

Scaling of the Time-Dependent Diffusion Coefficient by Molecular Dynamics Simulation

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The scaling behavior of the time-dependent diffusion coefficient $D(t)$ in a suspension is studied by means of a molecular dynamics simulation. We obtain a visual collapse of the curves by suitable scaling of time axis and vertical axis for $D(t)$ at different concentrations. However, the derivatives of $D(t)$ do not show such a scaling behavior. By analyzing the kinetic regime probed in this simulation we conclude that the absence of scaling is due to the fact that the dynamics is not completely dominated by hydrodynamics processes. This provides further evidence on the purely hydrodynamic origin of the scaling behavior.

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The time-dependent self-diffusion coefficient $D(t)$ is a simple quantity that describes the motion of a Brownian particle in a suspension. It is defined in either of two equivalent ways:

$$D(t) \equiv \frac{1}{6} \frac{d}{dt} \langle \Delta \mathbf{r}^2(t) \rangle = \int_0^t c(\tau) d\tau, \quad (1)$$

where $\langle \Delta \mathbf{r}^2(t) \rangle$ is the mean square displacement and $c(\tau) \equiv \frac{1}{3} \langle \mathbf{v} \cdot \mathbf{v}(\tau) \rangle$ is the velocity autocorrelation function (VAF). A different, but closely related definition of the time-dependent diffusion coefficient is given by

$$\tilde{D}(t) \equiv \frac{\langle \Delta \mathbf{r}^2(t) \rangle}{6t} = \frac{1}{t} \int_0^t D(t') dt'. \quad (2)$$

Very recently, the new technique of diffusing wave spectroscopy (DWS) [1] has allowed us to explore experimentally the very short time behavior of the time-dependent self-diffusion coefficient $\tilde{D}(t)$ [1,2]. In particular, a property of scaling of $\tilde{D}(t)$ at different concentrations has been reported [2], and it has also been confirmed by a lattice-Boltzmann simulation of a colloidal suspension [3]. However, it seems that this scaling is not obtained from recent theoretical studies of the transient hydrodynamics in colloidal suspensions at short times [4]. In this Letter we further investigate the scaling of the time-dependent self-diffusion coefficient with the aid of a molecular dynamics simulation. We regard as crucial for the validity of the scaling of $\tilde{D}(t)$ or, equivalently, $D(t)$ that the first derivative $c(t)$ and the second derivative [denoted as $\zeta(t)$] also present scaling. We find a visual scaling of $D(t)$ for different concentrations which is not a proper scaling as the first two derivatives do not exhibit such scaling. We offer an explanation for the discrepancy of our results with the experimental and simulation results.

Diffusing wave spectroscopy is specially suited for resolving extremely short time-space scales allowing for a study of the temporal dependence of the diffus-

ion coefficient. Using DWS, $\tilde{D}(t)$ has been measured for suspensions of monodisperse polystyrene latex spheres in water at different volume fractions [2]. The asymptotic value agrees with $D_s(\phi) = D_s^0(1 - 1.83\phi)$ and in addition, it is found that all the curves measured can be collapsed onto a master curve by suitable scaling of $\tilde{D}(t)$ and the time axis. This suggests that, for the volume fractions studied, the time-dependent diffusion coefficient behaves as $\tilde{D}(t) = D_s(\phi)d(t/\tau(\phi))$, where $d(x)$ is an adimensional scaling function with $d(x) \sim 1$ for large x and $D_s(\phi)$ and $\tau(\phi)$ are the scaling parameters. Therefore, a similar scaling should be observed for $D(t)$ [5].

The behavior of the self-diffusion coefficient in suspensions has been extensively studied numerically with different techniques such as molecular dynamics (MD) [6,7], Brownian dynamics [8], and lattice-Boltzmann simulations [3]. MD is a simple technique very suitable for studying very short time-space scales. The asymptotic self-diffusion coefficient of isotopic mixtures is studied in Ref. [7] with molecular dynamics. However, to our knowledge, there is no study of the effect of the concentration on the time-dependent diffusion coefficient with this technique. Brownian dynamics simulations [8] are based on Smoluchowski's equation, which means that the time scales described are larger than the correlation time of the velocity autocorrelation function. Therefore, this technique is not appropriate for this problem. The scaling of the self-diffusion coefficient has been studied with a novel numerical simulation via a fluctuating lattice-Boltzmann equation [3]. This technique considers the evolution of the solvent as a lattice gas with some stochastic noise added. The noise is designed in such a way that it simulates the effects of the hydrodynamic random stress tensor of the Landau-Lifshitz theory [9]. Finally, the Brownian particles evolve with Newtonian dynamics with stick boundary conditions. The results obtained from the simulation confirm the scaling behavior obtained experimentally, and extend the region of scaling to very short times

still not accessible experimentally [3].

