Like-Charge Attraction and Hydrodynamic Interaction

Todd M. Squires[1] and Michael P. Brenner[2]
[1]*Department of Physics, Harvard University, Cambridge, Massachusetts 02138*
[2]*Department of Mathematics, MIT, Cambridge, Massachusetts 02139*
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We demonstrate that the attractive interaction measured between like-charged colloidal spheres near a wall can be accounted for by a nonequilibrium hydrodynamic effect. We present both analytical results and Brownian dynamics simulations which quantitatively capture the one-wall experiments of Larsen and Grier [Nature (London) **385**, 230 (1997)], using a single unmeasured parameter.

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Colloidal spheres provide a simple model system for understanding the interactions of charged objects in a salt solution. Hence, it came as a great surprise when it was observed that two like-charged spheres can attract each other when the spheres are confined by walls [1–4]. Since both the charge densities and sizes of the spheres in question are in the range of large proteins, it would be expected that a change in sign of this interaction would have important implications for biological systems [5]. Theorems by Sader and Chan [6], Neu [7], and Trizac and Raimbault [8] demonstrate that under very general conditions the Poisson-Boltzmann equation for the potential between like-charged spheres in a salt solution will not admit attractive interactions. Explanations for the observed attraction have thus exclusively focused on deviations from the classical Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory.

Herein we propose that an apparently attractive interaction of two like-charged colloidal spheres measured in the presence of a single charged wall can arise from a nonequilibrium hydrodynamic effect. In a bulk solution, far from solid boundaries, an external force acting on two identical spheres cannot change their relative positions. This is a consequence of the kinematic reversibility of Stokes flow and of the symmetries inherent in the problem. However, these symmetries are broken in confined geometries, where the hydrodynamic effect of boundaries is important. In this situation, relative motion between the spheres could stem *either* from an interparticle force *or* from a hydrodynamic coupling caused by external forces acting on each of the spheres individually. In a typical experiment with charged polystyrene spheres, the charge density on the walls of the cell is of order the charge density on the spheres [9]. We demonstrate that the hydrodynamic coupling between two spheres caused by their repulsion from a wall leads to motion which, if interpreted as an equilibrium property, would appear to give an effective pair potential which has an attractive well. With a single unknown parameter (the charge density on the glass), our calculations quantitatively reproduce both the size and the shape of the experimental measurements for two spheres near a single charged wall.

The response of a particle to an external force is significantly changed near a wall because the flow field must vanish identically on the wall. For point forces, Lorenz determined this wall-corrected flow field [10], which Blake later expressed using the method of image forces [11], analogous to image charges used in electrostatics. Images of the appropriate strength on the opposite side of the wall exactly cancel out the fluid flow on the wall. When two spheres are pushed away from a wall, the flow field from one sphere's image tends to pull the other sphere towards it, and vice versa (Fig. 1). This decreases the projected distance between the spheres. All experiments which have directly measured an attractive pair interaction between like-charged colloids have based their conclusions on the spheres' relative motion projected onto the plane parallel to the wall.

The attractive interaction between two charged spheres in the presence of a single charged wall can now be understood with a simple picture. When the spheres are sufficiently close to the wall, they are electrostatically repelled from it. The net force on each sphere thus includes both their mutual electrostatic repulsion and their repulsion from the wall. How the spheres respond depends on their hydrodynamic mobility: when the spheres are close together (Fig. 2a), their mutual repulsion overwhelms any hydrodynamic coupling, and the spheres will separate as expected for like-charged bodies. However, when they

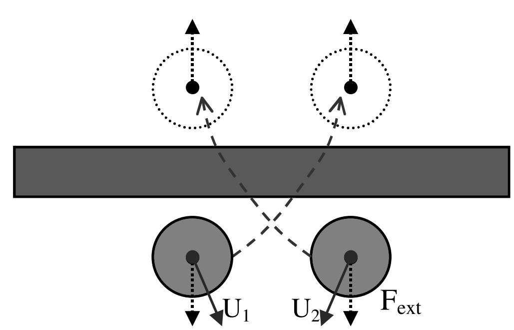

FIG. 1. Two spheres forced away from a wall are drawn together by hydrodynamic coupling, because the flow due to one sphere's image force pulls the other sphere towards it.

