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Hydrodynamic interaction in quasi-two-dimensional suspensions

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Abstract

Confinement between two parallel surfaces is found, theoretically and experimentally, to drastically affect the hydrodynamic interaction between colloid particles, changing the sign of the coupling, its decay with distance and its concentration dependence. In particular, we show that three-body effects do not modify the coupling at large distances as would be expected from hydrodynamic screening.

1. Introduction

The dynamics of colloid suspensions and macromolecular solutions are governed by hydrodynamic interactions, i.e., correlations in the motions of particles mediated by flows in the host liquid [1, 2]. In various circumstances colloids are spatially confined by rigid boundaries as in, for example, porous media, biological constrictions, nozzles, or microfluidic devices. Extensive studies have been devoted recently to colloid dynamics at the single-particle level, highlighting flow-mediated effects of the boundaries [3–7]. Confined suspensions have also been studied by computer simulations [8–10].

Hydrodynamic interactions in an unconfined suspension [11] decay with inter-particle distance r as $1/r$. They are positive, i.e., particles drag one another in the same direction. The long range of the interaction leads to strong many-body effects, manifest, for example, in an appreciable dependence of transport coefficients on particle volume fraction. A particularly important many-body effect is hydrodynamic screening [2]: over length scales much larger than the typical inter-particle distance the suspension responds to a slow disturbance as if it were a homogeneous medium with merely an increased viscosity. This implies that at large distances many-body effects change the prefactor of the $\sim 1/r$ pair interaction.

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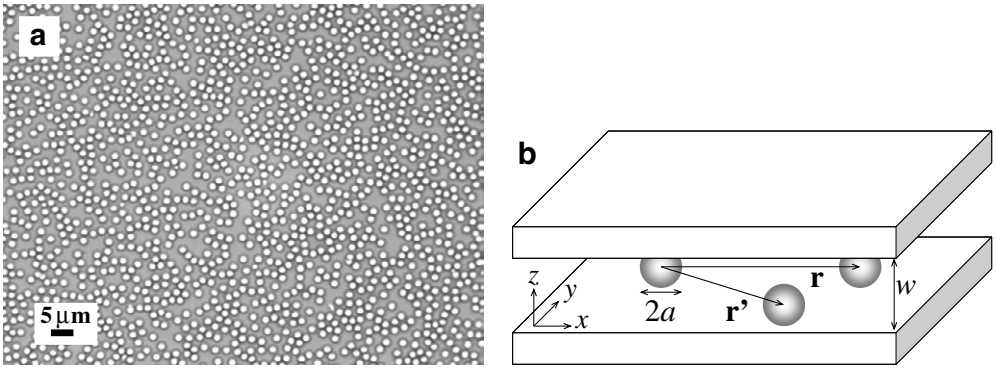

Figure 1. (a) Optical microscope image of the experimental Q2D suspension at area fraction $\phi = 0.338$. (b) Schematic view of the system and its parameters.

Our aim has been to investigate the effects of confinement on hydrodynamic interactions. Elaborating on our previous short publication [7], we consider here the case of confinement between two parallel plates, leading to a quasi-two-dimensional (Q2D) suspension (figure 1). In section 2 we define the problem and the corresponding nomenclature. In section 3 we address the hydrodynamic interaction between two isolated particles, and in section 4, the three-body correction at finite concentration. The experimental measurements are presented in section 5, and in section 6 we discuss the results.

2. Definition of the problem

The geometry considered in this work is depicted in figure 1(b). Identical, spherical particles of radius a are suspended in a liquid of viscosity η and temperature T, confined in a slab of width w between two planar solid surfaces. The x and y axes are taken parallel, and the z axis perpendicular, to the surfaces. The particles are assumed to behave as hard spheres with no additional equilibrium interaction. For simplicity we consider cases where particle motion is restricted to two dimensions, i.e., to a monolayer at the mid-plane, $z = 0$. We use the notation $\mathbf{r}(\boldsymbol{\rho}, z)$ for three-dimensional position vectors, where $\boldsymbol{\rho}(x, y)$ is a two-dimensional position vector in the monolayer. The area fraction occupied by particles is denoted by ϕ. The Reynolds number is assumed very low. (It is of order 10^{-6} in the experimental system.) The hydrodynamics, therefore, are well described by viscous Stokes flows [11]. The confining boundaries are assumed impermeable and rigid, imposing no-slip boundary conditions on the flow.

