

Scaling of the Dynamic Scattering Function of Concentrated Colloidal Suspensions

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By dynamic light scattering we have studied concentrated suspensions of “hard-sphere” colloidal particles in their equilibrium and metastable fluid states. We have found a simple, as yet unexplained, scaling procedure which collapses the measured intermediate scattering functions describing structural relaxation and self-diffusion onto the same master curve. [S0031-9007(96)00653-9]

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Understanding of Brownian motions of colloidal particles suspended at high concentrations in a liquid is still far from complete. They constitute a many-body problem, analogous to the motions of atoms in a liquid but complicated further by the effects of long-ranged, many-particle hydrodynamic interactions [1]. Improvements in the preparation of “model” colloidal particles and in the technique of dynamic light scattering (DLS) now allow the collection of high quality data. DLS measures the intermediate scattering function $f(Q, \tau)$, which describes the dynamics of spatial Fourier components of spontaneous fluctuations in the number density of particles. The challenge is to understand the full dependence of $f(Q, \tau)$ on both scattering vector Q and time τ .

In this Letter we describe the discovery of a remarkably simple scaling property of the measured intermediate scattering functions of suspensions of hard-sphere colloidal particles, embodied in Eqs. (1) and (2) and displayed in Figs. 2–4. This scaling applies at all particle concentrations up to the glass transition, and over an extended (but not the complete) range of Q which spans the main peak of the static structure factor $S(Q)$ of the suspensions. An interpretation of this finding suggests that the collective motion, or structural relaxation, of a particle and its cage of neighbors, which gives rise to the structure factor peak, is related to self-diffusion.

The particles used comprised cores of polymethylmethacrylate (PMMA) stabilized by thin layers of poly-12-hydroxystearic acid. Previous work on similar systems has shown that the interaction between the particles is well approximated by that of hard spheres [1–3]. We used two preparations of particles. The first set was suspended in *cis*-decalin, and had a mean radius $R = 178$ nm and size polydispersity $\sigma \sim 0.05$. These suspensions showed a crystallization, or disorder-order transition. As described elsewhere [2], sample volume fractions ϕ were calibrated by assuming the observed freezing concentration to be that of an assembly of hard spheres, $\phi = 0.494$. For studies in the metastable fluid region, $\phi > 0.494$, we used particles with $R = 207$ nm and $\sigma \sim 0.12$, suspended in a mixture of *cis*-decalin and tetralin. Because of the higher polydispersity, samples

of these particles did not crystallize over several days. It was thus possible to make long DLS measurements, without distortion from growing crystallites.

Measurements were made using two-color DLS (TCDLS) equipment, described in detail elsewhere [4]. The technique of TCDLS effectively suppresses multiple scattering. It is thus possible to study moderately turbid samples such as PMMA particles in *cis*-decalin. Since the strong single scattering dominates any scattering from dust and the walls of the sample cell and the multiple scattering is suppressed, data of high precision can be obtained. The technique measures the normalized intensity correlation function $g^{(2)}(Q, \tau) = \langle I(0)I(\tau) \rangle / \langle I(0) \rangle^2 = 1 + C_0 |f(Q, \tau)|^2$ where $\langle \dots \rangle$ represents a time average and C_0 an experimental constant smaller than 1. Dynamical information is contained in the normalized intermediate scattering function [1] $f(Q, \tau) = F(Q, \tau) / F(Q, 0)$, where $F(Q, \tau) = N^{-1} \sum_{i=1}^N \sum_{j=1}^N \langle \exp\{i\vec{Q} \cdot [\vec{r}_i(0) - \vec{r}_j(\tau)]\} \rangle$ and the static structure factor is $S(Q) \equiv F(Q, 0)$; N is the number of particles in the scattering volume, assumed to be large, and $\vec{r}_j(\tau)$ is the position of particle j at time τ .

