Anomalous hydrodynamic interaction in a quasi-two-dimensional suspension

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We have studied the correlated Brownian motion of micron-size particles suspended in water and confined between two plates. The hydrodynamic interaction between the particles exhibits three anomalies. (i) The transverse coupling is negative, i.e., particles exert “anti-drag” on one another when moving perpendicular to their connecting line. (ii) The interaction decays with inter-particle distance $r$ as $1/r^2$, faster than in unconfined suspensions but slower than near a single wall. (iii) At large distances the pair interaction is independent of concentration within the experimental accuracy. The confined suspension thus provides an unusual example of long-range, yet essentially pairwise correlations even at high concentration. These effects are shown to arise from the two-dimensional dipolar form of the flow induced by single-particle motion.

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Liquid suspensions containing particles of nanometer-to-micron size (colloids) are ubiquitous in industry and biology. In various circumstances the colloids are spatially confined, e.g., in porous media, biological constrictions, nozzles, and microfluidic devices. The dynamic behavior of suspensions is affected by flow-mediated velocity correlations. In unconfined suspensions these hydrodynamic interactions are positive (particles drag one another in the same direction), long-ranged (decaying with inter-particle distance $r$ as $1/r$), and involve many-body effects (i.e., depend on concentration). Considerable efforts have been devoted recently to studying colloids at the microscopic level, particularly in confinement, using digital video microscopy and optical tweezers. Particle dynamics near a single wall, between two walls, in a linear channel, and in a finite container were investigated. These studies have highlighted flow-mediated effects of the boundaries on particle dynamics. Quasi-two-dimensional (q-2D) suspensions have been studied recently also by computer simulations. In this Letter we demonstrate, using digital video microscopy, that the hydrodynamic interactions in a q-2D suspension are drastically different from those in less confined as well as more confined systems.

The experimental system consists of an aqueous suspension of monodisperse silica spheres (diameter $2a = 1.58 \pm 0.04$ µm, density 2.2 g/cm$^3$, Duke Scientific), tightly confined between two parallel glass plates in a sealed thin cell (Fig. 1). The inter-plate separation is $w = 1.76 \pm 0.05$ µm, i.e., slightly larger than the sphere diameter, $2a/w \approx 0.90$. Particles thus move essentially parallel to the plates, forming a q-2D suspension. The glass surfaces are coated with chlorine-terminated polydimethylsiloxane telomer (Glassclad 6C, United Chemical Products) to avoid particle sticking. Digital video microscopy and subsequent data analysis are used to locate the centers of the $N$ spheres in the field of view (area $A = 106 \times 80$ µm$^2$) and then extract time-dependent two-dimensional trajectories (time resolution 0.033 s). Details of the setup and measurement methods have been described elsewhere. Measurements were made at four packing fractions, $\phi \equiv N\pi a^2/A = 0.254, 0.338, 0.547, 0.619 \pm 0.001$. From equilibrium studies of this system we infer that, for the the current study, the particles can be regarded as hard spheres.

![FIG. 1: (a) Optical microscope image of 1.58 µm-diameter silica spheres suspended in water and confined between two glass plates at area fraction $\phi = 0.338$. (b) Schematic view of the system and its parameters.](image)

For a pair of particles in two dimensions, separated by a distance $r$, the coupled Brownian motion can be characterized by four diffusion coefficients, denoted $D^F_T(r)$ and $D^L_T(r)$. The longitudinal and transverse collective coefficients, $D^F_L$ and $D^L_T$, characterize the diffusion of the center of mass of the pair along and perpendicular to their connecting line. The relative coefficients, $D^F_L$ and $D^L_T$, relate to the fluctuations in length and orientation of the vector $r$ connecting the pair. These coefficients are measured as $D^F_T(r) = \langle (x_1(t) \pm x_2(t))^2 \rangle_r / (4t)$ and $D^L_T(r) = \langle (y_1(t) \pm y_2(t))^2 \rangle_r / (4t)$, where $x_i(t)$ and $y_i(t)$ are the displacements of particle $i$ during the time interval $t$ along and perpendicular to the line connecting it to its partner. The average $\langle \cdots \rangle_r$ is taken over all
observed pairs whose mutual distance falls in the range $r \pm 0.09 \mu m$. The time interval was kept sufficiently short ($t < 0.2$ s) that $r$ could be assumed constant within the $\pm 0.09 \mu m$ bin size. The pair diffusion coefficients are defined above such that, in the absence of correlations (e.g., when $r \to \infty$), all four reduce to the self-diffusivity of a single particle, $D_s$. (This is also verified experimentally.) Thus, the deviations of $D_{L,T}^{\pm}$ from $D_s$ serve as our measure of the pair hydrodynamic interaction.

$$\Delta_{L,T}^{\pm}(\rho) \equiv (D_{L,T}^{\pm} - D_s)/(D_0 a/w), \quad \rho \equiv r/w, \quad (1)$$

where $D_0 \equiv k_B T/(6 \pi \eta a)$ is the self-diffusivity of an isolated, unconfined sphere ($k_B T$ being the thermal energy and $\eta$ the viscosity). This rescaling yields, in the limit of small particles and low concentration, parameter-free functions describing solely the pair interaction [9]. The rescaled results are given in Fig. 3 where all long-distance measurements collapse onto the same four curves.