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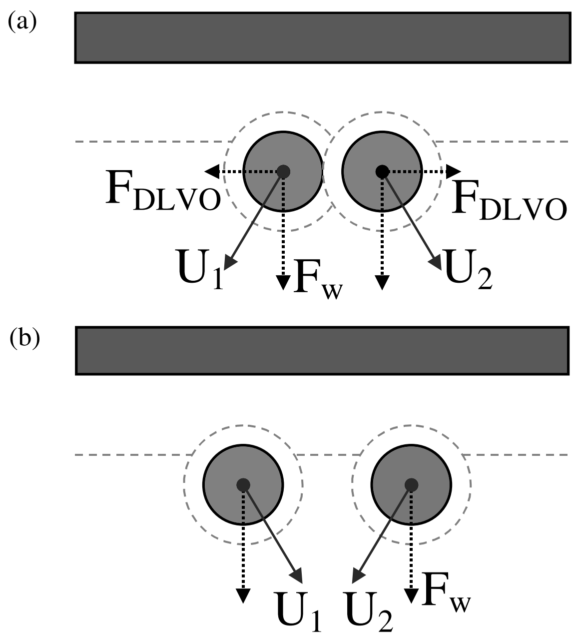

FIG. 2. (a) If the screening clouds of the two spheres overlap sufficiently, the mutual repulsion is stronger than the hydrodynamic coupling. (b) When the spheres are farther apart, the hydrodynamic coupling dominates.

are beyond some critical separation (Fig. 2b), the hydrodynamic coupling due to the wall force overcomes the electrostatic repulsion, so that the relative distance between the spheres decreases as they move away from the wall.

We are now in a position to make quantitative predictions for the role of hydrodynamic coupling in direct measurements of two-particle interaction. Two spheres of radius a initially located a distance r apart and a distance h from the wall move because of both interparticle forces and the repulsive force from the wall. The response of the two spheres to these forces is expressed by the hydrodynamic mobility tensor $\mathbf{b}(\mathbf{X}_1, \mathbf{X}_2)$, defined by

$$\mathbf{v} = \mathbf{b}(\mathbf{X}_1, \mathbf{X}_2) \cdot \mathbf{F}, \tag{1}$$

where $\mathbf{v} = (\dot{\mathbf{X}}_1, \dot{\mathbf{X}}_2)$ are the sphere velocities and $\mathbf{F} = (\mathbf{F}_1, \mathbf{F}_2)$ are the forces on the spheres. The two 3 by 3 blocks along the diagonal represent a sphere's response to a force applied directly to it, and are given by the (isotropic) Stokes mobility $(6\pi\mu a)^{-1}$, with (nonisotropic) wall corrections, where μ is the fluid viscosity. The off-diagonal blocks represent one sphere's motion due to a force on the other. Since small spheres in an external flow are simply advected with the flow, this coupling mobility is given by the fluid velocity at one sphere's position due to a force on the other. An explicit representation of the mobility tensor for these spheres using Blake's solution [11] for the flow due to a point force near a wall is given elsewhere [12].

For analytic tractability and intuitive clarity, we first consider an idealized non-Brownian experiment. Two spheres are initially held a distance r apart and a distance h from the wall, released for a small time Δt, and their *projected* relative displacement $\Delta r = \Delta x_2 - \Delta x_1$ recorded. If this relative displacement were interpreted to result exclusively from an effective interparticle force $F_{\text{eff}} = -\partial_r U_{\text{eff}}$, then one would infer F_{eff} to be given by

$$\Delta r = \{2(b_{X_2X_2} - b_{X_2X_1})|F_{\text{eff}}|\}\Delta t, \tag{2}$$

where $b_{X_2X_1}$ denotes the mobility of sphere 2 in the x direction due to a force in the x direction on sphere 1, and so on. We denote the x direction to lie along the line connecting the spheres, and the z direction to be perpendicular to the wall.