Figure 1(a) shows measured intermediate scattering functions for a sample at volume fraction $\phi = 0.465$; $\ln f(Q, \tau)$ is plotted against $Q^2\tau$ for different values of QR . In this representation, data for a dilute sample (no interparticle interactions) would lie on the same straight line with slope $-D_0$ [since in this case $f(Q, \tau) = \exp(-D_0 Q^2 \tau)$, where D_0 is the free-particle, or Stokes-Einstein, diffusion constant]. It is immediately apparent that interactions have a marked effect. First, $f(Q, \tau)$ departs strongly from a simple dependence on $Q^2\tau$ and second, its decay cannot be described by a single exponential. As shown in the inset of Fig. 1(a), at short times the decay of $f(Q, \tau)$ is linear in τ , $f(Q, \tau) = 1 - D_S(Q)Q^2\tau + \dots$, which defines the short-time, Q -dependent diffusion coefficient, $D_S(Q)$. A strong Q -dependence of $D_S(Q)$, plotted in reciprocal form for comparison with $S(Q)$ [5], is seen in Fig. 1(b). The theory for $D_S(Q)$ is well understood [1,2,6–8]; it can be written $D_S(Q) = D_0 H(Q) / S(Q)$, where $H(Q)$ reflects the effects of hydrodynamic interactions. Note the large

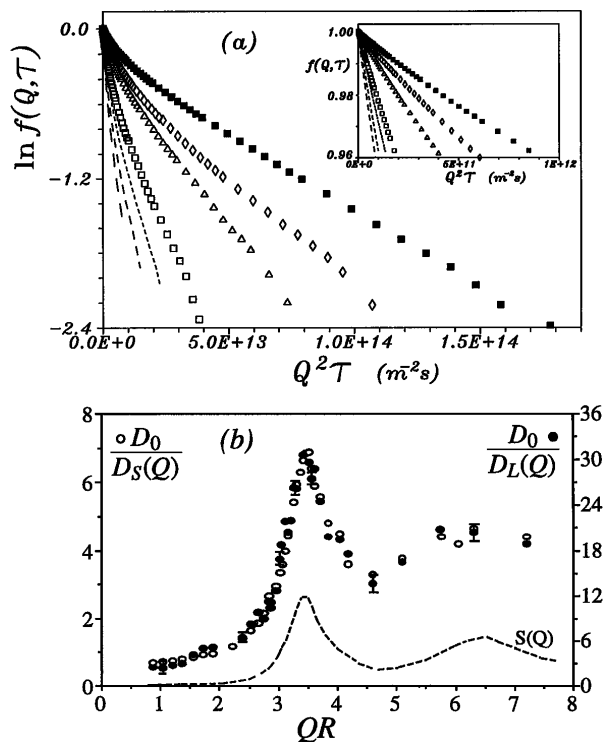


FIG. 1. TCDLS results for a suspension of PMMA spheres of polydispersity $\sigma \sim 0.05$ at volume fraction $\phi = 0.465$. The different symbols represent different values of QR (see Fig. 2(a) for legend). (a) Intermediate scattering functions; $\ln f(Q, \tau)$ is plotted against $Q^2 \tau$. Inset: short-time behavior. (b) Normalized short-time $D_0/D_S(Q)$, \circ (referred to left-hand axis), and long-time, $D_0/D_L(Q)$, \bullet (right-hand axis), diffusion coefficients. The dashed line is the theoretical static structure factor $S(Q)$ (left-hand axis) at $\phi = 0.465$.

difference between $D_0/D_S(Q)$ and $S(Q)$, particularly at $Q < Q_m$, indicate that hydrodynamic interactions play a large role in the dynamics of short-time diffusion.

Figure 1(a) also shows that the decay of $f(Q, \tau)$ at long times is roughly exponential, $f(Q, \text{large } \tau) \propto \exp[-D_L(Q)Q^2 \tau]$, defining a long-time diffusion coefficient $D_L(Q)$. Figure 1(b) also shows $D_0/D_L(Q)$ as a function of Q [note the different vertical scales for $D_S(Q)$ and $D_L(Q)$]. Surprisingly $D_S(Q)$ and $D_L(Q)$ have nearly the same dependence on Q and are related simply by a factor of ~ 4.3 (at $\phi = 0.465$). To our knowledge these are the first detailed measurements of long-time Q -dependent diffusion in concentrated hard-sphere suspensions in their equilibrium fluid state. In contrast to $D_S(Q)$, there are no theoretical predictions for $D_L(Q)$ which take proper account of hydrodynamic interactions.

The short-time processes can be associated with diffusion of the particles within their neighbor cages, and the long-time processes with diffusion on a time scale longer than that over which the cages break apart. The evolution from the short- to long-time regimes, associated with the breakdown of the cages, can be studied by defining a time-dependent diffusion coefficient $D(Q, \tau)$

in terms of the slopes of the data in Fig. 1(a), $D(Q, \tau) \equiv -(1/Q^2)d \ln f(Q, \tau)/d\tau$ [1]. Figure 2(a) shows $D(Q, \tau)$, obtained by numerical differentiation of the data in Fig. 1(a) and normalized by $D_S(Q)$, as a function of time τ . It is again surprising, and not predicted theoretically, that for $QR \geq 2.5$, the results superpose quite accurately on the same master curve, leading to

$$\frac{D(Q, \tau)}{D_S(Q)} = \chi'(\tau), \quad (1)$$

where $\chi'(\tau)$ is a Q -independent function of time.