We characterize the pair hydrodynamic interaction between two particles by the coupling mobilities $\Delta_{\mathrm{L,T}}(\rho)$ as functions of the inter-particle distance ρ. These are the off-diagonal terms in the mobility tensor of a particle pair, i.e., the proportionality coefficients relating the force acting on one particle with the change in velocity of the other. The two independent coefficients, Δ_{L} and Δ_{T}, correspond, respectively, to the coupling along and transverse to the line connecting the pair. (In [7] four coefficients were considered, $\Delta^{\pm}_{\mathrm{L,T}}$, whose relation with the ones considered here is $\Delta_{\mathrm{L,T}} = (\Delta^{+}_{\mathrm{L,T}} - \Delta^{-}_{\mathrm{L,T}})/2$.)

We use dimensionless quantities throughout this paper, scaling all distances by the confinement length w and all mobilities by $B_0 a/w$, where $B_0 = (6\pi\eta a)^{-1}$ is the Stokes mobility of a single, unconfined sphere. In places where we refer to dimensional quantities for clarity, a tilde symbol is used, e.g., $\tilde{r} = wr$.

3. Pair interaction at infinite dilution

We first examine the effect of confining boundaries on the flow due to a local disturbance such as the one created by single-particle motion. The flow field can be found by solving the Stokes and continuity equations subject to the appropriate boundary conditions [11]. This was done for a point force (stokeslet) in a Q2D geometry in [12]. However, by returning to the physical origin of the equations, one can gain a useful insight applicable to various geometries and particle sizes. The motion of a particle perturbs the local liquid momentum and displaces liquid mass. In an unconfined liquid the diffusion of the momentum disturbance, whose leading moment is a momentum monopole, creates a far flow decaying as $1/r$. The mass term, whose leading moment must be a mass dipole (since mass is neither created nor lost), adds to the far flow a much smaller contribution $\sim 1/r^3$.

In confinement, however, the situation is very different. It is the momentum perturbation which, while diffusing away, is absorbed by the boundaries and thus gives a contribution to the far field which is exponentially small in $r = \tilde{r}/w$ in both Q2D and Q1D geometries. The contribution from mass displacement propagates laterally, creating a far flow parallel to the boundaries. We conclude that the far flow field induced by single-particle motion in Q2D is that of a 2D mass dipole (source doublet). If the particle motion (mass dipole) is taken along the x direction, we thus have a far velocity field $\mathbf{v}(\mathbf{r})$ of the form

$$v_x(\mathbf{r}) \simeq f(z)(x^2 - y^2)/\rho^4, \qquad v_y(\mathbf{r}) \simeq f(z)(2xy)/\rho^4, \qquad v_z(\mathbf{r}) \simeq 0. \tag{1}$$

The 2D dipolar field must be modulated by a transverse profile $f(z)$ to make it vanish on the two confining surfaces. In 1D only a mass monopole creates flow. Hence, in a Q1D geometry (confinement in a linear channel) both the momentum and mass contributions are exponentially small in $\tilde{r}/w$, leading to a short-ranged hydrodynamic interaction [6]. (Note that the Q2D far flow, equation (1), differs from that in a purely 2D liquid. The latter is governed again by (2D) momentum diffusion, leading to a logarithmic distance dependence.)

Exact calculations of the flow due to a point force (stokeslet), i.e., the Oseen tensors in the confined geometries, confirm the above conclusions [12, 13]. Those exact results are relevant to colloid motion in the limit of very small particles, $a \ll w, \tilde{r}$. The strength of the heuristic arguments presented above is their general validity: the conclusions concerning the far flow should hold regardless of particle size or details of the confining boundaries. These arguments also imply that, for a spherical particle, particle rotation does not contribute to the far flow under confinement, since it perturbs only the liquid momentum.

