Time-Dependent Collective Diffusion of Colloidal Particles

Anthony J. C. Ladd

Lawrence Livermore National Laboratory, Livermore, California 94550

Hu Gang, J. X. Zhu, and D. A. Weitz

Exxon Research and Engineering Company, Route 22 East, Annandale, New Jersey 08801
(Received 29 June 1994)

We use a combination of numerical simulations and laboratory experiments to study the time-dependent collective diffusion coefficient $D(q,t)$ in concentrated colloidal suspensions. At short times, the particle configuration is frozen, and $D(q,t)$ probes the temporal and spatial evolution of hydrodynamic interactions, *via* their effects on the particle velocities. We find that $D(q,t)$ exhibits a surprising scaling behavior, with a single, q-dependent relaxation time, suggesting that the suspension behaves as an effective medium for hydrodynamic interactions over a wide range of length scales and time scales.

For many years there has been considerable interest in idealized suspensions of monodisperse hard spheres. In such systems, the dominant interactions are hydrodynamic; random forces, arising from thermal fluctuations in the fluid, excite fluctuations in the solid particle velocities which are subsequently damped by particle-induced viscous motion of the fluid. In the process, particles transmit hydrodynamic forces to one another on a time scale a^2/ν, where a is the particle radius and ν is the kinematic viscosity of the fluid. Since the diffusion coefficient of colloidal particles is about 5 orders of magnitude smaller than the viscosity, there is a substantial time regime (typically $10^{-8}-10^{-4}$ s) over which correlations in particle velocities specifically reflect the time evolution of the hydrodynamic interactions, without any additional complications due to the diffusion of the solid particles themselves. Light scattering measurements using diffusing-wave spectroscopy (DWS) have shown that the time-dependent self-diffusion of colloidal hard spheres can be characterized by a single relaxation time, independent of volume fraction [1,2]: If the mean-square displacement is scaled by its asymptotic value and the time is scaled by the inverse of the suspension viscosity, then the data for all particle volume fractions ϕ can be scaled onto a single, universal master curve, whose functional form can be calculated from the behavior of an isolated sphere [1]. Similar behavior was observed in numerical simulations based on a lattice Boltzmann model of the fluid [3]. Self-diffusion probes particle-particle correlations at small wavelengths, or scattering vectors q that are well beyond the first peak in the structure factor. By contrast, no reliable information about the behavior of collective diffusion, which probes the correlations at smaller q, has been obtained; yet it is at small values of qa that the dynamics directly reflect the effects of hydrodynamic interactions between one particle and its neighbors. Thus, to fully understand the hydrodynamic interactions between different particles, it is essential to extend these investigations to include the

low-q behavior. In this paper, we investigate, for the first time, the q-dependent time evolution of the hydrodynamic interactions between colloidal particles over the full range of q, from $q = 0$ to the high-q limit. By contrast, earlier simulations [3] and experiments [1] only studied one-particle self-diffusion, equivalent to the high-q limit of these studies. We use a novel combination of numerical simulations, based on a lattice Boltzmann model of the fluid [4,5], and experimental measurements, using DWS [6,7]. We show that collective diffusion also exhibits an unexpected scaling, remarkably similar to self-diffusion.

To characterize the time evolution of the hydrodynamic interactions over different spatial scales, we define the wave-vector-dependent analog of the mean-square displacement,

$$H(q,t) = \frac{1}{2D_0 t}\left\langle \frac{1}{N}\sum_{i,j=1}^{N} \hat{\mathbf{q}}\cdot\boldsymbol{\Delta}_i(t)\hat{\mathbf{q}}\cdot\boldsymbol{\Delta}_j(t)e^{i\mathbf{q}\cdot\mathbf{R}_{ij}}\right\rangle, \quad (1)$$

where $\boldsymbol{\Delta}_i(t) = \mathbf{R}_i(t) - \mathbf{R}_i(0)$, and $D_0 = k_B T/6\pi\eta a$ is the self-diffusion coefficient of an isolated sphere. For large values of q, terms with $i \neq j$ average to zero; in this limit the time-dependent hydrodynamic interaction function $H(q,t)$ reduces to the one-particle (or self-) interaction function $H_S(t)$, which is independent of q. Thus, it is useful to decompose $H(q,t)$ into the sum of $H_S(t)$ and an interaction contribution $H_I(q,t)$,

