Universal Self-Diffusion and Subdiffusion in Colloids at Freezing

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We provide a theoretical explanation for the observed quasiuniversality of the ratio of the long-time to short-time self-diffusion coefficients in colloidal liquids at freezing. We also predict that the mean-squared displacement at freezing, plotted against a suitably renormalized time, yields a universal curve showing a short-time subdiffusive regime and a long-time caged diffusion. We obtain $C_s(k,t)$, the intermediate scattering function, for all (k,t) and show that it implies strong non-Gaussian behavior in the probability distribution of the single-particle displacement at short times.

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In an interesting Letter [1], Löwen *et al.* made the empirical observation that the ratio of the long-time self-diffusion coefficient D_L to the short-time or bare value D_0 has a universal value close to 0.1 along the freezing line of several liquids interacting with different potentials. They based their conclusions on forced Rayleigh scattering experiments performed on charge-stabilized colloidal suspensions, as well as Brownian dynamics simulations on several Yukawa liquids, with the OCP (one-component plasma) and hard spheres as two extreme cases. The universal value of D_L/D_0 was offered as a useful dynamical freezing criterion. This observation also serves as a more incisive test of theories of mobility in liquids than mere fits of diffusivity as a function of temperature or density, since the latter allow too much latitude in the location of the point at which the extrapolated diffusivity appears to vanish.

In this Letter, we present a calculation of D_L/D_0, in a self-consistent one-loop approximation, for model systems of interacting Brownian particles. Our results, which should apply to colloidal systems in which the hydrodynamic interaction [2] can be neglected as well as to Brownian dynamics simulations, are as follows: (i) The observed dynamical universality of D_L/D_0 is in fact a direct consequence of the well-known [3] and well-understood [4] universal height of the static structure of simple liquids at freezing. However, our calculation of the ratio gives (universally) 0.05 rather than 0.1, a numerical discrepancy on which we comment at the end of this Letter. Our complete self-consistent calculation is carried out explicitly for two pair potentials, namely, hard spheres and $1/r^6$, but we show that the results should hold for a much wider class of systems. (ii) The mean-squared displacement (MSD) of a tagged particle in the colloid shows (Figs. 1 and 2) subdiffusive behavior (roughly $t^{0.45}$) at intermediate times, crossing over to a slow long-time (caged) diffusion. This is equivalent to nonexponential temporal relaxation of density correlations. (iii) The form of the intermediate (self-) scattering function $C_s(k,t)$ for a large number of values of the wave vector k and over all times implies (Fig. 3) a substantial departure from Gaussian behavior in the probability distribution of the particle displacement at short times. Experiments performed to measure such non-Gaussian [5] corrections will serve as a more demanding test of theories of the dynamics of dense liquids and colloids. (iv) The shape of the MSD vs time curve is effectively decoupled from the actual value of the long-time or renormalized diffusivity. By this we mean that the theoretical (present work) and simulation [6] plots of MSD in units of the mean interparticle distance σ vs time agree closely (see Fig. 1) if the time t in each case is measured in units of the *renormalized* diffusion time $\tau_R \equiv \sigma^2/D_L$ [where D_L is the *calculated* (for the theory) and *measured* (for the simulation) long-time diffusivity] [7]. The same figure also shows the corresponding plot

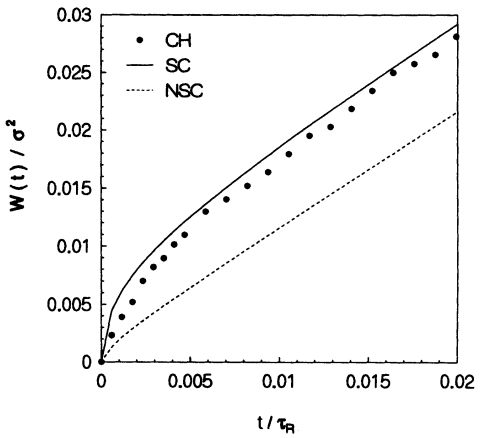

FIG. 1. We compare MSD data plotted against renormalized time for three different cases: the dots are points read off from graphs of the hard-sphere simulation data of [6] (CH); the solid curve is drawn through the data obtained at self-consistency in our calculation (SC); the dashed curve represents the non-self-consistent data in our calculation (to be compared with the theory of [2] (NSC). Both our sets of data have been computed from the correspondng $C_s(k,t)$ for $k\sigma = 0.2$ which is the lowest k value accessible numerically for very short times.