When the suspension is very dilute we may consider the interaction between two isolated particles. Suppose that the motion of particle 1 exerts on the liquid a unit force in the x direction. The disturbance will create a flow field which, in turn, will entrain particle 2 located at $\mathbf{r}$. Thus, the coupling mobilities at large distances are obtained as $\Delta_{\mathrm{L}} = v_x(\rho\hat{x})$ and $\Delta_{\mathrm{T}} = v_x(\rho\hat{y})$, where $\mathbf{v}(\mathbf{r})$ is given by equation (1) and $\hat{x}$, $\hat{y}$ denote unit vectors in the x and y directions, respectively. This yields

$$\phi \to 0: \qquad \Delta_{\mathrm{L}}(\rho \gg 1) = \lambda/\rho^2, \qquad \Delta_{\mathrm{T}}(\rho \gg 1) = -\lambda/\rho^2, \tag{2}$$

where λ is a coefficient which depends only on a/w. As found in equation (2), the pair hydrodynamic interaction in Q2D is very different from its unconfined counterpart. The decay with distance is faster, $\sim 1/r^2$ instead of $\sim 1/r$, yet the interaction is still long-ranged [14]. (Its decay is *slower* than near a single surface, where the interaction falls off as $1/r^3$ [3].) The transverse coupling is negative, i.e., particles exert 'anti-drag' on one another as they move perpendicular to their connecting line. (In the unconfined case one has $\Delta_{\mathrm{T}} = \Delta_{\mathrm{L}}/2$.) These properties are direct consequences of the far flow field inferred above. The $1/\rho^2$ decay is

that of the flow due to a 2D mass dipole. The negative transverse coupling is a result of the circulation flows in the dipolar field [7].

4. Three-body correction

As ϕ is increased, the pair hydrodynamic interaction should become affected by the presence of other particles. If hydrodynamic screening were to set in, we would expect the interaction at distances much larger than the typical inter-particle distance to have the form of equation (2), yet with a modified, ϕ-dependent prefactor. However, this is not the case, as is demonstrated below both theoretically and experimentally.

We begin again with particle 1, located at the origin and exerting a unit force in the x direction. This creates a flow of the form (1), which entrains particle 2, located at $\boldsymbol{\rho}$, with velocity $\mathbf{v}(\boldsymbol{\rho})$. We now introduce particle 3 at $\boldsymbol{\rho}'$. Particle 3 will obstruct the flow, thereby exerting an extra force $\mathbf{f}_3$ on the liquid. This force is related to variations of the flow $\mathbf{v}(\boldsymbol{\rho}')$ over the volume now occupied by particle 3. For example, in an unconfined, isotropic system, according to Faxen's first law [1], $\mathbf{f}_3 \sim \nabla^2\mathbf{v}(\boldsymbol{\rho}')$. In the anisotropic Q2D geometry this law is modified to

$$f_{3i} = C'_{ij}\nabla_\perp^2 v_j(\boldsymbol{\rho}', 0) + C''_{ij}\partial_{zz}|_{z=0} v_j(\boldsymbol{\rho}', z), \qquad i, j = x, y. \tag{3}$$

(This result is readily obtained by inspecting all the ways to produce a vector $\mathbf{f}_3$ from derivatives of another vector $\mathbf{v}$ while using the various symmetries of the field (1).) In equation (3), C', C'' are 2×2 coefficient tensors (which can be found by a more detailed calculation), and $\nabla_\perp^2 \equiv \partial_{xx} + \partial_{yy}$. Since the flow (1) satisfies $\nabla_\perp^2\mathbf{v} = 0$ and $\partial_z^2|_{z=0}\mathbf{v} \sim \mathbf{v}$, equation (3) is simplified to

$$f_{3i} = C_{ij} v_j(\boldsymbol{\rho}'). \tag{4}$$

This local relation between $\mathbf{f}_3$ and $\mathbf{v}$ must be invariant to rotation in the (x, y) plane, which leads to $C_{xx} = C_{yy} \equiv C_{\mathrm{L}}$ and $C_{xy} = -C_{yx} \equiv C_{\mathrm{T}}$. Since the problem is linear, the effect of the extra force on the velocity at $\boldsymbol{\rho}$ is found by projecting the same flow field, equation (1), from $\boldsymbol{\rho}'$ onto $\boldsymbol{\rho}$, $\delta v_x = v_i(\boldsymbol{\rho} - \boldsymbol{\rho}')f_{3i}(\boldsymbol{\rho}')$. We then get

