Influence of hydrodynamic interactions on the dynamics of long-range interacting colloidal particles

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Abstract. – We study the influence of hydrodynamic interactions on the self-diffusion of super-paramagnetic colloidal particles suspended in water. The colloids interact via repulsive dipolar forces due to an applied magnetic field, and their motion is effectively confined to two dimensions. By comparing experimental data with the results from extensive computer simulations, where the water flow fields are treated at the Rotne-Prager level, we show that the diffusivity is enhanced at all times due to hydrodynamic interactions. The enhancement effect becomes stronger with increasing particle density, but is almost unaffected by the temperature.

Introduction. – The dynamics of colloidal particles in suspensions are largely affected by hydrodynamic interactions (HI) mediated by the solvent [1]. In the presence of short-range interactions between the colloidal particles it has been shown that the self-diffusion of the colloids is *slowed down* by the HI [2]. This has been substantiated also by detailed mode-coupling calculations [1]. On the contrary, in the presence of long-range interactions the situation is less clear. It was conjectured recently [3] that the self-diffusion in this case may become *enhanced* by HI. This conjecture was based i) on a comparison of Brownian dynamics simulations *without* HI with experimental results, and ii) on (partially uncontrolled) theoretical approximations of the diffusion-coefficient within a moment expansion around $t = 0$. It is thus not really clear, whether the differences between simulations and experiments *for long times* are really due to HI.

In this letter we study in detail the role of HI on the diffusion of long-range interacting colloidal particles in two dimensions. To this end, we compare quantitatively the results from experiments of colloids interacting via a repulsive $1/r^3$ potential with the results from extensive computer simulations with HI. Our simulations provide excellent agreement with the experimental results. By comparison with Brownian dynamics simulations without HI we find that the HI enhance the diffusion for all times at all relevant temperatures and densities. We also demonstrate how the confined two-dimensional dynamics of dipolar colloidal particles in the presence of a three-dimensional solvent flow can be faithfully simulated.

Experimental setup. – Our system is composed of spherical colloidal particles of radius $a = 2.35\,\mu$m confined by gravity to the water/air interface of a drop that is suspended from a hollow glass cylinder due to surface tension. The top of the cylinder of 8 mm inner diameter and 1 mm height is sealed by a microscope cover sheet, which is glued onto the cylinder. To provide a flat interface the curvature of the water/air interface is adjusted by computer controlling the content of liquid using a micrometrical syringe. In this way a difference less than $1\,\mu$m in the height of the interface between the center and the border of the drop can be obtained. The experiments have been performed in the center of the drop where no appreciable changes ($< 1\%$) in the particle concentration could be observed. Also both the amplitude of capillary waves of the interface and thermal fluctuations of the vertical position of the particles can be estimated to be of the order of nanometers (the mass density of the particles is 1.7 g/cm^3). Our samples thus are almost ideal two-dimensional (2D) systems.

The particles are super-paramagnetic due to Fe_2O_3-doping and a magnetic field B applied perpendicular to the interface induces magnetic dipole moments M that lead to a repulsive interparticle potential $v(r) = (\mu_0/4\pi)\,M^2/r^3$. For the weak field intensities used we find $M = \chi_{\mathrm{eff}}B$ with an effective magnetic susceptibility of the particles $\chi_{\mathrm{eff}} = (7.62 \pm 0.2) \times 10^{-11}\,\mathrm{Am^2/T}$. Therefore, we can define a scaled interaction strength $\Gamma = (\mu_0/4\pi)(\chi_{\mathrm{eff}}B)^2 n^{3/2}/k_{\mathrm{B}}T$ (n denotes the 2D volume fraction of the particles).

An optical microscope is placed above the sample and images are monitored by means of a CCD-camera and evaluated on a PC. 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. About 10^3 particles are observed in a square box of $520 \times 440\,\mu$m^2, and averages are performed over typically 100 independent configurations.