It is straightforward to show that the scaling of $D(Q, \tau)$ implies that $f(Q, \tau)$ itself should also scale if plotted in the form $\ln f(Q, \tau)/D_S(Q)Q^2$ versus τ , i.e., that

$$\frac{\ln f(Q, \tau)}{D_S(Q)Q^2} = -\chi(\tau), \quad (2)$$

where, for a given concentration, $\chi(\tau)$ is related to $\chi'(\tau)$, Eq. (1), by $\chi'(\tau) = d\chi(\tau)/d\tau$. This is verified in Fig. 3. Figure 3(a) simply replots the data of Fig. 1(a) in the form $\ln f(Q, \tau)$ versus τ and the predicted collapse of the data is seen in Fig. 3(b).

As mentioned above, this scaling for $QR \geq 2.5$ has not been predicted theoretically. Some interpretation can be obtained from the following considerations. At large

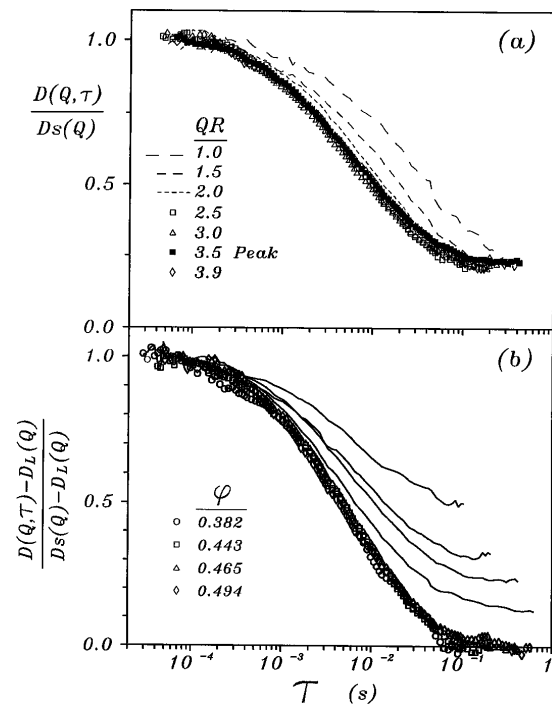


FIG. 2. Normalized time-dependent diffusion coefficients. (a) $D(Q, \tau)/D_S(Q)$ vs time for $\phi = 0.465$. $D(Q, \tau)$ is the (negative of the) local slope of the data in Fig. 1(a) (see text). (b) $[D(Q, \tau) - D_L(Q)]/[D_S(Q) - D_L(Q)]$, (symbols), and $D(Q, \tau)/D_S(Q)$, (solid lines, increasing concentration from top to bottom), vs time at different sample concentrations ϕ . For simplicity, only measurements near to the main peaks $Q \sim Q_m$ of the static structure factors $S(Q)$ are shown.

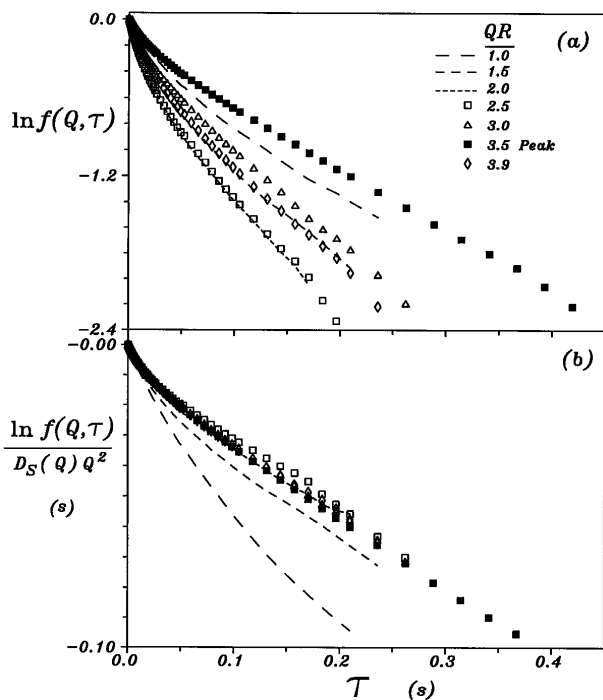


FIG. 3. Same data as Fig.1(a) plotted vs τ rather than $Q^2\tau$. (b) Same data plotted as $\ln f(Q, \tau)/D_S(Q)Q^2$ vs τ , showing collapse to master curve for $QR \geq 2.5$.