$$\begin{aligned}\delta v_x(\boldsymbol{\rho}, \boldsymbol{\rho}') = {} & C_{\mathrm{L}}[v_x(\boldsymbol{\rho} - \boldsymbol{\rho}')v_x(\boldsymbol{\rho}') + v_y(\boldsymbol{\rho} - \boldsymbol{\rho}')v_y(\boldsymbol{\rho}')] \\ & + C_{\mathrm{T}}[v_x(\boldsymbol{\rho} - \boldsymbol{\rho}')v_y(\boldsymbol{\rho}') - v_y(\boldsymbol{\rho} - \boldsymbol{\rho}')v_x(\boldsymbol{\rho}')].\end{aligned} \tag{5}$$

Equation (5) presents the correction to the x-velocity of the liquid at $\boldsymbol{\rho}$ given a fixed position $\boldsymbol{\rho}'$ of the third particle. We are interested, however, in the correction averaged over all possible positions $\boldsymbol{\rho}'$. This requires the probability density p of finding a particle a distance $\boldsymbol{\rho}'$, which we assume here to be uniform, $p = \phi/(\pi a^2)$. We average according to $\langle \delta v_x \rangle = \int \mathrm{d}^2\rho' p \delta v_x(\boldsymbol{\rho}, \boldsymbol{\rho}')$ and find

$$\langle \delta v_x \rangle(\boldsymbol{\rho}) = \epsilon\phi \int \mathrm{d}^2\rho'[v_x(\boldsymbol{\rho}')v_x(\boldsymbol{\rho} - \boldsymbol{\rho}') + v_y(\boldsymbol{\rho}')v_y(\boldsymbol{\rho} - \boldsymbol{\rho}')]. \tag{6}$$

The terms proportional to C_{T} cancel, leaving us with only one coefficient, $\epsilon = C_{\mathrm{L}}/(\pi a^2)$.

For $\rho' \gg \rho$ the integrand in equation (6) decreases as $(\rho')^{-4}$. Hence, the integrated contributions from far-away third particles should lead to a correction proportional to ϕ/ρ^2 which, as expected, would renormalize the prefactor of the leading $1/\rho^2$ term. However, carefully carrying out the convolution in equation (6), as shown in the appendix, proves this conclusion wrong. The specific angular dependence of the flow (1) leads to cancellation of terms, and the integral of equation (6) *vanishes*. Thus, the obstructions from numerous particles add up to nothing, and the long-range pair interaction (to linear order in ϕ) is identical to that in a particle-free liquid. Equation (2), therefore, remains unchanged for finite values of ϕ.