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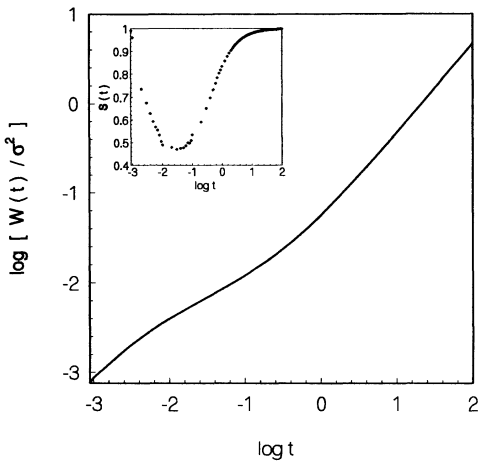

FIG. 2. We show MSD vs time on a log-log plot, clearly depicting an initial short-time diffusion, followed by a subdiffusive regime, and an asymptotic long-time diffusion. The inset shows a graph of the local slopes $S(t)$ of the log-log plot, highlighting the three different regimes indicated above.

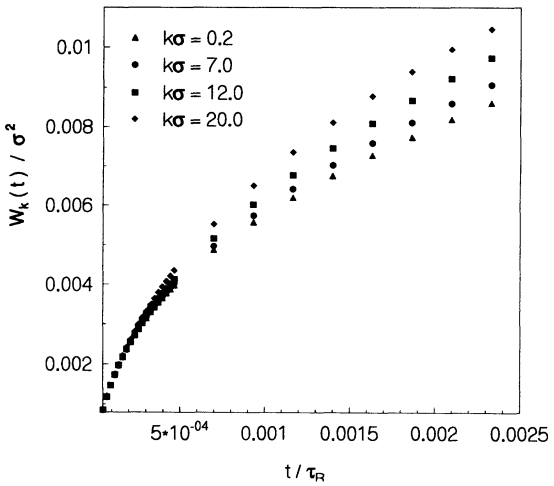

FIG. 3. This figure shows the strong k dependence of the quantity $W_k(t)/\sigma^2$ for short times. We look at k values covering 2 orders of magnitude, from $k\sigma = 0.2$ to $k\sigma = 20$; the figure is clearly indicative of non-Gaussian effects in $P[\mathbf{R}(t) - \mathbf{R}(0)]$, the probability distribution of the tagged particle position.

of the results of a "non-self-consistent" (hereafter NSC) calculation, similar to that of Medina-Noyola [2], which can be seen to deviate very substantially from the data. We believe that such a plot is the most useful comparison to make between experiments, simulations, and theory, since it captures the kinetics of the suspension for all times in much greater detail than plots of D_L/D_0 against density or temperature.

Most features of our results can be understood qualitatively as follows. Consider a specific ("tagged") particle in the suspension at temperature T. In the absence of other particles, it has a diffusion coefficient $D_0 = T/\Gamma_0$ where the *bare* friction coefficient Γ_0 is determined by the viscosity of the solvent. The presence of other particles interacting with ("caging") the tagged particle enhances the friction coefficient to a value $\Gamma \equiv \Gamma_0(1+\Sigma_0)$, leading to a reduced long-time diffusivity [8]

$$D_L = D_0/(1+\Sigma_0). \tag{1}$$

The "self-energy" Σ_0 is determined by the correlations and dynamics of the suspension particles, each of which is being slowed down in the same way. Thus, if we know the liquid-state correlations among the particles [say in the form of a static structure factor $S(q)$] the dynamics, including the self-diffusivity, can be determined self-consistently. The fact that the medium is highly correlated suggests that, at least at intermediate times, the particle motion should deviate from simple Brownian motion. Moreover, since the only input to the calculation is $S(q)$, whose height ($\approx$2.85) and shape at freezing are very similar [3,4] for a wide variety of simple liquid systems, it is reasonable to expect a universal suppression $1/(1+\Sigma_0)$ of diffusivity at freezing.

In more detail, note that the density of force in the equation of motion for the tagged-particle momentum density is [9]

$$\mathbf{F}(\mathbf{r},t) = -n_s(\mathbf{r},t)\nabla \int_{\mathbf{r}'} c(|\mathbf{r}-\mathbf{r}'|)\delta n(\mathbf{r}',t), \tag{2}$$

where δn is the deviation of the (collective) number density $n(\mathbf{r})$ from its equilibrium value n_0, n_s is the tagged-particle number density, and $c(r)$ is the direct pair correlation function of the liquid. This form is physically reasonable: the convolution of c and δn is simply the excess chemical potential μ due to interactions, and thus $-n_s\nabla\mu$ is the density of (osmotic) force. As a result of this nonlinear coupling, the local bare friction Γ_0 is replaced by a wave-number- (k) and frequency- (z) dependent damping rate

