q, t)$, i.e., $f(q \ll q_m, t) \approx \exp\{-q^2 D_S(q) t\}$ and $f(q \gg q_m, t) \propto \exp\{-q^2 W(t)\}$. Here, $q_m \approx 3.5/a$ is the principal peak position of the hard sphere $S(q)$. The large-q form is valid for negligible non-Gaussian corrections. Measuring $f(q, t)$ for $q > 2.5/a$ should give a q-independent master curve equal to $W(t)/d_S t$, when $-\ln f(q, t)/[q^2 D_S(q) t]$ is plotted versus t. Moreover, a single-exponential decay, $f(q, t) \propto \exp\{-q^2 D_L(q) t\}$, is predicted for long times and $q > 2.5/a$, with a long-time diffusion function

$$\frac{D_L(q)}{D_S(q)} \approx \frac{d_L}{d_S} \tag{2}$$

of the same q dependence as $D_S(q)$ and ratio d_L/d_S. Note that $D_L(q \to \infty) = d_L$ since $D_S(q \to \infty) = d_S$. An empirical rule for the onset of freezing by Löwen *et al.* [7] states that $d_L/d_S \approx 0.1$. Thus the $D_L(q)$ of a concentrated system is substantially smaller than its short-time counterpart.

The key question is whether Eqs. (1) and (2) are generic features of colloidal dispersions, not restricted to the neutral hard spheres studied by Segrè and Pusey. A recent study has challenged the validity of Eq. (2) even for the restricted class of hard-sphere-like systems: using XPCS and small-angle x-ray scattering (SAXS), Lurio *et al.* [11] measured the diffusion of charged polystyrene latex spheres in glycerol. The $S(q)$ in their system is indistinguishable from that of hard spheres, but $D_L(q)/D_S(q)$ was found to vary strongly in q at higher volume fractions ϕ, in conflict with Eq. (2). Lurio *et al.* argue that the violation of Eq. (2) may be due to a different hydrodynamic boundary condition on the surface of a charged latex sphere and a sterically stabilized neutral sphere.

In this Letter, we describe DLS experiments on fluid-ordered charge-stabilized trimethoxysilypropyl methacrylate (TPM) coated silica spheres [12], in an index-matching

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80:20 toluene-ethanol mixture at $T = 20\,^\circ\mathrm{C}$. The radius determined by SAXS is $a = 136$ nm, with size polydispersity of 0.06. The residual salinity is below 1 μM. Our precision measurements of $S(q,t)$ cover the full colloidal time regime and a broad q range, with ϕ extending up to the freezing transition value $\phi_f \approx 0.16$, where $S(q_m) \approx 3.2$. The DLS measurements were made using a setup by the ALV-Laservertriebsgesellschaft (Langen, Germany). The intensity autocorrelation function, $g_2(q,t)$, was recorded by an ALV-5000 multitau digital correlator, and the electric field autocorrelation function, $g_1(q,t) \propto S(q,t)$, was determined from $g_2(q,t)$ using the Siegert relation. We checked that there is no noticeable multiple scattering.

We will show that our results for $D_S(q)$ and d_S deduced from $S(q,t)$ are in good agreement with theoretical predictions for low-salt systems of strongly charged particles [9,13]. Moreover, our data at the crystallization point confirm two dynamic criteria for the freezing values of d_L/d_S [7] and the long-time cage-diffusion coefficient, $D_L(q_m)$ [13]. The latter quantifies the decay of density relaxations of wavelength $2\pi/q_m$. Most importantly, our data show that factorization scaling also applies approximately to charge-stabilized suspensions for ϕ up to the freezing value. We provide theoretical arguments supporting the applicability of factorization scaling for arbitrary pair potentials, but we also point to its approximate nature.