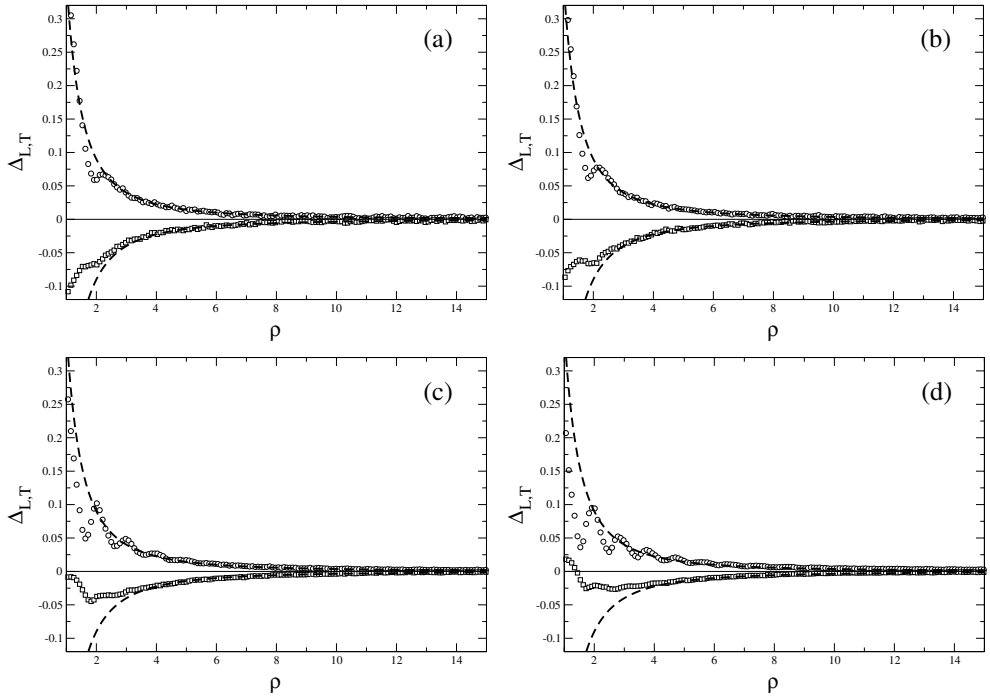

Figure 2. Longitudinal (Δ_L, circles) and transverse (Δ_T, squares) coupling diffusion coefficients as a function of inter-particle distance ρ. The coefficients are scaled by $D_0 a/w$ and the distance by w. Area fractions are $\phi = 0.254$ (a), 0.338 (b), 0.547 (c), and 0.619 (d). The dashed lines are a fit to $\pm\lambda/\rho^2$ with the same value of $\lambda = 0.36$ for all panels.

Deviations of the flow from the far-field dipolar form and the introduction of a non-uniform particle distribution (i.e., static pair correlations) lead to non-vanishing three-body effects. These corrections, however, are short-ranged and thus do not change the above result. (The short-ranged three-body effects will be addressed in a separate publication.)

5. Experimental results

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 (figure 1). The inter-plate separation is $w = 1.76 \pm 0.05$ μm, i.e., slightly larger than the sphere diameter, $2a/w \simeq 0.90$. Digital video microscopy and subsequent data analysis are used to locate the centres of the spheres in the field of view and then extract time-dependent two-dimensional trajectories. Details of the setup and measurement methods can be found elsewhere [15]. Measurements were made at four values of area fraction, $\phi = 0.254, 0.338, 0.547, 0.619 \pm 0.001$. From equilibrium studies of this system [16] we infer that, for the purpose of this study, the particles can be regarded as hard spheres.

The correlated Brownian motion of a particle pair is characterized by longitudinal and transverse coupling diffusion coefficients. Upon scaling by $D_0 a/w$, where $D_0 = k_B T/(6\pi\eta a)$ is the Stokes–Einstein diffusion coefficient of a single unconfined sphere, the two coefficients (thanks to the Einstein relation) become identical to the two mobilities Δ_L and Δ_T. The two coupling mobilities are thus directly extracted from measured particle trajectories as $\Delta_L(\rho) = \langle x_1(t)x_2(t)\rangle_\rho/(2D_0 ta/w)$ and $\Delta_T(\rho) = \langle y_1(t)y_2(t)\rangle_\rho/(2D_0 ta/w)$, where $x_i(t)$

and $y_i(t)$ are the displacements of particle i of the pair during a time interval t along and transverse to their connecting line, respectively. The average $\langle\rangle_\rho$ is taken over all pairs whose mutual distance falls in a narrow range ($\pm 0.09\ \mu$m) around $\tilde{\rho} = w\rho$.

The measured coupling diffusion coefficients are presented in figure 2. The leading behaviour for all ϕ values fits well the predicted $\pm\lambda/\rho^2$ dependence of equation (2). The negative sign of Δ_T confirms the predicted 'anti-drag' between particles located transverse to the direction of motion. The fact that the fitted value of $\lambda = 0.36$ does not change with ϕ demonstrates the absence of hydrodynamic screening up to an area fraction of 0.619. (Larger area fractions could not be checked because the suspension began to crystallize [16].)