Q ($QR \gg 3.5$), the coherent scattering function $f(Q, \tau)$ tends to the self (incoherent) intermediate scattering function $F^{\text{self}}(Q, \tau)$ [1]. If the displacement $\Delta\vec{r}(\tau)$ of a single particle is assumed to be a Gaussian variable, $F^{\text{self}}(Q, \tau)$ becomes

$$F^{\text{self}}(Q, \tau) = \exp[-Q^2\langle\Delta r^2(\tau)\rangle/6]. \quad (3)$$

(The Gaussian approximation is known to be reasonably accurate for colloidal suspensions in their equilibrium fluid states [1,9].) Requiring that Eq. (2) reduces to Eq. (3) in the high- Q limit then gives an expression for $\chi(\tau)$ so that $f(Q, \tau)$ can be written

$$f(Q, \tau) = \exp\left(-\frac{D_S(Q)}{D_S^{\text{self}}} Q^2\langle\Delta r^2(\tau)\rangle/6\right), \quad (4)$$

where $D_S^{\text{self}} = \lim_{Q \rightarrow \infty} D_S(Q)$ is the short-time self diffusion coefficient, $\langle\Delta r^2(\tau)\rangle = 6D_S^{\text{self}}\tau - \dots$. Thus Eq. (4) suggests that, for $QR \geq 2.5$, the coherent scattering function is determined by the diffusion of a single particle, scaled by the ratio of collective to self short-time diffusion coefficients. The behavior of the mean-square displacement, $\langle\Delta r^2(\tau)\rangle$, can be understood qualitatively in terms of the cage effect [1] and the coefficients $D_S(Q)$ and D_S^{self} are well-defined equilibrium averages.

It is apparent from Figs. 2(a) and 3(b) that the scaling of Eqs. (1) and (2) breaks down at small Q , $QR < 2.5$, which corresponds to fluctuations on length scales somewhat larger than the mean interparticle spacing. [Previously [10] we have discussed the decay of $f(Q_m, \tau)$, at the peak, $Q = Q_m$, of $S(Q)$, in terms of the structural

relaxation of a particle and its cage of neighbors.] Presumably, for $QR < 2.5$, collective particle motions of a different nature control $f(Q, \tau)$. These will be discussed in detail elsewhere [11].

The results shown in Figs. 2(a) and 3 are typical of those found in five other equilibrium fluid samples; $\phi = 0.382, 0.443, 0.470, 0.482$, and 0.494 [11]. In Fig. 2(b) we show time-dependent diffusion plots obtained in the scaling regimes for several different concentrations. Remarkably, when plotted in the form $[D(Q, \tau) - D_L(Q)]/[D_S(Q) - D_L(Q)]$, results for $0.38 \leq \phi \leq 0.494$ also scale approximately even though the ratio $D_S(Q)/D_L(Q)$ varies from 2 to 7 over this concentration range. The insight afforded by Eq. (4) allows some interpretation of Fig. 2(b) in terms of earlier work. The function $[D(Q, \tau) - D_L(Q)]/[D_S(Q) - D_L(Q)]$ can now be regarded as describing the evolution in time of a single particle through its cage. This was studied by Cichocki and Hinsen by Brownian dynamics simulations of hard spheres [12], neglecting hydrodynamic interactions. They found both a similar function form to that seen in Fig. 2(b) and the near independence of particle concentration.

The results discussed so far are limited to suspensions in their equilibrium fluid states at concentrations below freezing at $\phi = 0.494$. We now consider a higher con-