$$H(q,t) = H_S(t) + H_I(q,t). \quad (2)$$

With a suitable choice of relaxation time τ_S, the self-correlation function $H_S(t)$, normalized by its asymptotic values H_S, can be scaled onto the dilute system curve [1,3]. This relaxation time is dependent on volume fraction; in the low density limit it is equal to the single-sphere relaxation time $\tau_0 = a^2/\nu$. The interaction contribution $H_I(q,t)$ directly measures the effects of interparticle hydrodynamic interactions; it shows how the trajectory of one particle is affected by the motion of its neighbors. It can be most conveniently determined by

computer simulations in which both $H(q,t)$ and $H_S(t)$ are measured; $H_I(q,t)$ can then be determined from Eq. (2).

The numerical simulations are based on a combination of molecular dynamics, which is used to track the motion of the solid particles, and a fluctuating lattice Boltzmann model of the fluid [4]. These models are remarkably effective at reproducing the dissipative and the fluctuating hydrodynamic forces that occur in the dynamics of colloidal suspensions [5]. As a further check, we have compared the long time asymptote $H(q) = H(q, t \rightarrow \infty)$ with theory [8] and experiment [9]. The simulation data for $H(q)$ are in agreement with theoretical calculations [8] and experiment [9]. Although a detailed comparison with experiment is hindered by uncertainties in both the simulation and the experimental data, the general agreement is quite good; the peaks and troughs in $D_0/D(q)$ appear at the same values of qa and have similar magnitudes.

In Fig. 1, we show a small sample of our simulation results, for two characteristic wave vectors; $qa \approx 1.8$, a relatively long wavelength, and $qa \approx 3.6$, near the first peak of the structure factor. The q dependence of the correlation functions is similar at all volume fractions, but more pronounced at higher concentrations; we show results at a volume fraction $\phi = 45\%$ to indicate the maximum variation with q. The scaled self-diffusion contribution $[H_S(t/\tau_S)/H_S]$ is distinguishable from the theoretical curve for one sphere, shown in Fig. 1 by the solid line. By contrast, under these same scaling conditions, $H_I(q,t)$ exhibits dramatically different behavior that is strongly dependent on q.

For small q ($qa < 2$) the interaction contributions are negative. At first sight this might be a little surprising; because of hydrodynamic interactions, the motion of one
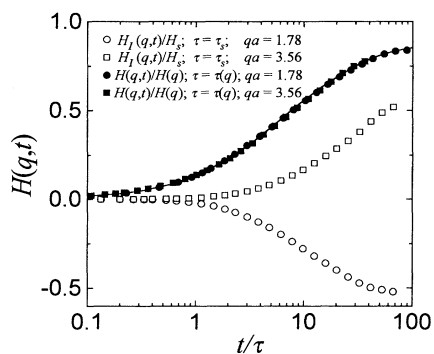
sphere tends to cause its neighboring spheres to move in the same direction. However, for sufficiently large volumes (i.e., for sufficiently small q), the average flow across any plane in the system must vanish. Thus, the motion of a particle induces a backflow of displaced fluid, which in turn sweeps the other particles along with it; this motion of particles and fluid opposes the motion of the primary sphere. Therefore, on sufficiently large length scales, there is an overall anticorrelation of particle velocities. By contrast, the wave vectors $qa \approx \pi$ probe primarily the first shell of neighbors; for such closely spaced particles the direct hydrodynamic interactions dominate the much weaker backflow effect, so that these contributions are positive. Finally, for very large q the interaction contribution vanishes.

