Hydrodynamic Interactions May Enhance the Self-Diffusion of Colloidal Particles

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(Received 27 March 1997)

We report experimental evidence for an enhancement, due to the hydrodynamic interactions (HI), of the self-diffusion function $D_s(t)$ of colloidal particles at intermediate and long times. Monolayers of paramagnetic polystyrene spheres confined to an air/water interface are studied using digital videomicroscopy. The interparticle potential tuned by an external magnetic field is accurately calibrated by comparing measured radial distribution functions with computer simulation results. This allows one to separate the effects of HI on $D_s(t)$ from those of the direct interactions. [S0031-9007(97)03503-5]

PACS numbers: 82.70.Dd, 05.40.+j, 47.15.Pn, 61.20.−p

During the last decades, the interest in the physical properties of colloids has grown tremendously because of their widespread technological applications and the availability of both calibrated model particles and new experimental techniques to study their static and dynamic properties [1,2]. Since the stability of colloidal suspensions arises from the combined action of Brownian motion, direct interactions (DI) between particles, and hydrodynamic interactions (HI) mediated by the solvent, a major challenge is to understand the nature of these forces and to describe their effects on the statics and dynamics of the suspension.

While Brownian motion of free particles is well understood, the dynamics of colloidal particles is much more complex when DI and HI become important. Many experiments and theories have focused on sterically stabilized suspensions (e.g., silica spheres) modeled as hard spheres and on charge stabilized suspensions (e.g., polystyrene spheres) modeled as suspensions of Yukawa particles. In hard spheres the diameter σ of the particles is the only interaction parameter; it is accurately determined by measuring the diffusion coefficient $k_BT/3\pi\eta\sigma$, in very diluted suspensions, η being the solvent viscosity. Then, the effects of HI on the self-diffusion function $D_s(t)$ can be isolated from those of DI; they are always found to *slow down* the self-diffusion of colloidal particles [3]. However, when the interaction potential is long range, different effects due to the coupling between the solvent velocity field and the interparticle interactions appear. Recent calculations have shown that the short-time [4] and long-time [5] self-diffusion coefficient of hard spheres may increase by putting charges on the particles. However, in charge stabilized suspensions the interaction potential remains a matter of debate [6] and the experimental determination of the interaction parameters is subject to large uncertainties. Therefore, in this kind of system it was impossible so far to separate the influence of HI and DI on $D_s(t)$.

Introducing a new colloidal model system, where the interaction parameters are determined with high accuracy and can be changed *in situ* in a simple and reversible manner, we were able to study the effects of HI on $D_s(t)$ directly and found first experimental evidence of how HI can help colloidal particles to diffuse faster. In addition, this effect is qualitatively accounted for theoretically.

Our system is composed of paramagnetic polystyrene spheres ($\sigma = 4.7$ μm) suspended on the water/air interface of a water drop pending from a glass plate [7,8]. The drop is confined by a hollow glass cylinder, which is glued onto the plate, of 8 mm inner diameter and 1 mm height. To provide a flat interface the curvature of the water/air interface is adjusted by computer controlling the drop's content of liquid using a micrometrical syringe [9]. A difference less than 1 μm in the height of the interface between the center and the border of the drop can be reached. The experiments have been performed in the center of the drop, and no appreciable changes ($<1\%$) on the particle concentration could be observed. In addition, it is easy to show that both the amplitude of capillary waves of the interface and thermal fluctuations of the vertical position of the particles are of the order of nanometers (the mass density of the particles is 1.7 g/cm^3). In this sense our samples are almost ideal two-dimensional (2D) systems.

The particles are superparamagnetic due to Fe_2O_3 doping [10]. Therefore an external magnetic field B perpendicular to the interface induces a magnetic dipole moment M on the spheres, which for the weak field intensities in our experiments is related to B by $M = \chi_{\text{eff}}B$. Here, χ_{eff} is the effective magnetic susceptibility of the particles. The interaction potential between two particles due to the induced moments is $u(r) = (\mu_0/4\pi)\, M^2/r^3$, r denoting the distance between their centers. Turning off the field, the particles are occasionally observed to collide. Therefore, at contact the screened electrostatic interactions are of order k_BT. The van der Waals forces are of the same order, because the thermal energy is able to separate particles in contact. Finally, since the particles are close to an interface, we have to consider surface tension forces. If the particles are not completely wetted, the contact angle between their surface and the interface introduces an additional force due to the Laplace pressure. However, by adding 0.5 mg/cm^3 of a surfactant, complete wetting is obtained. Finally a simple estimation reveals that the weak deformation of the interface due to the weight of the particles can also be neglected. Thus our system is entirely controlled by magnetic dipole interaction.