$$\Gamma(k,z) \equiv \Gamma_0\,(1+\Sigma(k,z)). \tag{3}$$

The starting point in the calculation of $\Gamma(k,z)$ is largely standard [9], and rests on a simple application of a fluctuation-dissipation theorem: the excess friction or self-energy Σ in (3) is proportional to the autocorrelation of the excess thermodynamic force $\mathbf{F}$. In a Gaussian decoupling approximation, this leads to

$$\Sigma(k,z) = \frac{1}{3}\int d^3q \int dz_1\, v(q)\, C_s(|\mathbf{k}-\mathbf{q}|, z-z_1)\, C_c(q,z_1), \tag{4}$$

which is bilinear in the self-density and collective-density correlations (C_s and C_c, respectively), and the Σ_0 which

appeared in the suppression factor in Eq. (1) is $\Sigma(k = 0, z = 0)$. Note that in (4) and hereafter, we express lengths and times in units of the mean interparticle distance $\sigma \equiv n_0^{-\frac{1}{3}}$ and the bare interparticle diffusion time σ^2/D_0, respectively. With (4) and (6) (below) in this dimensionless form, the fact that Σ depends only on $S(q)$, and should thus be universal at freezing, is very clear. In (4),

$$v(q) = q^2[n_0 c(q)]^2 \tag{5}$$

is the interaction vertex arising from (2), $c(q) = n_0^{-1}\left[1 - S^{-1}(q)\right]$ being the Fourier transform of the direct correlation function.

Although the mode-coupling expression (4) is superficially similar to that in earlier (NSC) treatments [2,10] of the effect of interaction on self-diffusion in colloids, there is a major difference in the form we take for the self-density and collective-density correlation functions:

$$C_s(k,z) = \frac{1}{z + \frac{ik^2}{1+\Sigma(k,z)}},$$

$$C_c(k,z) = \frac{S(k)}{z + \frac{ik^2 S^{-1}(k)}{1+\Sigma(k,z)}}. \tag{6}$$

In (6), the constant bare diffusivity which would appear in the correlation functions used in [2,10] is replaced by the wave-vector- and frequency-dependent quantity $D_0/[1+\Sigma(k,z)]$. This is a significant departure from earlier studies which were not, in this sense, self-consistent. One (partially self-consistent) approach [11] is noteworthy: it carries out essentially the same calculation as in [2] but interprets the diffusivity on both sides of the equation as the *zero-frequency* value $D(0)$. The final result is an algebraic equation for $D(0)$, which leads to a substantial reduction relative to D_0, but the intermediate-time dynamics is described no better than by NSC theories. The various approaches have very different predictions for the shape of the MSD vs time plot, as we shall see below.

In writing (6), we have assumed that C_s and C_c are renormalized in a similar manner. Although it has been observed [8,12] that the interaction contribution to the self-friction and collective friction are rather different in form at intermediate densities, our approximation is reasonable at the freezing densities considered here. For the important wave-number regime that contributes substantially to the integral in (4), the time decay is controlled by C_s, since the large values of $S(q)$ make C_c decay much more slowly. The magnitudes of the two renormalizations are likely to be very similar in this particular wave-number regime. It is clear from (4) and (6) that we have to solve an integral equation in four dimensions in order to evaluate $\Sigma(k,z)$ self-consistently.

It is useful to separate the question of the universality of D_L/D_0 at freezing from the actual numerical value of this quantity. A quick demonstration of the universality can be obtained from a preliminary NSC calculation —that is, one in which the *bare* ($\Sigma = 0$) self- and collective-density correlation functions are used on the right-hand side of (4). In that case the integral equation reduces to an integral, and $\Sigma(0,0)$ is trivial to evaluate. We used the freezing line data tabulated in Hansen and Schiff [13] for the static structure factors of soft-sphere potentials of the form $V(r) = \epsilon\left(\frac{\sigma}{r}\right)^n$ ($n = 1, 4, 6, 9, 12$), and the Percus-Yevick expression for the structure factor of hard spheres (at a density at which the peak height was 2.85) [14]. Gratifyingly, we found a robust value of $\simeq 0.35$ for D_L/D_0 in all these cases, confirming that the origin of the universality lies in the structure factor.