Figure 1 shows DLS data for the $g_2(q,t)$ of TPM coated silica spheres at q_m and for ϕ up to ϕ_f. The inset displays $\ln f(q,t)$ versus q^2t for $\phi = 0.14$ and q including the peak position value where $S(q_m) \approx 2.9$. The experimental $S(q)$ is shown in the inset of Fig. 2, together with the $S(q)$ calculated using the penetrating background rescaled mean spherical approximation (PBRMSA) scheme [14]. This analytic scheme provides accurate $S(q)$ [15]. The only adjustable parameter in this scheme is the effective particle charge in the Derjaguin-Landau-Verwey-Overbeek (DLVO) screened Coulomb potential, determined as $175e$ from fitting the experimental peak height. The good agreement between calculated and experimental $S(q)$ holds for all investigated ϕ. According to Fig. 1, $f(q,t)$ and $g_2(q,t)$ decay initially exponentially, followed by a nonexponential decay at intermediate times and an approximately exponential slower decay at long times. Similar to the neutral-sphere systems studied earlier [10,16], we have deduced $D_L(q)$ from these data. The inverse of $D_L(q)$ in Fig. 2 is compared with the inverse of $D_S(q)$ plotted on a different vertical scale. In accord with Eq. (2), $D_L(q)$ and $D_S(q)$ share practically the same q dependence, with ratio $D_L(q)/D_S(q) \approx 0.23$ at $\phi = 0.14$. This superpositioning is valid for ϕ up to ϕ_f. The solid curve in Fig. 2 is the prediction for $D_S(q)$ by the $\delta\gamma$ scheme of Beenakker and Mazur [17] using the PBRMSA $S(q)$ as input. The agreement with the experiment illustrates the accuracy of this scheme in predicting the $H(q)$ of charged systems [8,9].

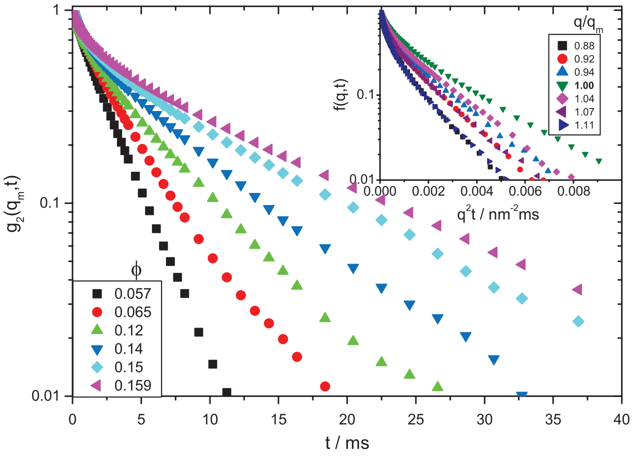

FIG. 1 (color). Scattering function $g_2(q,t)$ versus time t for TPM coated silica spheres in a toluene-ethanol mixture measured at $q = q_m(\phi)$ for ϕ values as indicated. Inset: $f(q,t)$ versus q^2t for $\phi = 0.14$ at q values as indicated.

To test Eq. (1) for its time dependence, in Fig. 3 we plot $-\ln f(q,t)/[q^2D_S(q)t]$ versus t for the same q's as in the inset of Fig. 1. To decent accuracy, the data collapse on a master curve for $q > 0.8q_m$. According to Eq. (1), this curve should be identified as $W(t)/(d_St)$ with long-time asymptote d_L/d_S. The long-time regime is reached for $t > 33$ ms, giving $d_L/d_S(\phi = 0.14) \approx 0.23$.