However, the spheres' relative motion arises because of both interparticle forces and the repulsive force from the wall. Utilizing symmetries of the mobility tensor, it is straightforward to show that Δr will be

$$\Delta r = \{2(b_{X_2X_2} - b_{X_2X_1})|F_{\text{p}}| + 2b_{X_2Z_1}F_{\text{w}}\}\Delta t, \tag{3}$$

where F_{p} and F_{w} are, respectively, the repulsive electrostatic sphere-sphere and sphere-wall forces.

Therefore, if one were to assume the measured displacement (3) to arise exclusively from F_{eff} as in (2), one would determine an effective pair potential given by

$$U_{\text{eff}}(r,h) = U_{\text{p}}(r) - \int_{\infty}^{r} \frac{b_{X_2Z_1}(r,h)F_{\text{w}}(h)}{b_{X_2X_2}(h) - b_{X_2X_1}(r,h)}\, dr, \tag{4}$$

where $U_{\text{p}}(r)$ is the true interparticle thermodynamic pair potential, r is the separation between spheres, and h is their distance from the wall. Since $b_{X_2X_1}(r,h) \ll b_{X_1X_1}(h)$, we neglect $b_{X_2X_1}$ and arrive at an explicit form for the inferred effective potential

$$U_{\text{eff}}(r,h) = U_{\text{p}}(r) - \frac{F_{\text{w}}}{1 - \frac{9a}{16h}} \frac{3h^3 a}{(4h^2 + r^2)^{3/2}}. \tag{5}$$

We use the DLVO potential [13] for the electrostatic interaction of two spheres in the form presented by Larsen and Grier [4],

$$\frac{U_{\text{DLVO}}}{k_B T} = Z^2 \lambda_B \left(\frac{e^{\kappa a}}{1 + \kappa a}\right)^2 \frac{e^{-\kappa r}}{r}, \tag{6}$$

where a and Z are, respectively, the radius and effective charge of each sphere, the Bjerrum length $\lambda_B = e^2/\varepsilon k_B T$, and the Debye-Hückel screening length $\kappa^{-1} = (4\pi n \lambda_B)^{-1/2}$, with a concentration n of simple ions in the solution. This formula is obtained using effective point charges in a linear superposition approximation. To determine the repulsive electrostatic force between each sphere and the wall, we used the same effective point-charge approach to obtain

$$\frac{U_{\text{w}}}{k_B T} = 4\pi Z \sigma_{\text{g}} \lambda_B \frac{e^{\kappa a}}{\kappa(1 + \kappa a)} e^{-\kappa h}, \tag{7}$$

where σ_{g} is the effective charge density on the glass wall. We note that while the functional form of this equation is correct, it is not clear that the effective charges in Eqs. (6) and (7) will be exactly the same, as geometric factors buried in each effective charge will vary from situation to situation. A more reliable description of sphere-sphere and wall-sphere interactions will be necessary for quantitative comparisons with independently measured charge densities.

Using all of Larsen and Grier's experimental parameters as inputs to the theory, we plot (5) to obtain the effective potential $U_{\rm eff}$. The only necessary parameter not measured is the surface charge density of the glass walls $\sigma_{\rm g}$, which we take to be $\sigma_{\rm g} = 0.4\sigma_{\rm p}$, well within the range of measured estimates [9]. Figure 3 shows this effective potential for various sphere-wall separations. The hydrodynamic coupling of collective motion away from the wall with relative motion in the plane of the wall leads to what appears to be an attractive component. It is important to emphasize that this hydrodynamic coupling is a *kinematic* effect, and has no thermodynamic significance—if one were to nail down the spheres and measure the forces acting on them, all forces would be repulsive.