The usual interpretation [2,3] is that the scaling in colloidal suspensions has a hydrodynamic origin. However, a puzzling question is why the scaling behavior extends to times shorter than the time needed for the hydrodynamic interactions to be established [2,3]. Ladd suggests a mechanism by which the viscosity of the suspension reaches almost instantaneously the value of an effective viscosity [3]. Therefore, the Brownian particles move freely in an effective medium from very short times.

The purpose of this Letter is to see whether in a binary mixture there also exists a scaling behavior for the time-dependent self-diffusion coefficient. The essential difference between colloidal suspensions and binary mixtures is the size of the Brownian particles involved, the colloidal particles being much larger in size than the solvent particles, whereas in a binary mixture the diffusing particles are of comparable size to the solvent particles. As a consequence, in a binary mixture there is a small scale separation between sound traversal and diffusion of vorticity. If ν is the kinematic viscosity of the solvent and σ is the radius of the solute particles, the time scale of the diffusion of vorticity is $\tau_\nu^0 = \sigma^2/\nu$ and $c\sigma/\nu \sim 1$ for a binary mixture (where c is the sound speed). This ratio may be orders of magnitude larger for a colloidal suspension. For this reason, the interaction of a colloidal particle with the solvent is dominated by hydrodynamics. Such hydrodynamic description may not be completely adequate in the case of diffusion of mixtures although hydrodynamic considerations enter into the analysis of the dynamics of liquids at a molecular scale [10].

We have performed a MD simulation in a periodic box of $N = 216$ particles interacting through a soft repulsive CWA (Coulomb wave function approximation) potential [11]. The CWA potential is a Lennard-Jones potential truncated at the minimum (which occurs at $r = 2^{1/6}\sigma$) and shifted vertically by an amount ϵ in such a way that it is a purely repulsive continuous potential. The Brownian particles are 5 times heavier than the solvent particles but have the same size. We have considered a number $N_B = 1, 10, 50, 100$ among the 216 particles as being Brownian. We have used the standard velocity Verlet algorithm with neighbor list [8]. The units of length, time, and energy are chosen to be the usual Lennard-Jones parameters σ , $(m\sigma^2/\epsilon)^{1/2}$, and ϵ , respectively. The time step is set to

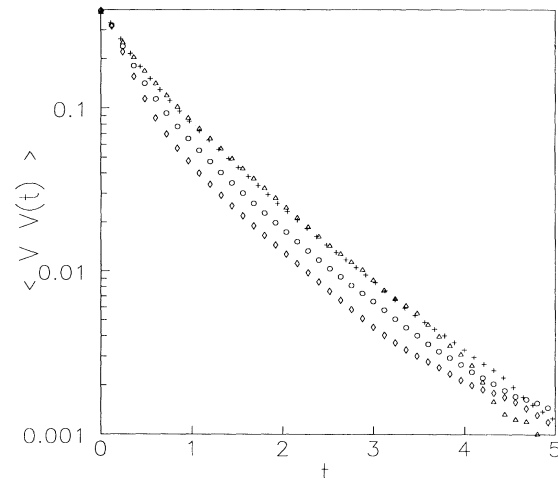


FIG. 1. Logarithm of the velocity autocorrelation function $\langle VV(t) \rangle$ for various numbers N_B of heavy particles in the box: $N_B = 1$ (Δ), $N_B = 10$ (+), $N_B = 50$ (\circ), $N_B = 100$ (\diamond).

0.004 in reduced units. The total number density ρ is fixed to 0.6 and the temperature to 2.00 ± 0.05 . Further details of the simulation will be given elsewhere. For $N_B = 1, 10, 50, 100$ we have 12 trajectories of 10^6 steps, 19 trajectories of 5×10^5 steps, 20 trajectories of 10^5 steps, and 90 trajectories of 7.5×10^4 steps, respectively. Standard statistical error analyses have been performed with these trajectories.