6. Discussion

Flows due to local disturbances in a Q2D geometry are governed by mass propagation rather than momentum diffusion. We have demonstrated the strong effect that this has on the pair hydrodynamic interaction between colloid particles. The $1/r^2$ decay of the coupling with distance is faster than in the unconfined case but slower than near a single surface. The transverse coupling becomes negative. Three-body effects do not renormalize the coupling coefficient, in contrast with the usual case of hydrodynamic screening. Since momentum diffusion does not contribute to the large-distance coupling, it is perhaps natural that the flow effects of numerous distant particles may not renormalize the viscosity, which is the transport coefficient associated with momentum diffusion.

The mass-dipole shape of the Q2D far flow, equation (1), applies as well to realistic 2D liquids where momentum leaks to the third dimension [17]. Thus, our results concerning the long-distance hydrodynamic interaction are valid for particles embedded in such liquids, for example, proteins in a biological membrane.

We have not treated the effect of particle motion perpendicular to the boundaries. Such fluctuations must exist in practice, yet our experimental results suggest that they have a minor effect on the long-distance behaviour. This is expected since the flows produced by transverse fluctuations decay exponentially with distance [12].

We have restricted the discussion to far-field effects. At small inter-particle distances various features are observed in the hydrodynamic interactions (see figure 2), which are related to the static particle pair correlation. We shall address these short-ranged effects in a forthcoming publication.

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Appendix

We wish to calculate the convolution integral appearing in equation (6):

$$I(\boldsymbol{\rho}) = \int \mathrm{d}^2\rho' [v_x(\boldsymbol{\rho}')v_x(\boldsymbol{\rho} - \boldsymbol{\rho}') + v_y(\boldsymbol{\rho}')v_y(\boldsymbol{\rho} - \boldsymbol{\rho}')], \tag{7}$$

where (omitting the prefactor)

$$v_x(\boldsymbol{\rho}) = (x^2 - y^2)/\rho^4, \qquad v_y(\boldsymbol{\rho}) = 2xy/\rho^4. \tag{8}$$

Calculating $I(\boldsymbol{\rho})$ by direct integration is quite tricky, for reasons similar to those encountered in electrostatics. Excluding two small areas $\sim a^2$ around the (integrable) singularities at $\rho' = 0$ and $\boldsymbol{\rho}' = \boldsymbol{\rho}$, we divide the integration into three domains (φ and φ' being the polar angles of $\boldsymbol{\rho}$ and $\boldsymbol{\rho}'$, respectively): (i) $a < \rho' < \rho - a$, $0 \leqslant \varphi' < 2\pi$; (ii) $\rho' > \rho + a$, $0 \leqslant \varphi' < 2\pi$; (iii) $\rho - a < \rho' < \rho + a$, $\varphi + a/\rho < \varphi' < \varphi + 2\pi - a/\rho$. The contribution from the inner domain (i) vanishes upon angular integration for any a. The outer domain (ii) contributes $\pi/\rho^2 + \mathrm{O}(a/\rho^3)$. However, integration over the intermediate narrow domain (iii) just cancels the outer contribution, yielding $-\pi/\rho^2 + \mathrm{O}(a/\rho^3)$. Thus, in the limit $a \to 0$ the result is $I = 0$. A finite value of a leads to a correction of $\mathrm{O}(a/\rho^3)$, which is negligible compared to the leading $1/\rho^2$ coupling at large enough distances.

The direct integration pitfalls can be circumvented altogether by switching to Fourier space, $\mathcal{F}[f(\boldsymbol{\rho})] \equiv f(\mathbf{q}) \equiv \int \mathrm{d}^2\rho \mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\boldsymbol{\rho}} f(\boldsymbol{\rho})$. The transformed velocity field is

$$v_x(\mathbf{q}) = -\pi(q_x^2 - q_y^2)/q^2, \qquad v_y(\mathbf{q}) = -\pi(2q_xq_y)/q^2. \tag{9}$$

Using equation (9) in the convolution readily gives

$$I(\boldsymbol{\rho}) = \pi^2\mathcal{F}^{-1}[1] = \pi^2\delta(\boldsymbol{\rho}). \tag{10}$$

Hence, $I = 0$ for any $\rho > 0$.

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