By extrapolating the diffusion coefficient $D(t) = \langle\Delta\mathbf{r}^2(t)\rangle/4t$ towards $t \to 0$ [4], we obtain the short-time self-diffusion coefficient D_0. In the range of 2D particle concentrations studied ($n < 6 \times 10^{-3}\mu$m^{-2}) we did not observe any dependence of D_0 upon n. We found $D_0 = (1.08 \pm 0.02)\,k_{\mathrm{B}}T/6\pi\eta a$, which is slightly higher than the value expected from the Stokes-Einstein equation. The difference of 8% may be attributed to the proximity of the particles to the interface: With respect to the hydrodynamic interactions, we can replace a system of spherical particles at a free interface (*i.e.* having slip boundary condition) by a layer of dumbbells in an infinite medium. These dumbbells diffuse in the plane of motion and take the solvent flow field caused by the water/air interface into account (method of images, see [5]). Since half of the friction coefficient of a dumbbell is less than that of the original sphere [6], one should expect the particles at the interface to have a higher D_0 than the Stokes-Einstein value.

Brownian dynamics simulations with HI. – The Brownian dynamics with HI can be described by the Smoluchowski equation for the probability $P(\mathbf{r}_1, \ldots, \mathbf{r}_N, t)$ to find the colloidal particles at positions $\mathbf{r}_1, \ldots, \mathbf{r}_N$ at time t [7],

$$\partial_t P = \partial_{i\mu} D_{i\mu,j\nu} \left(-\beta F_{j\nu} + \partial_{j\nu}\right) P\,. \tag{1}$$

Here $\partial_{i\mu} \equiv \partial/\partial x_{i\mu}$ (i denotes the particle index and μ the Cartesian component), $\beta = 1/k_{\mathrm{B}}T$, $F_{i\mu} = -\partial_{i\mu}\sum_j v(r_{ij})$ with $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, and we applied the summation convention with respect to repeated indices. $D_{i\mu,j\nu}$ is the hydrodynamic diffusion tensor appropriate for particles separated by large distances (far-field expansion up to the Rotne-Prager level [7]),

$$D_{i\mu,j\nu}^{(\mathrm{RP})} = \frac{3}{4}D_0\frac{a}{r_{ij}}\left[\left(1 + \frac{2}{3}\left(\frac{a}{r_{ij}}\right)^2\right)\delta_{\mu\nu} + \left(1 - 2\left(\frac{a}{r_{ij}}\right)^2\right)\frac{(x_{i\mu} - x_{j\mu})(x_{i\nu} - x_{j\nu})}{r_{ij}^2}\right]\,. \tag{2}$$

Equation (1) corresponds to the Langevin equation (in Ito-interpretation)

$$\dot{x}_{i\mu}(t) = \beta D_{i\mu,j\nu}F_{j\nu} + \partial_{j\nu}D_{i\mu,j\nu} + \sigma_{i\mu,j\nu}\eta_{j\nu}(t)\,, \tag{3}$$

where $\eta_{i\mu}(t)$ is a Gaussian-distributed noise with zero mean and correlator $\langle \eta_{i\mu}(t_1) \, \eta_{j\nu}(t_2) \rangle = 2\delta_{ij} \, \delta_{\mu\nu} \, \delta(t_1 - t_2)$; the matrix $\sigma_{i\mu,j\nu}$ results from a Cholesky decomposition of the diffusion tensor.

Equation (3) is discretized according to an Euler scheme and solved by using periodic boundary conditions. For calculating the direct dipolar forces $F_{i\mu}$, the simulation square is periodically continued in two dimensions. These calculations are speeded up by using interpolations of stored force values with respect to a dense grid of interparticle vectors (taking symmetry relations into account). For calculating the hydrodynamic forces associated with the solvent flow we periodically continue the system in the direction perpendicular to the plane of motion also. By employing this method of images, we ensure that the solvent flow through the drop surfaces is zero. The Ewald summation method [8] then is used to take into account the long-range nature ($\sim 1/r_{ij}$) of the Rotne-Prager tensor $D_{i\mu,j\nu}$. Our periodic continuation corresponds to a plane of motion located exactly in the middle of the upper and lower water drop surfaces. However, in the experiments the particles are close to the water/air interface. This discrepancy between the situations in the experiment and in the simulations is of minor importance for the far-distant images, but for the closest images should be corrected. As explained above, the particles together with their closest images on the other side of the water/air interface should be replaced by dumbbells [5] (for a recent detailed treatment of hydrodynamic boundary effects for both solid and free surfaces see also [9] and references therein). We approximate this situation by choosing spheres enclosing the dumbbells in the numerics, that means the effective particle diameter is twice as large as in the real system.