In Fig. 1, the velocity autocorrelation function $c(t)$ is plotted at different concentrations in a logarithmic plot. The initial behavior of the VAF is ballistic [at $t = 0$ the derivative of $c(t)$ is zero] and after a crossover region the decay becomes exponential. The result of an exponential fit $A \exp\{-\lambda t\}$ in this region is shown in Table I. There is a slight dependence of the exponential constant λ on the concentration within the error bars. After this exponential region (which occurs for times $1 \leq t \leq 2.5$) the decay is slower, presumably algebraic, although our simulations are too short to have good statistics for this to be detected unambiguously. In Fig. 2 we show $D(t)$ computed from the second identity in (1) for different concentrations. The plateau value $D_\phi(t_p)$ of the time-dependent diffusion coefficient decreases as the concentration increases (see Table I). A preliminary study shows that the asymptotic value of the self-diffusion coefficient

TABLE I. For various numbers of Brownian particles N_B , the exponential part of the VAF is fitted to $A \exp\{-\lambda t\}$. The plateau value $D_\phi(t_p)$ of the time-dependent diffusion coefficient is computed at time t_p . t_I is the typical time needed for a Brownian particle to travel half the typical separation $L_B/2$ between them. Scaling time τ for $D(t)$.

N_B	A	λ	t_p	$D_\phi(t_p)$	$L_B/2$	t_I	τ
1	0.27 ± 0.02	1.18 ± 0.03	5	0.2613 ± 0.013	7.11		0.678
10	0.26 ± 0.01	1.20 ± 0.03	10	0.2574 ± 0.014	1.25	1.68	0.670
50	0.20 ± 0.04	1.21 ± 0.01	10	0.2230 ± 0.011	0.55	0.60	0.578
100	0.15 ± 0.03	1.24 ± 0.01	10	0.1940 ± 0.006	0.35	0.36	0.485

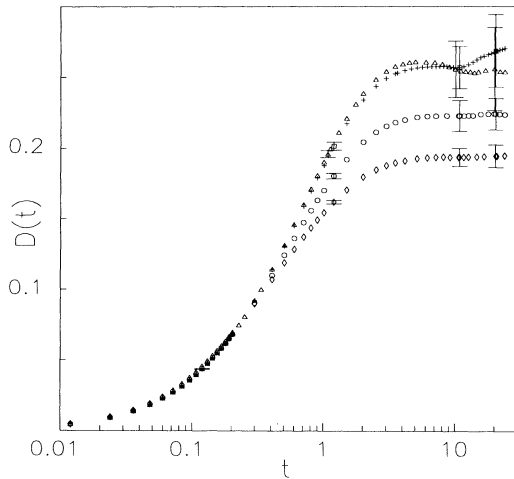


FIG. 2. Time-dependent self-diffusion coefficient $D(t)$ for various numbers N_B of heavy particles in the box: $N_B = 1$ (Δ), $N_B = 10$ (+), $N_B = 50$ (\circ), $N_B = 100$ (\diamond).

decreases with increasing mass ratio. In Fig. 3 we show the derivative $\zeta(t)$ of the VAF. This function vanishes at the origin due to the fact that the derivative of $c(t)$ is zero at $t = 0$. It presents a sharp maximum with variable amplitude and location depending on the concentration. The ballistic region of the VAF can be defined as the region of times before the maximum of $\zeta(t)$ is reached.

We have tried to scale $D(t)$ for different concentrations in Fig. 4. The vertical axis is scaled to the plateau value of $D_\phi(t_p)$ for each concentration. The time scaling in Fig. 4 is made in such a way that the times at which $D(t) = 0.6D(t_p)$ coincide for different concentrations. These scaling times are shown in Table I. This scaling gives the best visual superposition of the curves. We

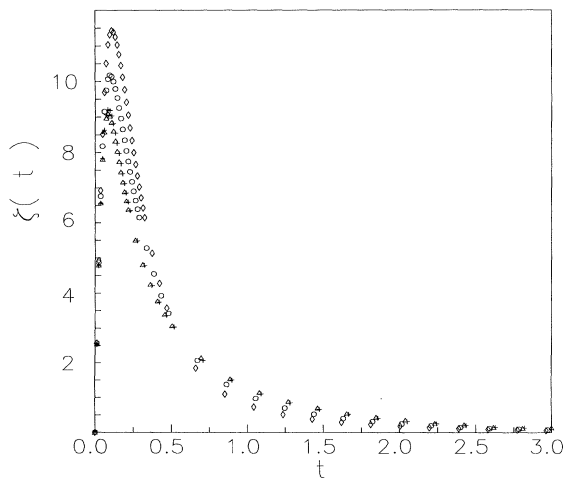


FIG. 3. Time derivative $\zeta(t)$ of the velocity autocorrelation function for various numbers of heavy particles: $N_B = 1$ (Δ), $N_B = 10$ (+), $N_B = 50$ (\circ), $N_B = 100$ (\diamond).