As a complement to this analytic approach and in order to make quantitative comparisons with Larsen and Grier's experiment, we simulate the dynamics of this system using (6) and (7) for the (repulsive) sphere-sphere and wall-sphere forces, respectively. We account for Brownian motion of the spheres in the standard Stokes-Einstein fashion, whereby the diffusion tensor is proportional to the mobility tensor, $\mathbf{D} = k_B T \mathbf{b}$ [14–16]. Using all experimental parameters and $\sigma_{\rm g} = 0.4\sigma_{\rm p}$ as explained above, we performed a computer version of Larsen and Grier's experiment, and analyzed the resulting data using their methods [17]. Our results suggest that this approach includes all of the essential ingredients necessary for quantitatively understanding their observations.

In Fig. 4, we present simulations for the two cases presented by Larsen and Grier: the first with the spheres 2.5 μm from the wall, so that they interact significantly with the charge double layer of the wall, and the second starting 9.5 μm from the wall, well outside of the wall's charge double layer. The simulated results show a shallower dip than the analytic ones because the spheres are released and their positions recorded at $1/60$ s intervals in the experiments, so that as they are forced away from the wall, the force from the wall decreases and the wall-driven hydrodynamic coupling becomes weaker. By contrast, the analytic treatment considers instantaneous measurements.

Our theoretical picture agrees quantitatively with measured data. Moreover, there are many consequences of the theory that can be tested experimentally: (1) Effective kinetic potentials can be predicted for different sets of conditions and quantitatively compared with experiments. (2) The hydrodynamic mechanism requires a net drift of the spheres away from the wall, which could be independently measured. In fact, a reexamination of the original data in the one-wall experiment under discussion has revealed an out-of-plane motion of the order of magnitude we predict, although a precise measurement has thus far proved elusive [18]. (3) Finally, the theory provides a simple explanation for the observation that the attraction disappears when the salt concentration is increased. While

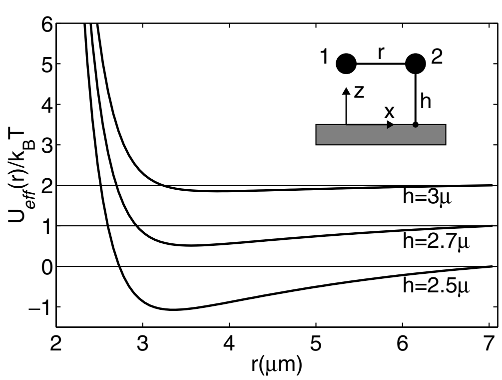

FIG. 3. Plot of the analytic effective potential (4) for three different wall separation distances. The simulated effective potentials (Fig. 4) are slightly shallower because the pair of spheres drifts off the wall into areas with a shallower well during the $1/60$ s measurement intervals.

