INTERACTIONS IN COLLOIDAL SUSPENSIONS

Electrostatics, Hydrodynamics and their Interplay

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Abstract These lecture notes address some recent advances in our understanding of macroionic interactions inspired in part by the evolution of new techniques for studying macroions’ dynamics.

1. INTRODUCTION

Charged colloidal particles suspended in water interact through hard core repulsions, van der Waals attractions, Coulomb interactions, and hydrodynamic coupling. The particles’ influence on the surrounding medium modifies these interactions, for instance leading to screening of Coulomb interactions by atomic-scale simple ions. It also can give rise to entirely new effects such entropically driven depletion interactions in heterogeneous suspensions and Casimir attractions in solvents near critical points. Bounding surfaces can modify all of these interactions, particularly if they carry their own charges. Competition and cooperation among these influences give rise to a bewildering variety of many-body phenomena including colloidal crystallization (of various kinds), gel formation (of various kinds), glass formation, and a host of shear- and field-induced transitions. Any confidence we might have in our ability to explain and control such cooperative behavior is undermined by the gnawing realization that colloid’s underlying interactions still hold mysteries.

This contribution addresses experimental investigations of interactions in dilute suspensions of monodisperse charge-stabilized spheres
whose behavior should be dominated by screened Coulomb and hydro-
dynamic interactions. Both classes of interactions have come under re-
newed scrutiny in recent years because of an accumulation of anomalous
observations. For example, spheres carrying the same sign charge ap-
pear to attract each other under circumstances for which theory leads
us to expect repulsion. Similarly, velocity fluctuations in sedimenting
spheres are predicted to diverge with system size, but instead appear to
be bounded by an as-yet unexplained mechanism [1]. In both cases, the
anomaly may result from a failure to properly account for many-body
contributions to the spheres’ dynamics.

2. EXPERIMENTAL TECHNIQUES

![Diagram of experimental apparatus](image)

Figure 1. Experimental apparatus for measuring colloidal interactions and dynamics. Based on a conventional optical microscope, this system combines video imaging with optical tweezer manipulation, total internal reflection (TIR) particle tracking, and optical microprobe single-particle light scattering. The entire system, including environmental control and monitoring for the sample, is computer controlled.
2.1. DIGITAL VIDEO MICROSCOPY

Colloidal spheres larger than a couple hundred nanometers are easily observed with a good quality light microscope. Their images can be captured by a video camera, digitized, and analyzed with a computer to obtain remarkably precise measurements of their positions in each video frame. In principle, the pattern of light scattered by a single sphere could be compared with calculated scattering patterns [2] to obtain the sphere's three-dimensional position relative to the microscope’s focal plane, as well as its size and index of refraction. These calculations are quite difficult, however, for spheres comparable in size to the wavelength of light. As a consequence, particle tracking is usually treated phenomenologically, a particle’s centroid being identified with the scattering pattern’s center of brightness [3]. Even this expedient yields high resolution data because a single sphere’s image can subtend several pixels in the imaging plane. The center of brightness for micron-scale spheres can be determined to within 10 nm to 20 nm in the plane with transmitted light microscopy [3]. Consecutive snapshots of $N$ particles’ positions then can be linked into trajectories $\vec{r}_i(t)$ with a maximum likelihood algorithm [3] to yield the particles’ in-plane distribution function

$$\rho(\vec{r}, t) = \sum_{i=1}^{N} \delta^{(2)}(\vec{r} - \vec{r}_i(t)).$$

(1.1)

This time-resolved trajectory data is the basis for all of the experimental results which follow. In many respects, it resembles the results of molecular dynamics simulations. The primary difference is that we will attempt to use these data to shed new light on the interactions responsible for colloidal dynamics rather than trying to discover the dynamics resulting from particular interactions.

2.2. OPTICAL TRAPPING

Simply watching colloidal suspensions’ behavior with single-particle resolution has yielded valuable insights regarding the fundamental mechanisms of structural phase transitions, processes responsible for aggregation and gelation, and the response of complex fluids to external forces. Complementary information becomes available with the ability to manipulate individual colloidal particles. Among the possible techniques, optical tweezers introduced by Ashkin, Dziedzic and Chu [4] offer an unparalleled combination of precision, simplicity, generality, scalability, and non-invasiveness.