Figure 3: (Color online) The same data as in Fig. 2 rescaled according to Eq. (1). Note the collapse of the long-distance data for different area fractions onto the same four curves (insets). The solid curves correspond to $\pm \lambda/\rho^2$ with $\lambda = 0.31$ [Eq. (3)]. The dashed curves in (b) are obtained from the rigorous solution in the limit $a \ll w$ [17] (see text).

In the longitudinal modes, the correlation has the expected positive sign—particles drag one another in the direction of motion, thus enhancing the collective motion and suppressing the relative motion [Fig. 3(a)]. The transverse interaction, however, has a surprising reverse sign—the collective motion is suppressed while the relative motion is enhanced [Fig. 3(b)], i.e., particles exert “anti-drag” on one another.
Since the liquid velocity vanishes on the plates (assuming no-slip boundary conditions), one might have expected suppression of locally induced flows and a cutoff in the hydrodynamic interaction at distances much larger than $w$. Such screening is found in q-1D suspensions \[14\] and in the electrostatic analogue of charges located between two conducting plates. However, all four diffusion coefficients are found to decay as $1/r^3$ for large $r$ (Fig. 3). This decay is faster than the $1/r^3$ dependence in unconfined suspensions but is still long-ranged—correlations at distances ten times $w$ are measurable. Moreover, the observed decay is \textit{slower} than the $1/r^3$ dependence of the interaction parallel to a single wall \[11\].

Other particles obstruct the flow induced by the monitored pair, thus affecting their measured interaction, as observed at short distances (Fig. 3) \[14\]. One would have expected that at large distances the combined contributions from numerous particles would shift the pair interaction by a factor proportional to $\phi$. This correction should have been significant already at small $\phi$ because of the long-range interaction. However, as can be seen in the insets of Fig. 3, within our experimental accuracy there is \textit{no} concentration effect even at large $\phi$ \[15\].

Since the Reynolds number is very low ($\sim 10^{-6}$), the hydrodynamic interactions are carried by linear Stokes flows \[16\]. Together with no-slip boundary conditions on the plates and particles the mathematical problem is well posed, yet very complicated to solve. The observations presented above can be accounted for, nonetheless, on simpler grounds. We focus on the flow due to the motion of a single particle parallel to the plates. The motion perturbs the liquid momentum distribution and displaces liquid mass. Far away from the particle one can consider only the lowest-order moments of the perturbation—a momentum monopole and a mass dipole. (Since mass is merely displaced, there is no mass monopole.) The momentum monopole undergoes diffusion with absorbing boundary conditions at the plates, and its contribution to the far field is therefore exponentially small in $r/w$. However, the mass-dipole perturbation is not absorbed by the boundaries and must propagate laterally. We thus expect the far field to be that of a \textit{two-dimensional mass dipole} (source doublet), which decays only as $1/r^2$. The entrainment of a second particle by this flow determines the pair hydrodynamic interaction, hence the $1/r^2$ decay in the measured correlations. Dipolar flow fields were previously encountered in various q-2D and 2D problems \[17\], \[18\], \[19\]. The above argument clarifies the generality of this result.

Consider a particle located on the midplane and exerting a force $f_1 \hat{x}$ on the liquid. The $y$ axis is taken as the second direction parallel to the plates, and $z$ perpendicular to the plates [Fig. 1(b)]. The far velocity field, arising from a two-dimensional mass dipole oriented along $x$, is given by $v_\alpha(r) = [f_1/(6\pi\eta w)] \Delta_\alpha(r)$, with

$$
\Delta_x(r) = h(z) \frac{x^2 - y^2}{(x^2 + y^2)^2}, \quad \Delta_y(r) = h(z) \frac{2xy}{(x^2 + y^2)^2},
$$

where $\Delta_z$ is exponentially small in $r/w$. The flow has a perpendicular profile $h(z)$ having a certain value at the midplane, $h(0) \equiv w^3 \lambda$, and vanishing on the two plates, $h(z = \pm w/2) = 0$. In the limit $a/w \ll 1$ $h(z)$ is parabolic and $\lambda = 9/16$ \[17\]. The dipolar flow pattern is depicted in Fig. 4(b), where it is contrasted with the flow in an unconfined medium [Fig. 4(a)]. Due to the circulation currents a second particle, located transversely to the particle motion, will evidently be entrained in the opposite direction, hence the negative transverse correlation.

