

Anomalous Hydrodynamic Interaction in a Quasi-Two-Dimensional Suspension

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We study the correlated Brownian motion of micron-sized 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 “antidrag” on one another when moving perpendicular to their connecting line. (ii) The interaction decays with interparticle 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 [1]. In various circumstances, the colloids are spatially confined, e.g., in porous media, biological constrictions, nozzles, and microfluidic devices [2]. The dynamic behavior of suspensions is affected by flow-mediated velocity correlations. In unconfined suspensions [1], these hydrodynamic interactions are positive (particles drag one another in the same direction), long ranged (decaying with interparticle distance r as $1/r$), and involve many-body effects (i.e., depend on concentration) [3]. A considerable effort has been devoted recently to studying colloids at the microscopic level, particularly in confinement, using digital videomicroscopy [4] and optical tweezers [5]. Particle dynamics near a single wall [6,7], between two walls [8], in a linear channel [9], and in a finite container [3] were investigated. These studies have highlighted flow-mediated effects of the boundaries on particle dynamics. Quasi-two-dimensional (Q2D) suspensions have been studied recently also by computer simulations [10]. In this Letter, we demonstrate, using digital videomicroscopy, that the hydrodynamic interactions in a Q2D 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 $2a = 1.58 \pm 0.04 \mu\text{m}$, density 2.2 g/cm^3 , Duke Scientific), tightly confined between two parallel glass plates in a sealed thin cell (Fig. 1). The interplate separation is $w = 1.76 \pm 0.05 \mu\text{m}$ [11], i.e., slightly larger than the sphere diameter, $2a/w \approx 0.90$. Particles thus move essentially parallel to the plates, forming a Q2D suspension. The glass surfaces are coated with chlorine-terminated polydimethylsiloxane telomer (Glassclad 6C, United Chemical Products) to avoid particle sticking. Digital videomicroscopy and subsequent data analysis are used

to locate the centers of the N spheres in the field of view (area $A = 106 \times 80 \mu\text{m}^2$) and then extract time-dependent two-dimensional trajectories (time resolution 0.033 s). Details of the setup and measurement methods have been described elsewhere [12]. Measurements were made at four packing fractions, $\phi \equiv N\pi a^2/A = 0.254, 0.338, 0.547, \text{ and } 0.619 \pm 0.001$. From equilibrium studies of this system [13] we infer that, for the current study, the particles can be regarded as hard spheres.

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 $D_L^\pm(r)$ and $D_T^\pm(r)$. The longitudinal and transverse collective coefficients, D_L^+ and D_T^+ , characterize the diffusion of the center of mass of the pair along and perpendicular to their connecting line. The relative coefficients, D_L^- and D_T^- , relate to the fluctuations in length and orientation of the vector \mathbf{r} connecting the pair. These coefficients are measured as $D_L^\pm(r) = \langle [x_1(t) \pm x_2(t)]^2 \rangle_r / (4t)$ and $D_T^\pm(r) = \langle [y_1(t) \pm y_2(t)]^2 \rangle_r / (4t)$, 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 $\langle \dots \rangle_r$ is taken over all observed pairs whose mutual distance falls in the range $r \pm 0.09 \mu\text{m}$.

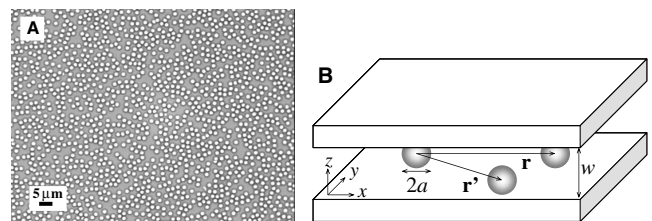


FIG. 1. (a) Optical microscope image of $1.58 \mu\text{m}$ -diameter silica spheres suspended in water and confined between two glass plates at area fraction $\phi = 0.338$. (b) Schematic view of the system and its parameters.