Having established the universality of D_L/D_0, we then performed the full self-consistent calculation. On the face of it (4) is a four-dimensional integral equation and hence numerically somewhat involved. This has prompted many workers studying similar problems in simple fluids [6,15,16] to *eliminate* the wave-number dependence in (4) by assuming a leading role for modes near the peak position q_0 of $S(q)$, replacing the problem (4) by a one-dimensional integral equation. Although this procedure is intuitively appealing, it cannot be justified in a systematic manner (and indeed [6,15,16] do not suggest that it can). However [17], we can use the spatial isotropy of the correlation functions (6) to render the problem effectively *two dimensional*, and evaluate (4) iteratively in a "pseudospectral" manner. We note that the right-hand side of (4) is the convolution of the functions $C_s(k,z)$ and $\tilde{C}_c(k,z) \equiv v(k)C_c(k,z)$ which are themselves isotropic, so that in real space-time, $\Sigma(r,t) = C_s(r,t)\tilde{C}_c(r,t)$. We therefore begin by obtaining the real space C_s and $\tilde{C}_c$ from (5) and (6) with $\Sigma = 0$, and evaluate (4) the first time around, using only two-dimensional transforms and avoiding convolutions. The resulting $\Sigma(k,z)$ is fed into (6) to give the new values for the correlation functions and the process iterated until $\Sigma(k,z)$ converges to within less than a percent over the entire range of (k,z). We make no assumptions whatsoever about the (k,z) dependence of Σ, C_s, or C_c at any stage in the iteration scheme.

We have carried out the self-consistent calculation outlined above for the $n = 6$ soft-sphere case and the Percus-Yevick hard-sphere case. The ratio D_L/D_0 is once again found to be universal with a value now of about 0.05. This is of course a factor of 2 smaller than the observed value, and we comment on this discrepancy below. We have not bothered to carry out the full self-consistent calculation for cases other than these two since the single iteration results discussed above leave no doubt that the result will be the same.

With the solution to (4) in hand, the remaining results presented at the beginning of this paper follow. Some remarks on these are in order. (a) The subdiffusive intermediate-time behavior is a natural conse-

quence of the "self-consistent" nature of the dynamics. The slowing-down effect of the collective modes builds in gradually as the tagged particle explores longer and longer time scales, so that the effective diffusivity is time dependent, crossing over gradually from its bare to its (smaller) long-time value. Equivalently, purely exponentially decaying forms for C_s and C_c are inconsistent with (4). (b) Recall that the tagged-particle density correlation is related to the particle position $\mathbf{R}(t)$ by $C_s(k,t) = \langle e^{i\mathbf{k}\cdot[\mathbf{R}(t)-\mathbf{R}(0)]}\rangle$. If the probability distribution $P[\mathbf{R}(t) - \mathbf{R}(0)]$ were Gaussian, we should have $C_s(k,t) = e^{-k^2W(t)}$ where $W(t) = \frac{1}{6}\langle[\mathbf{R}(t) - \mathbf{R}(0)]^2\rangle$ is the MSD. On the other hand, defining $W_k(t) \equiv -[\ln C_s(k,t)]/k^2$, any k dependence in $W_k(t)$ indicates that P is non-Gaussian. Figure 3 shows strong k dependence in $W_k(t)$ at short times. Further, a simple NSC calculation shows much weaker deviations from Gaussian behavior. It would be of considerable interest to compare $W_k(t)$ or individual moments of the distribution with experiment and simulation, again in a plot versus t/τ_R as defined at the start of this paper. (c) The reason why our self-consistent theory, unlike the NSC theories, yields a plot of MSD vs rescaled time plot that agrees well with experiment should be appreciated. In an NSC theory, the time scales of the modes contributing to the self-energy are set by the bare correlation function, so that all structure in time-dependent quantities appears at times of order the bare diffusion time σ^2/D_0. A plot against a reduced time in units of the renormalized diffusion time will inevitably have all structure pushed to very short times. In our approach as well as in experiments and simulations, however, all time scales are determined by the renormalized correlation functions, so that the shape is well predicted by the rescaling used in Fig. 1. (d) Last we turn to the fact that the calculated reduction D_L/D_0 is 0.05, not 0.1. This is a consequence of the mode-coupling scheme we have used: as in simple fluids, it will drive the system, if the peak in $S(q)$ is high enough, into an unphysical "glass" state with $D_L = 0$, because of an overestimation of self-consistent feedback effects [18]. The cutoff mechanism of Das and Mazenko [16] and Götze [19], if implemented here as well, might mitigate the feedback, giving a value of D_L/D_0 closer to 0.1.

We summarize by noting that our theory succeeds in explaining the universal suppression of self-diffusion at freezing in Brownian systems, predicts a rich crossover structure in the time domain including subdiffusive and non-Gaussian effects, all of which should be testable in experiments, and highlights the importance of the self-consistent approach in modeling interacting colloids. A more quantitative discussion of non-Gaussian effects as well as more details of our calculations will appear in a longer work [20]. In forthcoming work, we propose to improve our numerical estimate of the suppression and, more important, to include the effect of the hydrodynamic interaction.

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