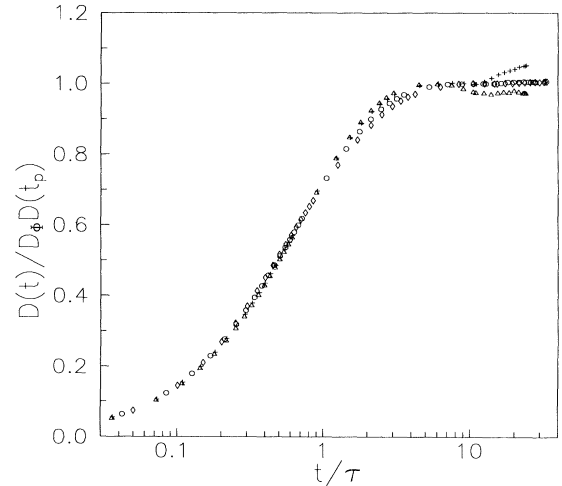


FIG. 4. Scaling of the time-dependent self-diffusion coefficient at several concentrations of heavy particles shown in Fig. 1. $D(t)$ is scaled by its asymptotic value $D_\phi(t_p)$ from Table I. The time is scaled so that all curves reach 60% of the asymptotic value at the same time. The scaling time τ is shown in Table I.

also scale $\zeta(t)$ for different concentrations in such a way that the maxima of all curves coincide in location and amplitude with the maximum corresponding to $N_B = 1$, as shown in Fig. 5. We observe that $\zeta(t)$ only scales for very short times, in the ballistic region. The conclusion is that, although an apparently good visual scaling is observed for the diffusion coefficient, it is not a proper scaling because the time derivatives of $D(t)$ do not scale. This is apparently observed in the velocity autocorrela-

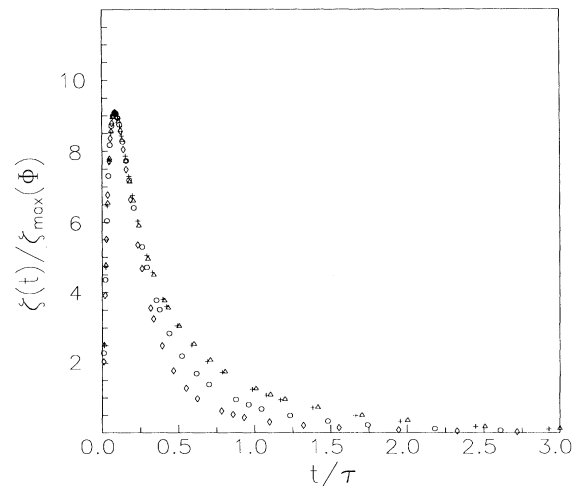


FIG. 5. Scaling failure of the time derivative of the velocity autocorrelation function. $\zeta(t)$ is scaled by its maximum value ζ_{\max} and time is scaled so the maximum values for all concentrations coincide in time. $N_B = 1$ (Δ), $N_B = 10$ (+), $N_B = 50$ (\circ), $N_B = 100$ (\diamond).

tion function in Fig. 1. During the exponential regime, the exponential parameter λ is almost independent of the concentration, thus precluding any scaling behavior. [If one tries to scale the time axis according to the scaling used for $D(t)$, the VAFS do not collapse onto the same curve.]

In order to investigate the time-space scales involved in this simulation we have computed the typical time t_I between collisions of Brownian particles. This is the time at which the square root of the mean square displacement equals half the typical distance L_B between heavy particles. This interparticle distance is computed according to $L_B = (N/N_B \rho)^{1/3} - 0.8\sigma$. The value 0.8σ is a rough estimation of the effective radius of the particles. The values of t_I and $L_B/2$ at different concentrations are presented in Table I. It is clear that during the times in which the velocity autocorrelation is still appreciably different from zero ($t \sim 2$) for all the concentrations the diffusing particles have traveled a distance larger than $L_B/2$. This means that in the transient regime of $D(t)$ there exist direct interactions between the heavy particles. In the language of colloidal suspensions we would be measuring the long-time self-diffusion coefficient.