The time interval was kept sufficiently short ($t < 0.2$ s) that r could be assumed constant within the $\pm 0.09 \mu\text{m}$ bin size. The pair diffusion coefficients are defined above such that, in the absence of correlations (e.g., when $r \rightarrow \infty$), 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.

Figure 2 shows the measured values of $D_{L,T}^\pm(r)$ as functions of r at different area fractions ϕ . As ϕ is increased, the curves shift to lower values (i.e., D_s expectedly decreases with concentration) and, at short distances, become more structured [14]. We focus in this Letter on the long-distance pair interaction. To get a

more unified presentation in this domain, we rescale diffusion coefficients and distances according to

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

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 η 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.

In the longitudinal modes, the correlation has the expected positive sign—particles drag one another in the direction of motion, thus enhancing the collective

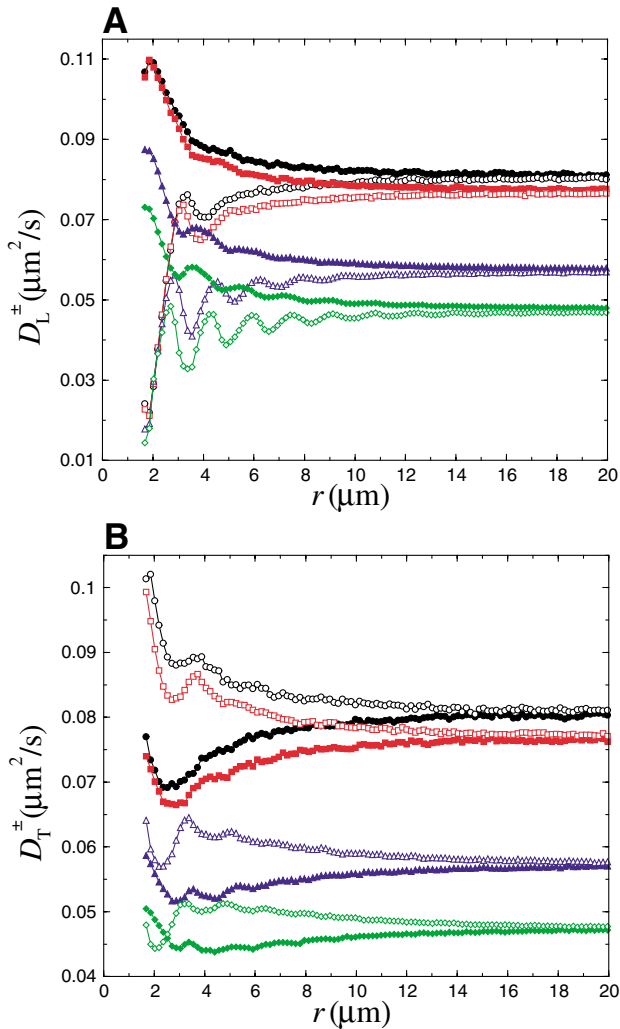


FIG. 2 (color online). Longitudinal (a) and transverse (b) pair diffusion coefficients as functions of interparticle distance. Filled and open symbols correspond, respectively, to collective and relative coefficients. Symbol shapes and colors correspond to different area fractions: $\phi = 0.254$ (black circles), 0.338 (red squares), 0.547 (blue triangles), 0.619 (green diamonds). Note the long range of the interaction and the sign reversal of the transverse coupling.