The natural time scale used in the system is given by $\tau_0 = 1/nD_0$, which is the time needed for a particle to move a typical interparticle distance $n^{-1/2}$ in the absence of any interactions. (Note that by considering quantities normalized with respect to D_0 the experimental enhancement effect discussed above is scaled out.) We have used a fixed time step $5 \times 10^{-4}\tau_0$ to integrate eq. (3).

Comparison and discussion of the experimental and numerical results. – First we check the reliability and quality of the numerical scheme in comparison with the experiments. Figure 1 shows, for $\Gamma = 8.2$ and $n = 3.24 \times 10^{-3}\mu\mathrm{m}^{-2}$, the pair correlation functions $g(r)$ as a function of $rn^{1/2}$ obtained from the experiments (full circles, [3]), the simulations without HI (solid line), and the simulations with HI (dashed line). As expected, all curves agree perfectly, since the HI is not affecting any static properties.

In fig. 2 we consider the normalized diffusion coefficient $D(t)/D_0$ as a function of time t/τ_0 corresponding to the data presented in fig. 1. As can be seen from the figure, only the results for $D(t)$ from the simulations with HI agree with the experimental data, and $D(t)$ is for *all* times t larger than the "Brownian diffusivity" $D^{(\mathrm{B})}(t)$ in the absence of HI. As was shown in [3], an enhancement effect can already be recognized at short times by considering the initial slope $D'(0)$. In general we can write, based on a short-time expansion of the Smoluchowski equation (1), $D'(0) = -D_0^2 \langle K_{i\mu} K_{i\mu} \rangle / 4N$, where $K_{i\mu} = D_{i\mu,j\nu} F_{j\nu}/D_0$, N is the number of particles and $\langle K_{i\mu} K_{i\mu} \rangle / 4N$ might be calculated from static structure functions. The basic mechanism leading to an increase of $D'(0)$ becomes already clear, however, by considering only two particles and the HI in Oseen approximation [7], for which we obtain $K_\mu^{(12)} = (1 - 3a/2r_{12}) \, F_\mu^{(12)}$. Thus the effective force $K^{(12)}$ is smaller than $F^{(12)}$ due to the HI and accordingly $D'(0)$ is enhanced. The important point seen in fig. 2 is that the enhancement effect increases with t and is largest for the long-time diffusivity D_∞.

In order to show how the HI effect varies with the interaction strength and the density, we plot in fig. 3 the time-dependent diffusion coefficient for a) various n and fixed $\Gamma = 8.2$, and b) various Γ and fixed $n = 1.86 \times 10^{-3}\mu\mathrm{m}^{-2}$. All simulated curves show an excellent agreement
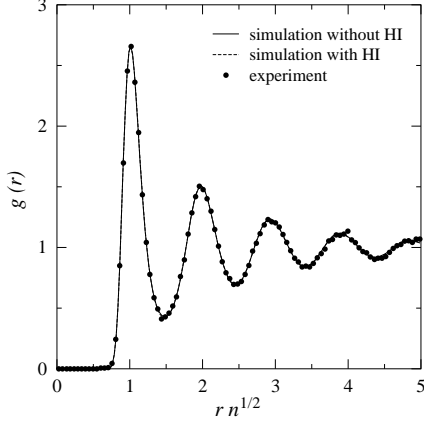
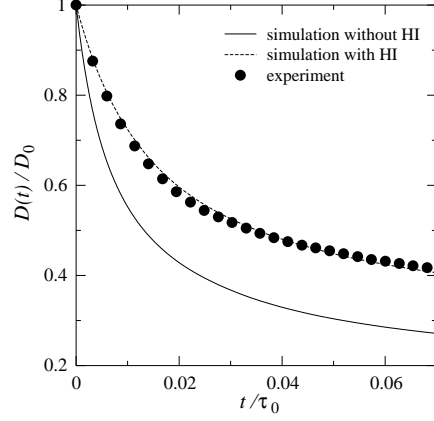Fig. 1   Fig. 2

Fig. 1. – Comparison of the pair correlation functions in the experiments with those in the simulations for $\Gamma = 8.2$ and $n = 3.24 \times 10^{-3} \mu\text{m}^{-2}$.

