Like-Charge Attraction through Hydrodynamic Interaction

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Abstract

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 385, 230, 1997).
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 \[6\] and Neu \[7\] 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 attractive interaction of two like-charged colloidal spheres measured in the presence of a single wall can arise from a non-equilibrium hydrodynamic effect. The idea is that the relative motion between two spheres depends on both the forces acting between them and in addition, their hydrodynamic coupling. 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 particles could stem from either an interparticle force, or from a hydrodynamic coupling caused by forces acting on each of the particles individually. In a typical experiment with charged colloidal spheres, the charge density on the walls of the cell is of order the charge density on the spheres \[8\]. 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, is consistent with an effective potential between the spheres with an attractive well. Our calculations quantitatively reproduce the experimental measurements of these potentials.

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, Lorentz determined this wall-corrected flow field \[9\], which Blake later expressed using the method of image forces \[10\], 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 particles are pushed away from a wall, the flow field from one particle’s image tends to pull the other particle towards it, and vice versa (Fig. 1). This decreases the distance between the particles.
FIG. 1. Two spheres forced away from a wall are drawn together by hydrodynamic coupling, because the image force of one particle pulls the other particle towards it.

The attractive interaction between two charged spheres in the presence of a 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 are beyond some critical separation (Fig. 2b), the hydrodynamic coupling due to the wall force overcomes the electrostatic repulsion, so that the particles move together as they move away from the wall.
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 further apart, the hydrodynamic coupling dominates.

Although this decrease in mutual separation is a non-equilibrium kinetic effect, it could be interpreted as the result of an attractive equilibrium pair-potential. This is most clearly understood without Brownian motion. Two particles initially located a distance \( r \) apart move because of both interparticle forces and the repulsive force from the wall. The response of these two particles to forces \( \mathbf{F}_1 \) and \( \mathbf{F}_2 \) is expressed by the hydrodynamic mobility tensor \( \mathbf{b}(\mathbf{X}_1, \mathbf{X}_2) \), defined by

\[
\mathbf{v} = \mathbf{b}(\mathbf{X}_1, \mathbf{X}_2) \cdot \mathbf{F},
\]

where \( \mathbf{v} = (\dot{\mathbf{X}}_1, \dot{\mathbf{X}}_2) \) are the particle velocities and \( \mathbf{F} = (\mathbf{F}_1, \mathbf{F}_2) \) are the forces on the particles. Thus, the distance between the spheres (measured in the plane parallel to the walls) will change by an amount \( \Delta r = \Delta x_2 - \Delta x_1 \) in a small time \( \Delta t \), where we denote the \( x \)-direction to be along the line connecting the spheres, and the \( z \)-direction to be perpendicular to the wall. Utilizing symmetries of the mobility tensor, it is straightforward to show that \( \Delta r \) will be

\[
\Delta r = \left\{ 2(b_{X_2X_2} - b_{X_2X_1})|F_p| + 2b_{X_2Z_1}F_w \right\} \Delta t,
\]

where \( F_p \) and \( F_w \) are respectively the repulsive electrostatic sphere-sphere and sphere-wall forces. The tensor component \( b_{X_2Z_1} \) refers to the \( x \)-motion of particle 2 due to a force in the \( z \)-direction on particle 1, and so on.

If this system were assumed to be in equilibrium, then the relative motion would be interpreted as the result of an effective potential, so that an effective force \( \mathbf{F}_{\text{eff}} = -\partial_r U_{\text{eff}} \)

\[
\Delta r = \left\{ 2(b_{X_2X_2} - b_{X_2X_1})|\mathbf{F}_{\text{eff}}| \right\} \Delta t,
\]

so that one would determine this effective potential to be given by
\[ U_{\text{eff}}(r, h) = U_p(r) - F_w \int_{\infty}^{r} \frac{b_{XX_z}(r, h)}{b_{XX_z}(h)} - b_{XX_z}(r, h) \, dr, \quad (4) \]

where \( U_p(r) \) is the interparticle thermodynamic pair potential, \( r \) is the separation between particles, and \( h \) is their distance from the wall.