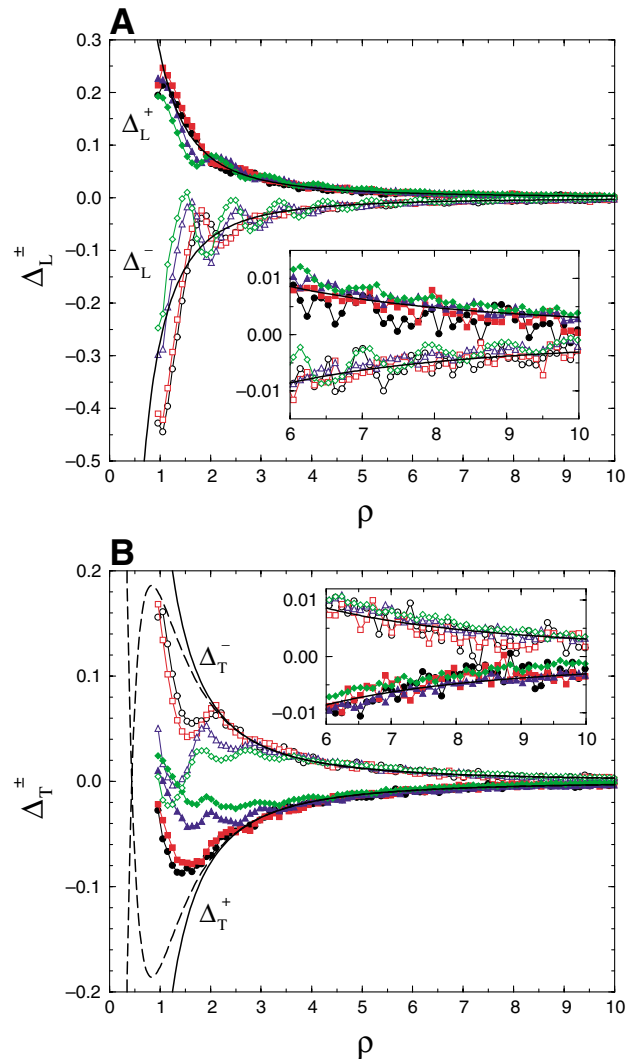


FIG. 3 (color online). The same data as in Fig. 2 rescaled according to Eq. (1). Note the collapse of the long-distance data for different area fractions onto the same four curves (insets). The solid curves correspond to $\pm\lambda/\rho^2$ with $\lambda = 0.31$ [Eq. (3)]. The dashed curves in (b) are obtained from the rigorous solution in the limit $a \ll w$ [16] (see text).

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 antidrag 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 Q1D suspensions [9] and in the electrostatic analogue of charges located between two conducting plates. However, all four diffusion coefficients are found to decay as $1/\rho^2$ for large ρ (Fig. 3). This decay is faster than the $1/\rho$ dependence in unconfined suspensions but is still long ranged—correlations at distances 10 times w are measurable. Moreover, the observed decay is *slower* than the $1/\rho^3$ dependence of the interaction parallel to a single wall [7].

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 ϕ . This correction should have been significant already at small ϕ because of the long-range interaction. However, as can be seen in the insets of Fig. 3, within our experimental accuracy there is *no* concentration effect even at large ϕ [17].

Since the Reynolds number is very low ($\sim 10^{-6}$), the hydrodynamic interactions are carried by linear Stokes flows [18]. 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 perturbations—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 *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 encountered in various Q2D and 2D problems [16,19,20]. 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 perpendicu-

lar to the plates [Fig. 1(b)]. The far velocity field, arising from a two-dimensional mass dipole oriented along x , is given by $v_\alpha(\mathbf{r}) = [f_1/(6\pi\eta w)]\Delta_\alpha(\mathbf{r})$, with

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

while Δ_z is exponentially small in r/w . The flow has a perpendicular profile $h(z)$ having a certain value at the midplane, $h(0) \equiv w^2\lambda$, and vanishing on the two plates, $h(z = \pm w/2) = 0$. [In the limit $a/w \ll 1$ $h(z)$ is parabolic and $\lambda = 9/16$ [16].] The dipolar flow pattern is depicted in Fig. 4(b), where it is contrasted with the flow in an unconfined medium [Fig. 4(a)]. Because of the circulation currents a second particle, located transverse to the moving particle, 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 $\Delta_x(r\hat{y})$. Thus, from Eq. (2),

$$\Delta_L^\pm(\rho \gg 1) = \pm\lambda/\rho^2, \quad \Delta_T^\pm(\rho \gg 1) = \mp\lambda/\rho^2. \quad (3)$$