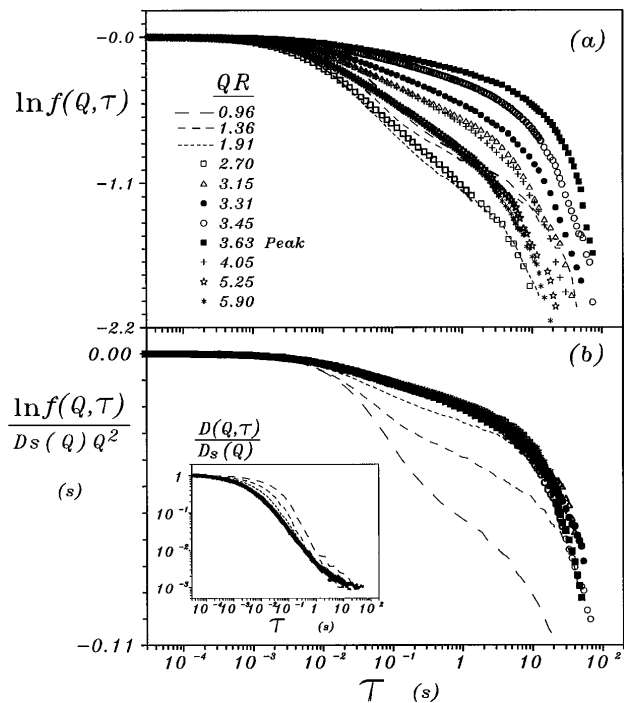


FIG. 4. Intermediate scattering functions for a suspension of PMMA spheres of polydispersity $\sigma \sim 0.12$ and volume fractions $\phi \sim 0.57$, near to the glass transition. (a) $\ln f(Q, \tau)$ is plotted vs τ ; the time axis is logarithmic because of the strongly stretched decays. (b) $\ln f(Q, \tau)/D_S(Q)Q^2$ versus τ , showing collapse, or scaling, for $QR \geq 2.7$. Inset: $D(Q, \tau)/D_S(Q)$ vs τ .

centration sample of the more polydisperse particles at volume fraction $\phi \sim 0.57$, near to the glass transition [13]. The correlation functions, Fig. 4(a), are qualitatively similar to those found in a previous study [14], comprising three distinct relaxation regimes. The short time decays, $\tau \leq 5 \times 10^{-4}$ s, yield values of $D_S(Q)$ which display a Q dependence similar to that shown in Fig. 1(b). The stretched intermediate decays extending to $\tau \sim 5$ s, are termed β -relaxation in the glass transition literature and can be associated with the evolution of the practice cages prior to their complete breakdown [15]. At the longest times $\tau > 5$ s, the α -relaxation corresponds to long-distance diffusion. Despite the more complex form of $f(Q, \tau)$ for this sample, compared to those at lower concentrations (Fig. 3), the data for $QR > 2.7$ still collapse reasonably well when plotted as $\ln f(Q, \tau)/D_S(Q)Q^2$ and $D(Q, \tau)/D_S(Q)$ versus τ as shown in Fig. 4(b).

As mentioned above, the complexity of interparticle hydrodynamics has so far precluded any firm theoretical predictions of the long-time dynamics of concentrated colloidal suspensions. However, there are some relevant theories and simulations for concentrated suspensions in which hydrodynamic interactions are (hypothetically) neglected, including those of de Schepper *et al.* [16], who also suggest a connection between structural relaxation and self-diffusion, Härtl *et al.* [17], and Cichocki and Felderhof [18]. However, none of these approaches appears to lead directly to the scaling property found in this Letter.

Mode-coupling theories for fluids close to the glass transition predict specific scaling properties for the α - and β -relaxations [15] which have been observed in PMMA suspensions similar to those studied here [14]. It is not yet clear how these relate to the simple scaling that we have found [11]. We note that Eqs. (1) and (2) indicate a factorization property of $\ln f(Q, \tau)$ and $D(Q, \tau)$; both quantities can be approximately written as the product of separate functions of Q and τ only.

Finally, we mention some results of recent DLS studies on two other types of strongly interacting suspensions. Nearly monodisperse emulsion droplets of oil in water can behave like hard spheres at the concentrations and time scales of interest here. Unpublished DLS measurements [19] on such a system at $\phi \sim 0.5$ gave scattering functions $f(Q, \tau)$ and scaling almost identical to those found with the PMMA particles. On the other hand, the scattering functions of dilute aqueous suspensions of charged polystyrene spheres [20], which interact through long-ranged Coulombic repulsions but weaker hydrodynamic interactions, do not exhibit accurate scaling though they look qualitatively similar to those shown in Fig. 1(a).

We have found an approximate, but quite accurate, scaling property of the intermediate scattering functions $f(Q, \tau)$ of concentrated colloidal suspensions which ap-

plies for a range of scattering vectors, $QR > 2.7$, which encompasses most of the strong Q -variation of the static structure factor $S(Q)$. This property suggests that the "structural relaxation" of a particle and its cage of neighbors is related to self-diffusion.

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