In summary, in this Letter we have calculated the time-dependent self-diffusion coefficient in a binary mixture as a function of the concentration. The behavior of the system is not dominated by hydrodynamics as can be seen from the following facts: the decay of the velocity autocorrelation during the transient regime in which the time-dependent diffusion reaches its plateau value is mainly exponential. Second, in this transient region there are direct interactions between the heavy particles and, finally, there is a dependence of the plateau value of the self-diffusion coefficients on the mass of the heavy particles. In contrast, the experiments [2] and the lattice-Boltzmann simulation [3] are fully dominated by hydrodynamics because the transient regime is mainly power law, the asymptotic value of the self-diffusion coefficient is well represented by the hydrodynamic formula $D = D_0(1 - 1.83\phi)$, and there are no direct interactions between the colloidal particles in the transient regime.

Regarding scaling, our results show that, in spite of the visual collapsing of the self-diffusion curves, there is no actual scaling because the time derivatives of the time-dependent self-diffusion coefficient do not show such scaling. This is a very useful test to discriminate the scaling property. We suggest that by looking at higher derivatives (particularly in computer simulations as in [3] where the statistical errors at short times are very small), it must be possible to discriminate among the different scaling schemes proposed in [2]. One should note that the second derivative contains a rich structure at

short times which allows us to test scaling at these short times. We expect that for the time scales where hydrodynamic interactions begin to operate (this is signaled by the algebraic decay in the velocity autocorrelation), even in the binary mixture system a scaling should be obtained. The algebraic regime should appear at shorter times for a suspension of heavy particles with larger sizes, and a numerical simulation is being conducted in order to precisely discriminate the time scales where scaling is satisfied. Unfortunately, the algebraic time scales are very difficult to probe with actual computer resources. The fact that we do not observe scaling of the time-dependent self-diffusion coefficient gives strong support to the purely hydrodynamic origin of the scaling in colloidal suspensions [2,3], as we show that the scaling does not extend to very short times. Further work has to be done both theoretically and numerically. It is a challenging problem to obtain scaling from pure hydrodynamic theory extending the work in Ref. [4] by including many-body hydrodynamics interactions.

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- [1] D.J. Pine, D. Weitz, P. Chaikin, and E. Herbolzheimer, *Phys. Rev. Lett.* **60**, 1134 (1988); D. Weitz, D. Pine, P. Pusey, and R. Tough, *Phys. Rev. Lett.* **63**, 1747 (1989).
 - [2] J.X. Zhu, D.J. Durian, J. Müller, D.A. Weitz, and D.J. Pine, *Phys. Rev. Lett.* **68**, 2559 (1992); M. Kao, A. Yodh, and D. Pine, *Phys. Rev. Lett.* **70**, 242 (1993).
 - [3] A. Ladd, *Phys. Rev. Lett.* **70**, 1339 (1993).
 - [4] H. Clercx and P. Schram, *Physica (Amsterdam)* **174A**, 293 (1991); **174A**, 325 (1991).
 - [5] The scaling of $\dot{D}(t)$ implies the scaling of $D(t)$ because $D(t) = \dot{D}(t) + t\ddot{D}(t) = D_s(\phi)\{d(t/\tau(\phi)) + [t/\tau(\phi)]d'(t/\tau(\phi))\}$.
 - [6] P. Herman and B. Alder, *J. Chem. Phys.* **56**, 987 (1973); G. Jackson, J. Rowlinson, and F. van Swol, *J. Phys. Chem.* **91**, 4907 (1987); J. Erpenbeck, *Phys. Rev. A* **39**, 4718 (1989); H. Schaink and C. Hoeisel, *Phys. Rev. A* **45**, 8559 (1992).
 - [7] I. Ebbsjö, P. Shofield, K. Sköld, and I. Waller, *J. Phys. C* **7**, 3891 (1974).
 - [8] M. Allen and D. Tildesley, *Computer Simulation of Liquids* (Clarendon Press, Oxford, 1987).
 - [9] L. Landau and E. Lifshitz, *Fluid Mechanics* (Pergamon, New York, 1959).
 - [10] B. Alder and T. Wainwright, *Phys. Rev. A* **1**, 18 (1970).
 - [11] J. Hansen and I. McDonald, *Theory of Simple Liquids* (Academic Press, New York, 1986).