This result is in good agreement with the data of Fig. 3 using $\lambda(a/w \simeq 0.45) \simeq 0.31$. In Fig. 3(b), we present also the results of the full solution in the limit $a \ll w$ [16], multiplied by $0.31/(9/16) = 0.55$ to match the long-distance behavior. This calculation reproduces the nonmonotone behavior of Δ_T^+ at short distances [21].

We now outline the analysis of the three-body effect [15]. 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 $r, r' \gg w$ [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

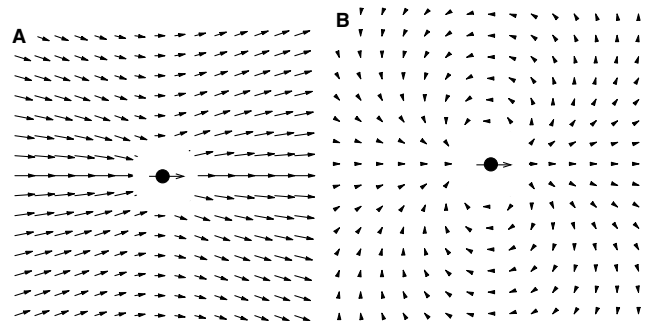


FIG. 4. Flow velocity field away from a particle moving to the right (indicated by circle and arrow at the center), in (a) unconfined liquid [18] and (b) liquid confined between two plates [Eq. (2)]. Shown are cross sections of the three-dimensional fields along the plane of particle motion. Note the dipolar shape of the confined flow.

$a^2 \partial^2 v_\alpha / \partial z^2|_{z=0} \sim (a^2/w^2) v_\alpha$ [22]. We can therefore write the force exerted by particle 3 as $f_{3,\alpha} = (6\pi\eta a^3/w^2) C_{\alpha\beta} v_\beta(\mathbf{r}')$, 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 \mathbf{f}_3 perturbs the velocity of particle 2 in the x direction by $\delta v_x(\mathbf{r}) = (6\pi\eta w)^{-1} \Delta_\alpha(\mathbf{r} - \mathbf{r}') f_{3,\alpha}$, and the perturbation should be averaged over all third-particle positions \mathbf{r}' . The interparticle 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 \mathbf{r}' . Combining this with the results for \mathbf{f}_3 and δv_x and rescaling, we find the following corrections to the pair interactions:

$$\delta\Delta_{L,T}^\pm(\rho) = \pm(a/\pi w)\phi C_L \int d^2\rho' [\Delta_x(\boldsymbol{\rho} - \boldsymbol{\rho}') \Delta_x(\boldsymbol{\rho}') + \Delta_y(\boldsymbol{\rho} - \boldsymbol{\rho}') \Delta_y(\boldsymbol{\rho}')], \quad (4)$$

where $\delta\Delta_L^\pm$ and $\delta\Delta_T^\pm$ are obtained by setting, respectively, $\boldsymbol{\rho} = \rho\hat{\mathbf{x}}$ and $\boldsymbol{\rho} = \rho\hat{\mathbf{y}}$. The integral in Eq. (3), however, vanishes. The leading corrections to this result that are linear in ϕ are found to decay faster than $1/\rho^2$ [15] and, hence, the vanishing of the three-body term is asymptotically exact.

This approach can be extended to the four-body effect [15], resulting in finite, small corrections. We find, e.g., $\delta\Delta_L^\pm/\Delta_L^\pm = (1/8\pi)\lambda^2(C_L^2 + C_T^2)(a/w)^2\phi^2$. At our largest ϕ , 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 Q2D 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 interparticle 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 [23] or microfluidic transport [2].

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