Fig. 2. – Comparison of the normalized time-dependent diffusion coefficients in the experiments with those in the simulations for the same parameters as in fig. 1.

with the experimental results (only a slight deviation occurs in the case of the highest density $n = 6.02 \times 10^{-3} \mu\text{m}^{-2}$ and the largest interaction strength $\Gamma = 8.2$). The diffusivity becomes smaller with decreasing n and increasing Γ. More important, while it is difficult to determine the long-time diffusivities $D_\infty = \lim_{t \to \infty} D(t)$ in the experiments [10], this is no problem in the simulations and we can thus quantify the enhancement effect in the long-time limit. As shown in the inset of fig. 3a, the difference between D_∞ and $D_\infty^{(\text{B})} = \lim_{t \to \infty} D^{(\text{B})}(t)$ becomes, for fixed Γ, larger with increasing n. Note that $D_\infty^{(\text{B})}$ does not depend on n for fixed Γ, *i.e.* density variations can be fully taken into account by a simple rescaling of Γ. This is due to
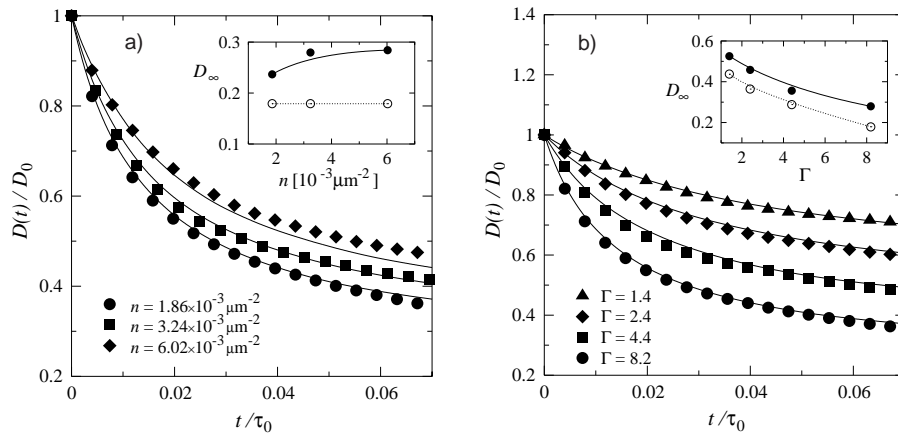

Fig. 3. – Diffusion coefficents $D(t)/D_0$ as a function of time t, a) for fixed $\Gamma = 8.2$ and various densities n, and b) for fixed density $n = 1.86 \times 10^{-3} \mu\text{m}^{-2}$ and various Γ. The symbols are from experiment, the lines from simulation. The insets show the long-time diffusion constants D_∞ (closed symbols, with HI) and $D_\infty^{(\text{B})}$ (open symbols, without HI). The lines in the insets are drawn as a guide for the eye.

the dipolar interaction potential, which provides no characteristic length scale. For fixed n, the enhancement is almost independent of temperature (Γ), see the inset of fig. 3b.

Concluding remarks. – We have achieved an almost full quantitative agreement between simulations and experiments despite of our approximate way to model the influence of the water/air interface on the flow field [11]. This approximation may cause the slight deviations to occur, which we found at the highest density and interaction strength. Less dominant contributions to these deviations may arise from the neglected polydispersity in the particle interactions and particle diameters, the small curvature of the water/air interface at the bottom of the drop, and the slightly imperfect confinement of the particle motion. In addition we have neglected the rotational degrees of freedom of the colloidal particles, which in general couple to the translational degrees of freedom.

Our simulations have convincingly shown that HI lead to an increase of the time-dependent diffusivity of colloidal particles interacting via a repulsive $1/r^3$ potential in two dimensions. This also holds in the long-time limit. We expect the enhancement for long-range interactions to be present also in higher dimensions, as is suggested by an approximate mode-coupling calculation for a three-dimensional system of particles interacting via screened longer-range Coulomb potential [12]. From a general viewpoint, when considering a repulsive potential of form $1/r^\alpha$, the question arises whether there exists a critical value α_c, above which HI no longer enhance but slow down the diffusion, as is usually observed for short-range interacting particles.

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