A discussion is in order here on the validity of the factorization scaling and the existence of the exponential long-time mode in $f(q,t)$ as its necessary prerequisite. The occurrence of a long-time mode and its q dependence were explored theoretically by Cichocki and Felderhof [18,19] for dilute to moderately dense hard-sphere systems without HIs. They analyzed the spectral distribution, $p_q(\lambda) \geq 0$, of relaxation rates λ,

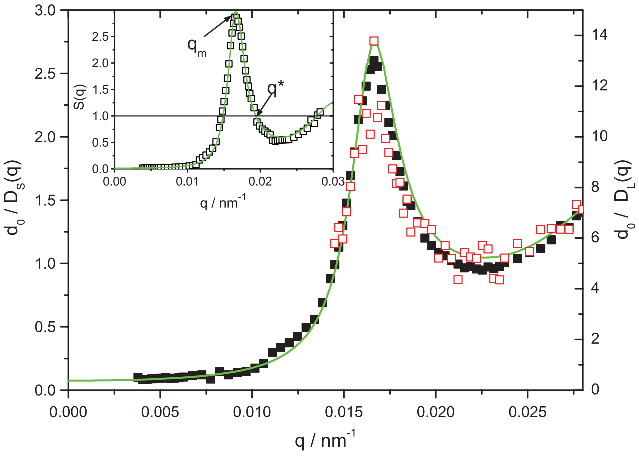

FIG. 2 (color). DLS results for the normalized inverse short-time diffusion function $d_0/D_S(q)$ (■, scale on left axis) and inverse long-time diffusion function $d_0/D_L(q)$ (□, scale on right axis) of TPM coated silica spheres at $\phi = 0.14$. Inset: static structure factor. Lines: theoretical predictions for $d_0/D_S(q)$ by $\delta\gamma$ scheme with PBRMSA input for $S(q)$.

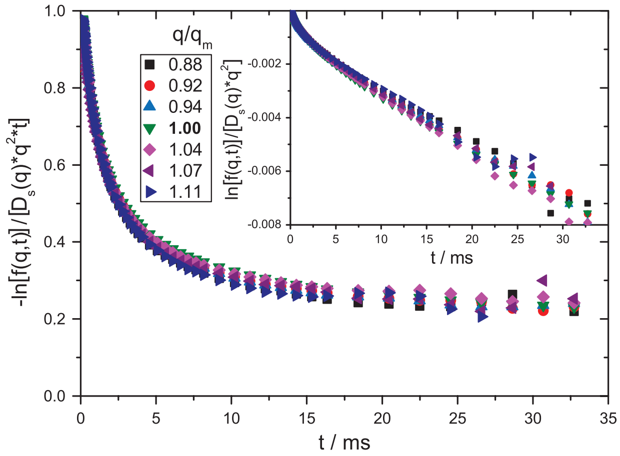

FIG. 3 (color). Same data as in the inset of Fig. 1, plotted here as $-\ln[f(q,t)]/[q^2 D_S(q)t]$. Inset: $\ln[f(q,t)]/[q^2 D_S(q)]$ versus t. Scaling is found for $q/q_m \geq 0.8$.

$$f(q,t) = \int_0^\infty d\lambda\, p_q(\lambda) \exp\{-\lambda t\}, \tag{3}$$

characterizing the strictly monotonous decay of $f(q,t)$. Using a contact Enskog approximation (CEA) exact to first order in ϕ, they showed that for $S(q)$ sufficiently large at the considered q, the long-time decay of $f(q,t)$ is dominated indeed by an exponential mode arising from a delta peak contribution to $p_q(\lambda)$, in a low λ gap, where the continuous part of $p_q(\lambda)$ is zero [18,19]. The associated $D_L(q)$ relates to the center of mass diffusion of a pair of particles. At a q different from q_m where $S(q)$ is small, e.g., at the first minimum in $S(q)$ to the right of q_m, the delta peak can mold with the continuous spectral part, but still a pronounced peak in $p_q(\lambda)$ may remain. If sufficiently strong, this peak describes approximately a long-time mode. Quite interestingly, $D_L(q)/D_S(q)$ obtained in CEA using $D_S(q) = d_0/S(q)$ for zero HIs varies significantly with q [19].

The feature of an approximate long-time mode for hard spheres without HIs, observed for $\phi \geq 0.2$ [20], should survive when particles with soft interactions, and many-body correlations not accounted for in CEA, are considered. Indeed, mode coupling theory (MCT) without HIs predicts a long-time mode both for charged spheres with strong electrostatic interactions and dense hard-sphere systems [20]. No sharp long-time mode occurs when the system is weakly structured or when $S(q)$ at the considered q is small.