The most remarkable result shown in Fig. 1 is that, although the interaction contributions (open symbols) do not scale to the single-sphere curve, the sum of the self-contribution and the interaction contribution at a particular wave vector (solid symbols) does scale to the single-sphere curve, but with a different normalization—$H(q)$ rather than H_S—and a different relaxation time $\tau(q)$. This is a general result, independent of q and independent of ϕ. This scaling implies that the hydrodynamic interactions are determined by a single time scale at each value of q, suggesting that the suspension is behaving as an effective medium at all length scales, and at all time scales. Although we do not claim that this scaling is necessarily exact over the whole time range, nevertheless, within the accuracy of the simulations we cannot detect any significant deviations from scaling.

The relaxation times required to scale the simulation data to the single-sphere master curve are shown in Fig. 2. The relaxation time scale is quite short at low q; it peaks around $qa = \pi$, and then, at large q, reaches the asymptotic value expected for the self-diffusion coefficient. The q dependence of the relaxation times is similar to the long-time asymptote $H(q, \phi)$, although there are noticeable deviations at small values of q ($qa < 1$); overall, this is reasonably consistent with a single relaxation time for $H(q,t)$.

We do not, as yet, have a complete explanation for these observations. At asymptotically long times the velocity correlation functions $\langle U_i(t)U_j(0) \rangle$ are known to decay with an algebraic $t^{-3/2}$ dependence, regardless of the separation between the spheres [10]. Thus any spatially weighted average of these correlation functions will also decay as $t^{-3/2}$ with some effective relaxation time [11]. However, the most interesting observation is that the correlation functions apparently see the same single-time-scale relaxation mechanism, regardless of spatial scale and concentration, modulated only be a wave vector and ϕ dependent effective viscosity; the origin of this is not understood.

To ascertain the validity of this remarkable scaling behavior, we compare our numerical results to experimental
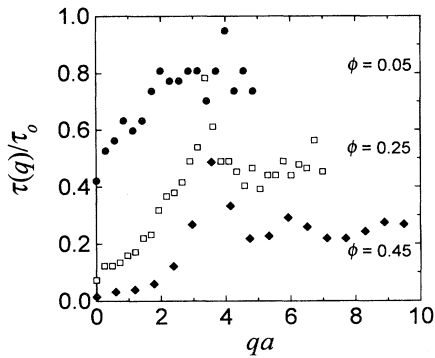
FIG. 1. Wavelength-dependent mean-square displacements at a volume fraction $\phi = 0.45$. Simulation data for $H(q,t)$ from a 128 sphere system (filled symbols), normalized by the long-time asymptote $2D_0tH(q)$, have been scaled to the single-sphere curve by adjusting the relaxation time $\tau(q)$. The wave vectors are $qa = 1.78$ and $qa = 3.56$. The open symbols indicate the interaction contributions $H_I(q,t)$ at the two wave vectors, scaled in the same way as the single-particle correlation function $H_S(t)$.

319

FIG. 2. Wavelength-dependent relaxation times $\tau(q)$, determined from plots similar to Fig. 1, are shown for a range of volume fractions. In a single-relaxation-time approximation $\tau(q) = H(q)$. The data at $\phi = 0.25$ are for a 1024-sphere system; the other results are for $N = 128$.

FIG. 3. Measurements of $[H(t)]$ for several volume fractions with 0.099 μm radius particles. The dashed line is the theoretical prediction for a single sphere; data for the lowest volume fraction are in good agreement with this. The upper curve illustrates that the data for all ϕ collapse onto a single master curve, whose functional form is determined by the single sphere theory. The amplitudes of the data are normalized by the long-time value $[H]$, and the relaxation times are scaled by a new, volume-fraction and particle-size dependent scaling time $[\tau]$.

results obtained using DWS [6,7]. DWS probes the very short time dynamics of colloidal suspensions, allowing the time evolution of hydrodynamic interactions to be measured. Measurements with DWS enable us to determine an average over many wave vectors [12,13]:

$$[H(t)] = \frac{\int_0^{q_{max}} q^3 F(q,a) H(q,t)\, dq}{\int_0^{q_{max}} q^3 F(q,a)\, dq}, \qquad (3)$$

where $F(q,a)$ is the form factor for spheres of radius a. Thus DWS measures an average over all values of q between 0 and $q_{max} = 2k_0$, where k_0 is the incident wave vector. Since this average is weighted by q^3, the dominant contributions to the DWS average arise from the largest values of the wave vector. Thus, if the radius of the particle is significantly greater than the wavelength of the laser light, DWS measurements probe very large values of qa, and hence reflect the self-diffusion of the particles. By contrast, if smaller particles are used, DWS measurements also contain a significant contribution from collective diffusion, allowing its behavior to be measured also.