An optical tweezer uses forces engendered by optical intensity gradients to drive small particles to the focal point of a tightly focused laser.
beam. A high degree of convergence is necessary to prevent the particles from being dispersed by radiation pressure. Consequently, most optical tweezers are built around optical microscopes, as shown in Fig. 1 taking advantage of the objective lens’ high numerical aperture and optimized optics to achieve a diffraction-limited focus. A collimated laser beam entering an infinity corrected objective’s back aperture comes to a focus and forms a trap in the microscope’s focal plane. In practice, a few hundred microwatts of visible light exerts enough force to localize a micrometer-scale dielectric particle against random thermal forces. Multiple beams entering the objective’s back aperture form multiple optical traps, with the necessary configuration of beams being created with beam splitters [5], holograms [6, 7], spatial light modulators [8] or by timesharing a single beam with high-speed deflectors [9, 10].

The combination of optical tweezer manipulation and digital video microscopy tracking makes possible precise measurements of colloidal interactions and dynamics [3, 5]. In the following sections, we apply these methods to test long-accepted and still-evolving theories for colloidal interactions.

3. ELECTROSTATIC INTERACTIONS

The Coulomb interaction between charged colloidal particles dispersed in a polar solvent is moderated and mediated by a diffuse cloud of surrounding ions. These simple ions are much smaller than the macroionic colloid, and carry much smaller charges. The resulting disparity in dynamical time scales encourages us to define an effective colloidal interaction averaged over the simple ions’ degrees of freedom. How to define and interpret this effective interaction has inspired spirited debate for more than 50 years.

Experimental observations reported over the past few years have raised the surprising possibility that like-charged colloidal spheres sometimes attract each other. If we view the spheres in isolation, their attraction seems counterintuitive. Recalling instead that the overall suspension is electroneutral suggests that unexpected features in the spheres’ effective pair potential must reflect unanticipated dynamics in the surrounding medium. The phenomena discussed in the following sections are noteworthy because they appear to be inconsistent with existing mean field theories. Such discrepancies raise concern about mean field theory’s broader application to macroionic problems as diverse as protein folding, DNA complexation, and the stability of industrial suspensions.
3.1. THE DLVO THEORY

The partition function for \( N \) simple ions of charge \( q_i \) arrayed at positions \( \vec{r}_i \) in the stationary potential \( \phi(\vec{r}) \) is

\[
Q = Q_0 \int_{\Omega} d\vec{r}_1 \cdots d\vec{r}_N \exp \left[ -\beta V(\{\vec{r}_i\}) \right],
\]

where

\[
V(\{\vec{r}_i\}) = \frac{1}{\epsilon} \sum_{i=1}^{N} q_i \phi(\vec{r}_i).
\]

The prefactor \( Q_0 \) results from integrals over momenta and \( \beta^{-1} = k_B T \) is the thermal energy at temperature \( T \). All charged species in the system, including the fixed macroions, contribute to \( \phi(\vec{r}) \). The macroions also exclude simple ions from their interiors, so their volumes are excluded from volume of integration \( \Omega \). Equation (1.3) implicitly adopts the primitive model, approximating the solvent’s influence through its dielectric constant \( \epsilon \).

The partition function can be expressed through the Hubbard-Stratanovich transform as a functional integral over all possible simple-ion distributions

\[
Q = Q_0 \int' Dn \exp \left( -\beta f[n] \right),
\]

where

\[
n(\vec{r}) = \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i),
\]

is one particular distribution whose activity is approximately given by

\[
f[n] \approx V[n] + k_B T \int_{\Omega} n \ln n \, d\Omega.
\]

The prime on the integral in Eq. (1.4) indicates that the simple ions’ number is conserved: \( \int_{\Omega} n \, d\Omega = N \).

Equation (1.6) differs from the exact activity by terms accounting for higher-order correlations among simple ions. Dropping these terms, as we have in Eq. (1.6), yields a thermodynamically inconsistent theory [11], whose redeeming virtue is tractability. Minimizing \( f[n] \) to implement the mean field approximation yields the familiar Poisson-Boltzmann equation

\[
\nabla^2 \phi = -\frac{4\pi}{\epsilon} \sum_{\alpha} n_{\alpha} q_{\alpha} \exp \left( -\beta q_{\alpha} \phi \right),
\]

\( D \) R A F T September 14, 2000, 3:36 pm D R A F T
where the subscript $\alpha$ denotes the various species of simple ions.