We expect that HIs cause no qualitative changes. However, earlier findings for neutral spheres and our data for charged silica spheres suggest that HIs tend to smooth out the q variations in $D_L(q)/D_S(q)$ present otherwise. The existence of a long-time mode with $D_L(q) \propto D_S(q)$ does not necessarily imply validity of the q-t factorization in $\ln f(q,t)$. To check the validity of Eq. (1) for a dense hard-sphere system, we performed MCT calculations of $W(t)$ and $f(q,t)$, each shown to be in good agreement with Brownian dynamics simulations [15]. According to MCT, the t dependence in Eq. (1) is only approximate, especially at intermediate times. There is no reason for Eq. (1) to be exact with HIs.

Since the self-intermediate scattering function, $G(q,t)$, related to self-diffusion is not measurable by DLS, we use an approximate procedure by Pusey to extract d_S and d_L directly from $S(q,t)$ [21], at a wave number $q^* > q_m$ (see inset of Fig. 2) where the distinct structure factor, $S_d(q) = S(q) - 1$, is zero. On assuming that the time-dependent generalization, $S_d(q^*,t) = S(q^*,t) - G(q^*,t)$, remains small as compared to $G(q^*,t)$, it follows $S(q^*,t) \approx G(q^*,t)$, and consequently $S(q^*,t) \approx \exp\{-(q^*)^2 W(t)\}$ when non-Gaussian contributions are ignored. This identifies d_S with $D_S(q^*)$. Simulations of neutral and charged spheres [9] show that d_S is determined by this procedure to within 5%–10%. A similar accuracy can be expected for d_L. This is supported by MCT results for charged particles where we compare $-\ln S(q^*,t)/(q^*)^2$ to $W(t)$, observing an agreement within 10% deviations at intermediate times. Our experimental data confirm the theoretical prediction, $d_s/d_0 = 1$–$2.5\phi^{4/3}$ [9,20], for all considered ϕ. The $\phi^{4/3}$ dependence is characteristic of charged particles at low salinity where $q_m \propto \phi^{1/3}$.

The d_L and d_s decrease in general monotonically with increasing ϕ, to an extent depending on parameters such as salinity and Z. To discuss their generic behavior, our data for d_L/d_0, $D_L(q_m)/d_0$, and $D_L(q_m)/D_S(q_m) \approx d_L/d_s$ are plotted in Fig. 4 versus $S(q_m)$ and compared to theoretical predictions. $S(q_m)$ quantifies the strength of static correlations. The MCT curve for the ratio, d_L/d_S, of hard spheres has been corrected for HIs by a short-time hydrodynamic rescaling procedure [2,20], describing experimental data very well [13]. At freezing where $S(q_m, \phi_f = 0.494) = 2.85$ for hard spheres, $d_L/d_S \approx 0.1$ is in accord with Löwen's criterion. Short-time rescaling works well for neutral spheres [2], but not for low-salinity systems of charged particles, where opposite to hard spheres long-time diffusion is enhanced [3,13,22].

The MCT curve for d_L/d_S of charged spheres was obtained without HIs. It matches rather closely the d_L/d_S curve for hard spheres, giving $d_L/d_0 \approx 0.1$ at $S(q_m) = 2.85$, and $d_L/d_0 \approx 0.06$ at the experimental value $S(q_m) = 3.2$ where the silica system freezes. The freezing value for $S(q_m)$ varies from 2.85 for hard spheres to about 3.1–3.3 for low-salt suspensions [23,24]. From the silica system data, we note $d_L/d_S \approx D_L(q_m)/D_S(q_m) \approx 0.12$ at freezing, in decent agreement with Löwen's criterion. Another remarkable finding is that the experimental freezing value, $D_L(q_m)/d_0 \approx 0.05$, is close to the value 0.06 predicted by MCT at the peak height where hard spheres freeze. At the experimental peak height of the silica system at freezing, MCT predicts $D_L(q_m)/d_0 \approx 0.03$.