The DWS measurements are made in the transmission geometry, enabling particle motion at very short time scales to be resolved [1]. The samples were polystyrene latex spheres with a screening length sufficiently short to ensure that the interactions are essentially those of hard spheres. The smallest particles had a radius of 0.099 μm, corresponding to $2k_0a = 3.2$, which is sufficiently small to ensure that the DWS measurements probe collective diffusion effects. We plot the measured $[H(t)]$, for several different volume fractions, in Fig. 3. The dashed line is the value calculated for the limit of low volume fractions, where there are no contributions from hydrodynamic interactions with the neighboring particles. The data at the lowest volume fraction ($\phi = 0.5\%$) agree well with the $\phi = 0$ theory, but as ϕ increases, the data fall further and further below this curve. Nevertheless, all this data can be scaled onto the single-sphere master curve, as
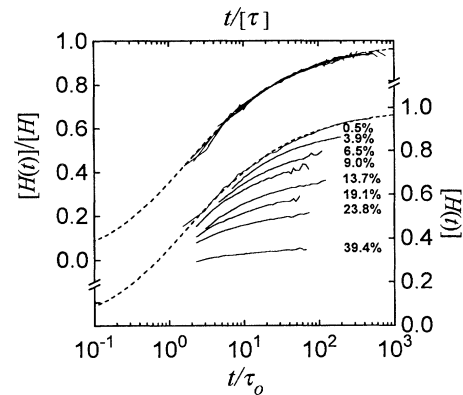
shown at the top of Fig. 3, by allowing both the time scale and the amplitude to vary. As in the simulations, very good scaling is observed, both for the small spheres shown in Fig. 3 and for larger size spheres as well.

The scaling of the data is strikingly similar to our earlier observations for large particles. However, the effects of the collective hydrodynamic interactions are very evident in the behavior of the time scale, shown in Fig. 4. At a given volume fraction ϕ, the experimentally measured ratio $[\tau]/\tau_0$ decreases rapidly with decreasing particle size. At first sight, the monotonic decrease of the measured $[\tau]$ seems inconsistent with the variation in $\tau(q)$ shown in Fig. 2. To investigate the origin of this apparent discrepancy, we used the q-dependent simulation results to calculate the average value, $[H(t)]$. We used the expected DWS weighting factors which were determined from Mie theory for each size sphere, averaged over all scattering vectors, and weighted by q^3 [13]. The behavior of the DWS-weighted simulation data is then consistent with experimental observations; the results for different particle sizes and different concentrations can again be scaled to the single-particle curve, with a relaxation time that decreases monotonically with decreasing particle radius, as well as with concentration. Thus the more subtle variations with q observed in the simulations are washed out by the averaging over wave vectors inherent in the DWS experiment. However, the experimentally measured relaxation times are much shorter (by at least a factor of 2 for small particles) than would be expected, either from the simulation data or from experimental measurements of the wave-vector-dependent diffusion coefficient (see Ref. [9]). Moreover, for the smallest
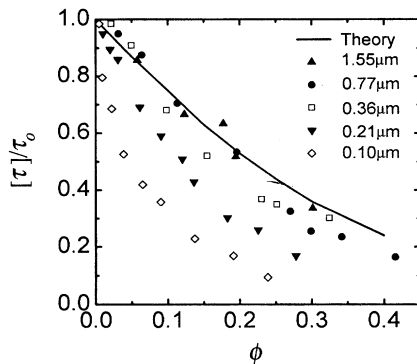
FIG. 4.   Volume-fraction dependence of the scaling times for different size spheres. The scaling times $[\tau]$ are normalized by their values at $\phi = 0$, corresponding to the hydrodynamic time scale $(\tau_0 = a^2/\nu)$ for each set of spheres. The solid line indicates the viscous scaling time $[\tau] = \rho a^2/\eta$, which describes the data for the largest spheres.