Our samples were studied using digital videomicroscopy. An optical microscope is placed above the sample and images are monitored by means of a CCD camera. From the filmed configurations, particle coordinates are extracted and both radial distribution functions $g(r)$ and mean square displacements $\langle[\Delta\mathbf{r}(t)]^2\rangle$ calculated. Typically about 10^3 particles were observed in a square box of $520 \times 440\ \mu\mathrm{m}^2$, and statistics were gathered for about 10^2 configurations. The time step between two successive pictures was chosen between 3 and 5 s, depending on the number density of particles. Given a value $D_0 \simeq 0.1\ \mu\mathrm{m}^2/\mathrm{s}$ of the self-diffusion coefficient, a time step corresponds to a mean displacement of the particles of $\approx 1\ \mu\mathrm{m}$, which approximately equals the lateral optical resolution. In the following, D_0 denotes the self-diffusion coefficient at high dilution. We found $D_0 = (1.08 \pm 0.02) k_B T / 3\pi\eta\sigma$, which is slightly higher than the value expected from the Stokes-Einstein equation. This difference, characterized by $\alpha = 1.08$, is due to the proximity of the particles to the interface since the diffusing particles have to push less solvent as compared to the three-dimensional (3D) case.

The particle motion can be described by the generalized Smoluchowski equation. Since our systems are 2D only regarding the motion of the colloidal particles (the solvent can move in all directions), it seems necessary to consider this equation in its 3D form. However, it is straightforward to show that its 2D version becomes correct, if the components of the 3D diffusion tensors are used as input for the elements of the 2D diffusion tensors. Furthermore, following Ermak and McCammon [11], the generalized Smoluchowski equation can be rewritten as the stochastic finite differences equation

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \beta \sum_{j=1}^{N} \mathbf{D}_{ij} \cdot \mathbf{f}_j(t)\Delta t + \nabla_j \cdot \mathbf{D}_{ij}\Delta t + \delta\mathbf{r}_i\,, \qquad (1)$$

provided the time step Δt is restricted to $\tau_B \ll \Delta t \ll \tau_I$, where τ_B and τ_I are, respectively, the momentum and structure relaxation times. Here, $\mathbf{r}_i(t)$ is the position vector of particle i at the time t, $\mathbf{D}_{ij}$ the diffusion tensors, $\mathbf{f}_j(t)$ the instantaneous force acting on particle j due to DI, $\delta\mathbf{r}_i$ the Brownian random displacement due to solvent-particle interactions, and $\beta = 1/k_B T$. The Cartesian components of $\delta\mathbf{r}_i$ are random variables with a $2N$-variate Gaussian distribution with zero means, and covariance matrix $\langle\delta\mathbf{r}_i\delta\mathbf{r}_j\rangle = 2\mathbf{D}_{ij}\Delta t$. In our simulations, we apply this algorithm neglecting HI, i.e., replacing $\mathbf{D}_{ij}$ by $D_0\delta_{ij}$. We allow 900 particles to move according to Eq. (1) in a square box with periodic boundary conditions, using $\Delta t = 10^{-4}\ (nD_0)^{-1}$, where n is the 2D number density of particles. After equilibrium is reached, statistics were gathered for typically 20 000 time steps.

At this point, it is useful to make the following comments. Equation (1) produces the same $g(r)$, independent of the input for $\mathbf{D}_{ij}$, since HI do not affect the static structure. Thus $n^{-1/2}$ is the natural structure scale of our systems. As a consequence, all systems with the same value of the scaled interaction amplitude $\Gamma = \beta(\mu_0/4\pi)\chi_{\mathrm{eff}}^2 B^2 n^{3/2}$ have the same $g(r)$, when plotted vs $rn^{1/2}$. Therefore, Eq. (1) will depend only implicitly upon n through $\mathbf{D}_{ij}$ and Γ, if $\tau_I = 1/nD_0$ is used as the natural time unit of the systems. Thus, if HI are neglected ($\mathbf{D}_{ij} = D_0\delta_{ij}$) all normalized self-diffusion functions $D_s(t)/D_0$, with $D_s(t) = \langle[\Delta\mathbf{r}(t)]^2\rangle/4t$, corresponding to the same value of Γ should be represented by one master curve, when plotted vs nD_0t. Any deviation from this scaling law in $D_s(t)/D_0$ is imputable to HI.