As shown in [13,20], a universal 1:1 relation between d_L/d_0 and $S(q_m)$, and a corresponding relation between $D_L(q_m)/d_0$ and $S(q_m)$, should apply approximately to all

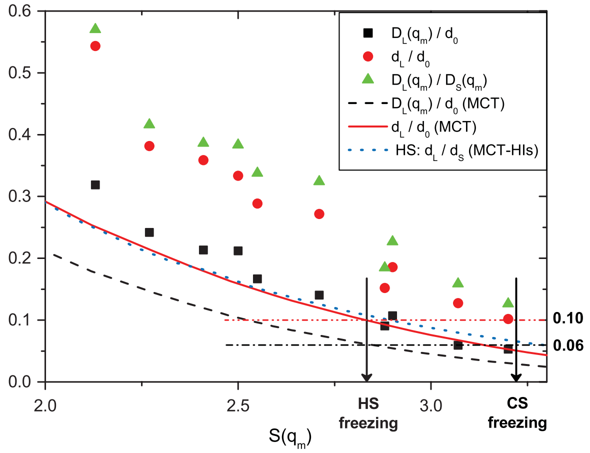

FIG. 4 (color). Long-time cage-diffusion coefficient $D_L(q_m)/d_0$ and self-diffusion coefficient d_L/d_0, and self-diffusion ratio d_L/d_S versus $S(q_m)$. Filled symbols: experimental data for charged silica spheres. Lines: MCT prediction for charged spheres (CS) without HIs (denoted by MCT) and HI-corrected MCT predictions for hard spheres (HS) denoted by MCT HIs.

low-salt systems characterized by a single length scale $r_m \approx \rho^{-1/3} \propto 1/q_m$, where ρ is the particle number density. With HIs, radius a comes into play as a second length so that d_L/d_0 and $D_L(q_m)/d_0$ become moderately dependent on r_m/a [13]. Inclusion of HIs moves the theoretical curves for d_L/d_0 and $D_L(q_m)/d_0$ closer to the experimental values, which otherwise are larger roughly by a factor of 2. The reason for the upward shift is that, according to theory and simulations [3,13,22], d_L is enlarged by the far-field part of the HIs dominating in low-salinity systems by a factor of 1.15–1.35. Since $D_L(q_m) \sim d_L$, a similarly pronounced hydrodynamic enforcement can be expected for $D_L(q_m)$, but there are to date no simulation results to corroborate this. According to our experiments, d_S of low-salt systems is smaller than d_0 by a factor of 1–$2.5\phi^{4/3}$, so that d_L is further upshifted when normalized by d_S in lieu of d_0. One should not expect quantitative agreement with experimental data even after inclusion of HIs. MCT is an approximate approach after all, becoming less accurate for less strongly structured systems.

In summary, we have shown that factorization scaling of $f(q, t)$, with q-independent ratio $D_L(q)/D_S(q)$ for $q > 0.8q_m$, also applies to charge-stabilized suspensions. This approximate feature should be observable, to a varying degree of accuracy, in any suspension of rigid spherical particles, provided these are correlated sufficiently strongly. Our data confirm theoretical predictions for the freezing values of d_L/d_S and $D_L(q_m)$, the ϕ dependence of d_S, and the q dependence of $D_S(q)$. We expect dynamic scaling to apply approximately even for soft spherical particles such as microgel spheres [25] and core-shell particles [26], where dynamic differences to rigid particles arise mainly from solvent permeability and correspondingly weakened HIs. A strong interplay of intra- and interparticle dynamics can be expected for very soft and flexible particles such as soft giant micelles [27], which might severely affect dynamic scaling. Exploring this interplay requires more theoretical and experimental work.

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