(0.099 μm) particles, the measured relaxation time is even shorter than the $q = 0$ relaxation time, $H(0)\tau_0$, which is the shortest time one would have expected to observe. Although there are many sources of uncertainty in both the simulations and the experiments, which we will discuss in detail in a longer paper, we believe the discrepancy has a physical origin.

When a sphere undergoes a fluctuation in its velocity, an impulse of momentum is transferred to the fluid. Part of this momentum impulse diffuses by viscous flow and gives rise to correlations which require some time to take effect (of the order of a^2/ν; see Fig. 1). However, additional momentum is carried by sound waves, which are another source of correlation in the velocities of *different* particles. These correlations arise essentially instantaneously, on time scales of the order of a/c, where c is the speed of sound in the fluid. Thus the velocities of different spheres can be correlated by sound propagation even at very short times, $t \ll a^2/\nu$. The total momentum carried off by sound waves is independent of particle mass; it depends only on the mass of the equivalent volume of fluid. Thus for particles with mass densities much larger than the surrounding fluid this effect is small, and almost all the momentum transfer is by viscous flow. However, for neutrally buoyant particles, the momentum in the sound waves is a significant fraction of the total (1/3). The DWS experiments are carried out with neutrally buoyant spheres; however, for computational reasons, the simulations were carried out using particles with a much larger mass density than the surrounding fluid, typically 10:1 and occasionally

5:1. Here we see a possible explanation for the discrepancy in the simulated relaxation times and the experimental measurements. In the experiments there are instantaneous correlations in particle velocities which are essentially absent for the more massive spheres used in the simulations. If the sound waves do indeed play a significant role in the propagation of hydrodynamic interactions, as is suggested by these result, their contribution would have to be included in future theories of the time evolution of hydrodynamic interactions. In particular, this may account for the apparent range of the scaling of the self-diffusion coefficient, which continues to time scales that are considerably shorter than τ_0.

In this work we have discovered that the scaling relations first observed for the self-diffusion coefficient apply to collective diffusion as well. These results suggest that monodisperse suspensions behave hydrodynamically as continuous media, for a substantial range of space and time scales, with only a varying effective viscosity. By a detailed comparison of simulation and experimental data we have discovered that sound wave propagation may play a vital role in the development of hydrodynamic interactions.

[1] J. X. Zhu *et al.*, Phys. Rev. Lett. **68**, 2559 (1992).
[2] M. H. Kao, A. G. Yodh, and D. J. Pine, Phys. Rev. Lett. **70**, 242 (1993).
[3] A. J. C. Ladd, Phys. Rev. Lett. **70**, 1339 (1993).
[4] A. J. C. Ladd, J. Fluid Mech. **271**, 285 (1994).
[5] A. J. C. Ladd, J. Fluid Mech. **271**, 311 (1994).
[6] G. Maret and P. E. Wolf, Z. Phys. B **65**, 409 (1987).
[7] D. J. Pine, D. A. Weitz, P. M. Chaikin, and E. Herbolzheimer, Phys. Rev. Lett. **60**, 1134 (1988).
[8] C. W. J. Beenakker and P. Mazur, Physica (Amsterdam) **126A**, 349 (1984).
[9] W. van Megen, R. H. Ottewill, S. M. Owens, and P. N. Pusey, J. Chem. Phys. **82**, 508 (1985).
[10] W. V. Saarloos and P. Mazur, Physica (Amsterdam) **120A**, 77 (1983).
[11] S. T. Milner and A. J. Liu, Phys. Rev. E **48**, 449 (1993).
[12] J.-Z. Xue, X.-L. Wu, D. J. Pine, and P. M. Chaikin, Phys. Rev. A **45**, 989 (1992).
[13] D. A. Weitz *et al.*, Phys. Scr. **T49**, 610 (1993).