In order to compare our results with experiments, we determine the hydrodynamic mobilities in the point-force limit, using Blake’s solution \cite{10}. We use the DLVO potential \cite{11, 13} for the electrostatic interaction of two spheres in the form presented by Larsen and Grier \cite{4},

\[ \frac{U_{\text{DLVO}}}{k_B T} = Z^2 \lambda_B \left( \frac{e^{\kappa a}}{1 + \kappa a} \right)^2 e^{-\kappa r} \quad (5) \]

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

\[ \frac{U_{\text{wall}}}{k_B T} = Z \sigma_g \lambda_B \frac{e^{\kappa a}}{\kappa(1 + \kappa a)} e^{-\kappa h} \quad (6) \]

where \( \sigma_g \) 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 equations (5) and (6) 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 numerically integrate (4) to obtain this apparent effective potential. The only necessary parameter not given is the surface charge density of the glass walls \( \sigma_g \), which we take to be \( \sigma_g = 5 \sigma_p \), consistent with Kepler and Fraden’s measurements \cite{1}. Fig. 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 an attractive component. It is important to emphasize that this hydrodynamic coupling is a \textit{kinematic} effect, and has no thermodynamic significance—all forces acting on the spheres are purely repulsive.
FIG. 3. Plot of the analytic effective potential \((\text{4})\) 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.

We note as well that a simple approximate expression exists for the hydrodynamic term in the effective potential \((\text{4})\), since \(b_{X_2X_2}(h)/b_{X_2X_1}(r, h) \sim O(h/a) \gg 1\). Approximating the denominator in the integrand as simply \(b_{X_2X_2}\), we explicitly evaluate the integral to give

\[
U_{\text{eff}}(r, h) = U_p(r) - \frac{F_w}{1 - \frac{3a}{16b}} \frac{3h^3a}{(4h^2 + r^2)^{3/2}}.
\]

(7)

As a complement to this analytic approach, we simulate the dynamics of this system, using (3) and (6) for the sphere-sphere and wall-sphere forces, respectively. We account for Brownian motion of the particles in the standard Stokes-Einstein fashion, whereby the diffusion tensor is proportional to the mobility tensor, \(D = k_B T \mu\). Using all experimental parameters and \(\sigma_g = 5\sigma_p\) 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 microns from the wall, so that they interact significantly
with the charge double layer of the wall, and the second starting 9.5 microns from the wall, well outside of the wall’s charge double layer.

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 µ), and far from the wall (h=9.5 µ). These are offset by 1 $k_B T$ 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 $\sigma_g = 5\sigma_p$.

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 particles away from the wall, which could be independently measured. (3) Finally, the theory provides a simple explanation for the observation that the attraction disappears when the salt concentration is increased. While this at first seems counterintuitive—the particles are mutually attractive only when they are mutually repulsive—the significance of the wall-driven hydrodynamic coupling makes this clear.

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. Besides the one wall experiment under discussion, attractive pair potentials have been observed for two spheres trapped between two walls [3], and for a suspension of spheres trapped between two walls [1,2]. 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 [18]. Similarly, voids in colloidal crystals take much longer to close than
expected [19]. It is not clear how the theory presented here will bear upon these experiments.

The theory presented in this paper offers a non-equilibrium hydrodynamic explanation for the attractive potential in the single-wall experiments without invoking a novel thermodynamic attraction. We have found quantitative agreement with experimental results when the effective wall charge density is chosen to be $\sigma_g = 5\sigma_p$, which is in the ballpark of measured estimates. Without a quantitative measurement of this parameter, this work does not strictly rule out the possibility that a novel attraction exists. This situation can be definitively resolved by more quantitative comparisons with experiments.

Acknowledgments: We are indebted to D. Grier and E. Dufresne for introducing us to their experiments, and for a stimulating collaboration. Useful discussions with J. Crocker, H. Stone, and D. Weitz are gratefully acknowledged. This research was supported by the Mathematical Sciences Division of the National Science Foundation, the A.P. Sloan Foundation, and the NDSEG Fellowship Program (TS).
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