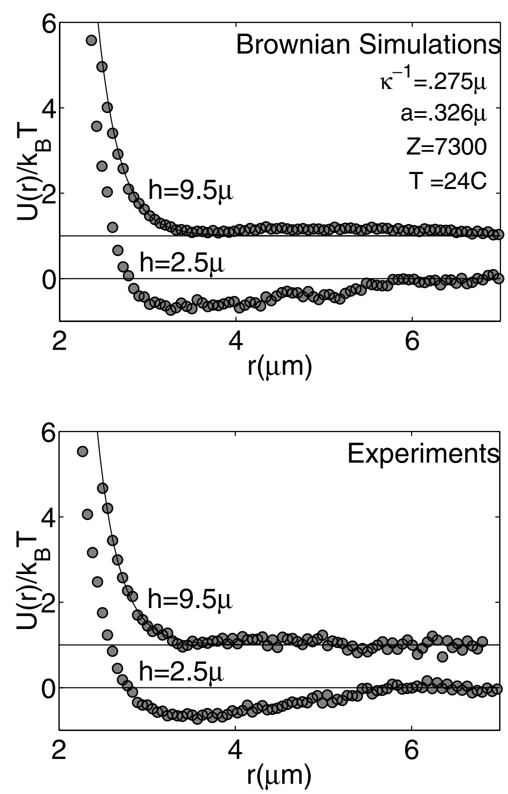

FIG. 4. Comparison between Brownian dynamics simulations and experiments [4] for the effective potential between two colloidal charged spheres near a wall. Two situations are presented: spheres close to the wall ($h = 2.5$ μm) and far from the wall ($h = 9.5$ μm). These are offset by $1k_BT$ for clarity. The simulations were carried out using standard methods [15,16], taking all parameters for the DLVO potential as those measured in the experiments [4]. The simulations were analyzed using the same techniques used in the experiments [17]. The only parameter that is not precisely measured is the charge density on the wall, which we take to be $\sigma_{\rm g} = 0.4\sigma_{\rm p}$.

this at first seems counterintuitive—the spheres are mutually attractive only when they are mutually repulsive—the significance of the wall-driven hydrodynamic coupling makes this clear.

Given that colloidal spheres immersed in a viscous fluid must obey the laws of hydrodynamics, there are only three ways to interpret the present results: (1) hydrodynamic coupling accounts for the entire dip in the measured one-wall pair potential, and therefore no attractive pair potential exists in this geometry; (2) hydrodynamic coupling accounts for some, but not all, of the apparent attraction; or (3) any putative attraction in the pair potential must be smaller than the noise in the present measurements. The second possibility, however, would require the putative attraction to have exactly the same shape as the hydrodynamic coupling—which seems unlikely, although not strictly ruled out.

Several pieces of experimental evidence have been collected which seemed to suggest the existence of an attractive minimum in the thermodynamic pair potential of like-charged colloidal particles in confined geometries. Attractive pair potentials have been observed for two spheres trapped between two walls [3], using methods similar to the one-wall experiment under discussion, and also in experiments using suspensions of spheres trapped between two walls [1,2], in which pair potentials are obtained after accounting for many body effects. In addition, it has been shown that metastable colloidal crystals take orders of magnitude longer to melt than would be expected without a thermodynamic attraction [19]. Similarly, voids in colloidal crystals take much longer to close than expected [20].

The theory presented in this paper applies only when there is a net force pushing spheres off of a wall. It therefore does not apply to the suspension measurements [1,2], since the suspensions are in equilibrium and the spheres fluctuate about the equilibrium position between the two walls. It also would not apply to the direct measurements of two spheres trapped between two walls [3] if it were certain that the two spheres were always placed exactly at the equilibrium position. However, any uncertainty in the centering of the spheres relative to the equilibrium position gives a force off of the nearer wall which leads to a hydrodynamic coupling mimicking an attractive interaction. Furthermore, in these experiments, the spheres' positions are reset with laser tweezers in every measurement, so that any uncertainty in the initial out-of-plane positions occurs systematically in all measurements. Since the uncertainties in wall separation and initial sphere positions are typically ±300–500 nm, which is somewhat more than the spheres move in our one-wall simulations, it not unreasonable to imagine that this directly measured attractive pair interaction could also be hydrodynamic in origin. We have not attempted a quantitative comparison with the experiments due to the large number of unknown experimental parameters.

The theory presented in this paper offers a nonequilibrium hydrodynamic explanation for the attractive potential in the single-wall experiments without invoking a novel thermodynamic attraction. Using exclusively repulsive forces and taking careful account of the hydrodynamics, we have found quantitative agreement with experimental results when the effective wall charge density is chosen to be $\sigma_g = 0.4\sigma_p$, well within the range of measured estimates. Whether the attractive effects observed in experiments are a consequence of many body effects or whether an attractive pair potential exists can be determined only by further experiments which allow a quantitative account for the effects of hydrodynamic coupling.

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