Figure 1 shows $g(r)$ vs $rn^{1/2}$ for two different systems with the same density n, but different values of B. The full circles are simulation results obtained by fitting the height of the first peak of the experimental $g(r)$'s (lines), using Γ as fitting parameter. Excellent agreement between simulation and experiment is observed, indicating that the magnetic dipole potential largely dominates the interaction and suggesting that the fitted values of Γ, 8.2 and 1.44, are correct. While the accuracy of Γ can be improved by exploiting more configurations in the averaging, the statistical errors in Fig. 1 are already smaller than the size of the circles. In the inset of Fig. 2 the fitted values of Γ are shown as a function of B for four different values of n. If the abscissa is rescaled plotting $B^2n^{3/2}$ (main body of Fig. 2), all curves collapse onto a master curve, proving the expected relation among Γ, n, and B to hold over the entire range of Γ, i.e., over 2 orders of

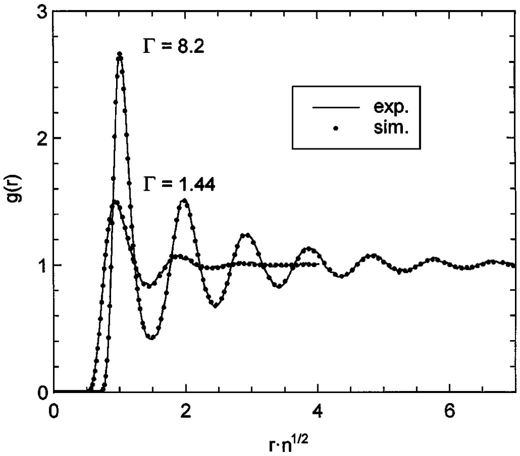

FIG. 1. Experimental pair correlation functions $g(r)$ of superparamagnetic colloidal particles in 2D and their simulation fits obtained by adjusting the scaled interparticle potential amplitude Γ (see text). For reasons of clarity the curves corresponding to $\Gamma = 1.44$ are represented only for $rn^{1/2} < 4$, n being the particle number density.

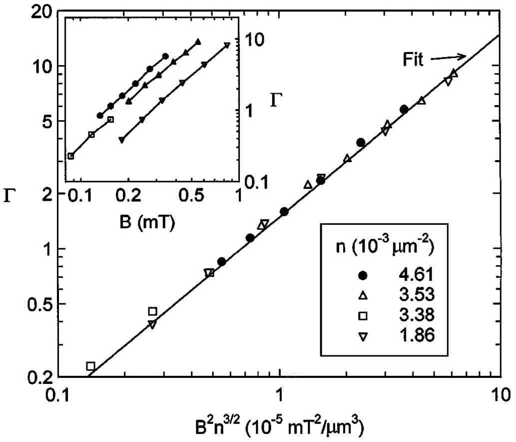

FIG. 2. In the inset the fitted values of Γ are represented as a function of the magnetic field B, for four different densities n. If the abscissa is rescaled plotting $B^2 n^{3/2}$, all curves collapse to one master curve, proving the expected scaling behavior $\Gamma \propto B^2 n^{3/2}$.

magnitude. A linear fit was used to determine the effective susceptibility $\chi_{\mathrm{eff}} = (7.62 \pm 0.2) \times 10^{-11}$ A m^2/T, which is in agreement with independent results from magnetophoresis experiments [9].

Figure 3 displays $D_s(t)/D_0$ vs nD_0t for three samples with different densities, but for the same value $\Gamma = 8.2$ (symbols), obtained experimentally by adjusting the magnetic field for given n. The corresponding simulation result (line) was obtained using the same value of Γ as in the experiments. First we note that the decay time τ of $D_s(t)$ is much smaller than τ_I, since the particles almost instantaneously feel each other due to the long range nature of DI. Therefore, the long- and short-time regimes have to be determined with respect to τ, and not to τ_I. It is in this sense that we speak of measurements of $D_s(t)$ at short ($\tau_B \ll t \ll \tau$) and long ($t \gg \tau$) times. Within experimental error (comparable to the size of the symbols in Fig. 3), the short-time, self-diffusion coefficient $D_s(t \to 0)$ of all studied systems has been observed to agree with D_0. However, a strong discrepancy between experiment and simulation is observed for intermediate and long times. As discussed earlier, this must be due to HI. All experimental curves lie above the simulations and, in addition $D_s(t > 0)/D_0$ *increases* with n. This observation is in contrast to earlier experiments on hard spheres systems, where HI are always found to *slow down* self-diffusion [3].