To leading order in $a/r$, the longitudinal and transverse pair interactions are given, respectively, by $\Delta_x(r\hat{x})$ and $\Delta_y(r\hat{y})$. Thus, from Eq. (2),

$$
\Delta^\mp_x(\rho \gg 1) = \mp \lambda/\rho^2, \quad \Delta^\mp_y(\rho \gg 1) = \mp \lambda/\rho^2.
$$

This result is in good agreement with the data of Fig. 3 using $\lambda(a/w \approx 0.45) \approx 0.31$. In Fig. 3b we present also the results of the full solution in the limit $a \ll w$ \[17\], multiplied by $0.31/(9/16) = 0.55$ to match the long-distance behavior. This calculation reproduces the non-monotone behavior of $\Delta^x_+ \Delta^-_y$ at short distances \[20\].

We now outline the analysis of the three-body effect \[21\]. Particle 1 exerts a force $f_1 \hat{x}$, yet now in the presence of particle 2 at $\mathbf{r}$ and particle 3 at $\mathbf{r}'$, where both $\mathbf{r}, \mathbf{r}' \gg w$ [Fig. 1(b)]. The leading effect of particle 3 on the pair interaction between 1 and 2 arises from variations of the induced flow over the volume it occupies. Because of symmetries of the midplane and Eq. (2) we find that the only derivative contributing to this effect is $a^2 \partial^2 v_\alpha/\partial z^2|_{z=0} \sim (a^2/w^2)v_\alpha$ \[22\]. We can therefore write the force exerted by particle 3 as

![FIG. 4: Flow velocity field away from a particle moving to the right (indicated by circle and arrow at the center), in (a) unconfined liquid \[16\] and (b) liquid confined between two plates [Eq. 2]. Shown are cross-sections of the three-dimensional fields along the plane of particle motion. Note the dipolar shape of the confined flow.](image-url)
\[ f_{3,\alpha} = (6\pi \eta a^3/w^2)C_{\alpha\beta}v_\beta(r') \], where \( C_{\alpha\beta} \) are dimensionless coefficients which, in principle, could be obtained from a detailed calculation. From rotational symmetry \( C_{xx} = C_{yy} \equiv C_L \) and \( C_{xy} = -C_{yx} \equiv C_T \). The force \( f_3 \) perturbs the velocity of particle 2 in the \( x \) direction by \( \delta v_x(r) = (6\pi \eta w)^{-1}\Delta_n(r - r')f_{3,\alpha}, \) and the perturbation should be averaged over all third-particle positions \( r' \). The inter-particle distances being much larger than \( a \), we can assume a uniform probability per unit area, \( \phi/(\pi a^2) \), to find a third particle at \( r' \). Combining this with the results for \( f_3 \) and \( \delta v_x \) and rescaling, we find the following corrections to the pair interactions:

\[
\delta \Delta_{L,T}^\pm(\rho) = \pm(a/\pi w)\phi C_L \int d^2\rho' [\Delta_x(\rho - \rho')\Delta_x(\rho') + \Delta_y(\rho - \rho')\Delta_y(\rho')],
\]

(4)

where \( \delta \Delta_L^\pm \) and \( \delta \Delta_T^\pm \) are obtained by setting, respectively, \( \rho = \rho x \) and \( \rho = \rho y \). The integral in Eq. (4), however, vanishes. The leading corrections to this result that are linear in \( \phi \) are found to decay faster than \( 1/\rho^2 \) [21] and, hence, the vanishing of the three-body term is asymptotically exact.

This approach can be extended to the four-body effect [21], resulting in finite, small corrections. We find, e.g., \( \delta \Delta_L^\pm/\Delta_T^\pm = (1/8\pi)\lambda^2(C_L^2 + C_T^2)(a/w)^2\phi^2 \). At our largest \( \phi \) this amounts to \( \sim (3 \times 10^{-4})(C_L^2 + C_T^2) \) which (unless \( C_L,T \) are unexpectedly large) would be smaller than the experimental noise. For most practical purposes the hydrodynamic interaction at large distances is thus a long-ranged, yet purely pairwise effect even at high concentrations. This result is unique to the q-2D geometry.

Perpendicular particle motion is restricted in our system by the large \( a/w \) ratio and possible repulsion from the plates [13]. The flow induced by such motion decays exponentially with \( r/w \). Increasing the spacing \( w \) is expected, therefore, to shift the validity range of our results to larger inter-particle distances. This effect, however, requires further experimental study. Since diffusion coefficients are proportional to mobility coefficients, the results presented here for Brownian motion should apply as well to overdamped driven motion, as in sedimentation [24] or microfluidic transport [2].

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