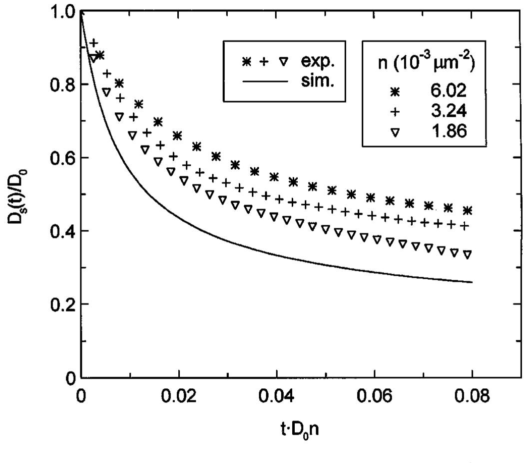

FIG. 3. Normalized self-diffusion function $D_s(t)/D_0$ in three samples with different densities, but at the same value of Γ. The corresponding computer simulation results are also shown.

In order to explain the above discrepancy, let us note that the curves for $D_s(t)/D_0$ in Fig. 3 never cross. Therefore, the smaller the value of the initial slope of $D_s(t)$, $D_s'(0) = [dD_s(t)/dt]_{t=0}$, the larger the value of $D_s(t > 0)$. Thus, although we do not have at the moment a theory for $D_s(t > 0)$, we can make qualitative predictions for $t > 0$ using theoretical schemes for $t = 0$. Specifically, from a moment expansion of the autocorrelation function at $t = 0$ [2], we have

$$\begin{aligned} D_s(0) &= -\frac{1}{q^2}\, m_s^{(1)}(q)\,, \\ D_s'(0) &= -\frac{1}{2q^2}\,\{m_s^{(2)}(q) - [m_s^{(1)}(q)]^2\}\,, \end{aligned} \tag{2}$$

where $\mathbf{q}$ is the scattering vector and

$$\begin{aligned} m_s^{(1)}(q) &= -\langle q^a q^b D_{11}^{ab} \rangle\,, \\ m_s^{(2)}(q) &= \langle q^a q^b q^c q^d D_{11}^{ab} D_{11}^{cd} + q^b q^d (\partial_j^c D_{i1}^{ab})(\partial_i^a D_{j1}^{cd}) \\ &\quad + \beta q^b q^d D_{i1}^{ab} (\partial_i^a \partial_j^c U) D_{j1}^{cd} \rangle\,, \end{aligned} \tag{3}$$

are the first and second moments. Here, the indices (i, j) are running over particles and $(a, \cdots, d)$ over Cartesian components. The sum convention for repeated indices is applied, and U is the total interaction energy $U = \frac{1}{2}\sum_{i,j=1\,(i\neq j)}^{N} u(|\mathbf{r}_i - \mathbf{r}_j|)$. In order to evaluate $D_s(0)$ and $D_s'(0)$, it is necessary to obtain an input for $\mathbf{D}_{ij}$. The effect of the interface on the velocity field of the solvent can be described by replacing the real system by an isolated smectic layer of dumbbells in 3D. These dumbbells, made of two spherical particles at contact, connected through their centers by an axis perpendicular to the layer, are confined to move in the layer plane. The underlying physical idea is that the water/air interface reflects the flow field of the solvent [12]. Therefore, we take for $\mathbf{D}_{ij}$ in our equations the corresponding expression for dumbbells obtained in an infinite 3D space, which can be written as

$$D_{ij}^{ab} = D_0 \delta_{ij}^{ab} + \delta_{ij} \sum_{k=1}^{N} (1 - \delta_{ik}) A_{ik}^{ab} + (1 - \delta_{ij}) B_{ij}^{ab}\,. \tag{4}$$

The tensors A_{ik}^{ab} and B_{ik}^{ab} are known as expansion in powers of (σ/r). For dilute systems B_{ik}^{ab} can be approximated by the Oseen tensor and the first term of A_{ik}^{ab} is of order $(\sigma/r)^4$ [4]. Thus, to leading order in (σ/d) we find

$$\frac{D_s(0)}{D_0} = 1 - \frac{15}{64}\frac{\pi}{\alpha}\left(\frac{\sigma}{d}\right)^4 \int_0^\infty dr\,\frac{g(r)}{r^3},$$

$$\frac{D_s'(0)}{nD_0^2} = -\frac{9\pi\Gamma}{2}\int_0^\infty dr\,\frac{g(r)}{r^4} + \frac{63}{8}\frac{\pi\Gamma}{\alpha}\frac{\sigma}{d}\int_0^\infty dr\,\frac{g(r)}{r^5}, \tag{5}$$

where r is scaled with $d = n^{-1/2}$. Strictly speaking, σ as appearing in the second term of $D_s(0)/D_0$ is an effective dumbbell diameter, but since we are only interested in the order of magnitude of this correction we use the diameter of our spheres. For highest particle concentrations ($d \simeq 3\sigma$) $D_s(0)/D_0$ is lowered by approximately 1%. This is well below the experimental error and, consistently, we found no dependence of $D_s(0)$ on the density. The first term in $D_s'(0)/nD_0^2$, which has its origin in the DI, predicts a drastic decrease of $D_s(t)$ as a function of t. The second one represents a correction—in the opposite direction—due to the coupling between HI and DI; i.e., it leads to an increase of $D_s(t)$, as compared to the case without HI. As the latter scales with σ/d, an enhancement of $D_s(t)$ is observed with increasing density. The bars in Fig. 4 represent the initial slopes $D_s'(0)/nD_0^2$ of several experimental $D_s(t)/D_0$ curves with $n = 1.86 \times 10^{-3}$ μm^{-2}, for different values of Γ. $D_s'(0)/nD_0^2$ is determined by a fit based on the simple exponential approximation [13] and compared to Eq. (5) with HI (circles) and without HI (squares). These results show that the Oseen approximation for HI describes qualitatively well the experimental curves.

To give an intuitive picture for the enhancement of $D_s(t)$, let us note that the Oseen tensor, which determines the HI correction to $D_s'(0)/nD_0^2$ in Eq. (5), corresponds to a tensor field which acts in the direction of motion of the particles. Thinking in terms of field lines, it is easy to see that the flows induced on the solvent by the tracer will push away the particles in front of it. On the other hand, the particles behind it will experience a drag and be pulled closer by. The first effect opens a "window" through which the tracer can diffuse, and the second one provides additional momentum on the tracer in the direction of its motion. Thus the Oseen term leads to an increase of the self-diffusion. The fundamental difference between our systems and the suspensions of hard spheres is the structure scale d. In contrast to our systems, where $d \gg \sigma$, d is comparable to σ in hard sphere suspensions. Thus, the term A_{ij}^{ab} ($\propto (\sigma/d)^4$), which determines the short time self-diffusion $D_s(0)$, is negligible in our case, while for hard spheres it significantly lowers $D_s(0)$. As a consequence, we observe an overall enhancement of the self-diffusion due to HI, in contrast to hard sphere systems.

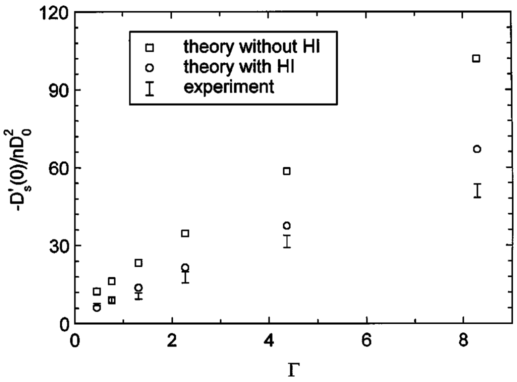

FIG. 4. Initial slope $D_s'(0)/nD_0^2$ of the normalized self-diffusion function of several experimental $D_s(t)/D_0$ curves with $n = 1.86 \times 10^{-3}$ μm^{-2}, for different values of Γ. They are compared to theoretical results with HI (circles) and without HI (squares).

In conclusion, introducing a novel 2D colloidal model system where the direct interparticle interaction is absolutely calibrated and controlled over several orders of magnitude, we were able to evaluate quantitatively the role of the hydrodynamic interactions on the self-diffusion function. This system also opens the possibility to probe experimentally the accuracy of integral equation theories of simple liquids.

We acknowledge useful discussions with G. Nägele and R. Klein, and one of us (JMMA) thanks CONACyT-Mexico for financial support.

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