By considering only the ionic distribution $n_0(\vec{r})$ which minimizes $f[n]$, the mean field approximation ignores contributions from fluctuations as well as higher-order correlations. Even this simplified formulation is intractable for all but the simplest geometries. In developing the classical theory for colloidal electrostatic interactions, Derjaguin, Landau [12], Verwey and Overbeek [13] (DLVO) invoked the Debye-Hückel approximation, linearizing the Poisson-Boltzmann equation, and solved for the potential

$$\phi(r) = -\frac{Ze}{\epsilon} \frac{e^{\kappa a}}{1 + \kappa a} \frac{e^{-\kappa r}}{r}$$

outside a sphere of radius $a$ carrying charge $-Ze$. The decay of correlations within the simple ion distributions is described by the Debye-Hückel screening length, $\kappa^{-1}$, given by

$$\kappa^2 = \frac{4\pi}{\epsilon k_B T} \sum_\alpha n_\alpha q_\alpha^2.$$  

(1.9)

For the rest of this discussion, we will consider only monovalent simple ions: counterions carrying a single charge $+e$ and coions carrying $-e$.

The Debye-Hückel approximation cannot be valid near the surface of a highly charged sphere. The hope, however, is that nonlinear effects will be confined to a small region very near the sphere’s surface and thus may serve only to renormalize the sphere’s effective charge at longer length scales [14, 15, 16, 17, 18].

We obtain the effective pair potential by integrating Eq. (1.8) over the surface of a second sphere separated from the first by a center-to-center distance $r$. This integration is facilitated by assuming the second sphere’s presence does not disrupt the first sphere’s ion cloud. The resulting superposition approximation yields a screened Coulomb repulsion for the effective inter-sphere interaction,

$$U(r) = \frac{Z^2 e^2}{\epsilon} \left( \frac{e^{\kappa a}}{1 + \kappa a} \right)^2 \frac{e^{-\kappa r}}{r}.$$  

(1.10)

The DLVO theory was developed principally to explain colloidal suspensions’ stability against flocculation under van der Waals attraction. However, dispersion attractions are negligible for well-separated spheres [19, 20] and are omitted from $U(r)$.

### 3.2. PAIR REPULSIONS

Since its development, the DLVO theory has profoundly influenced the study of macroionic systems. Testing its predictions directly through
Figure 2  Left: Colloidal interactions are measured in the carefully controlled environment of a hermetically sealed glass sample container shown here in cross-section. Two spheres are selected with optical tweezers and alternately trapped and released, their motions being recorded at 1/30 sec intervals as shown in the sequence of images. Spheres appear brighter when trapped because of light backscattered from the optical tweezers. Right: Interaction potentials for pairs of polystyrene sulfate spheres dispersed in deionized water at $T = 25^\circ$C. Sphere radii are indicated next to each curve. Solid lines are nonlinear least squares fits to Eq. (1.10). Dashed lines are fits to the Sogami-Ise theory, Eq. (1.14).

measurements on pairs of spheres has only become possible with the recent development of experimental techniques capable of resolving colloids’ delicate interactions without disturbing them. These fall into three categories: (1) measurements based on the equilibrium structure of low density suspensions [21, 22, 23], (2) measurements based on the nonequilibrium trajectories [5, 24, 25, 26] of spheres positioned and released by optical tweezers [27] and (3) measurements based on the dynamics of optically trapped spheres [20, 28]. All rely on digital video microscopy [3] to track the spheres’ motions and consequently would not have been possible before computerized image analysis became readily available.

Methods (1) and (2) take advantage of the Boltzmann relationship

$$\lim_{\rho \to 0} g(r) = \exp[-\beta U(r)]$$

(1.11)
between the spheres’ pair potential and their equilibrium pair correlation function
\[ g(r) = \langle \frac{1}{\bar{\rho} \Omega} \int \rho(\vec{x} - \vec{r}, t) \rho(\vec{x}, t) \, d\vec{x} \rangle, \]  
(1.12)
where \( \bar{\rho} \) is the mean concentration of spheres in area \( \Omega \) and the angle brackets indicate an average over both time and angles. The two approaches differ in how they measure \( g(r) \), but agree in their principal result: isolated pairs of spheres, far from walls and unconfined by their neighbors, repel each other.

Nonequilibrium optical tweezer measurements, such as the examples in Fig. 2 use a pair of optical traps to position two spheres at reproducible separations in a microscope’s focal plane. Extinguishing the traps eliminates any perturbing influence of the intense optical field and frees the particles to move under random thermal forces and their mutual interaction. Their motions are captured at \( \tau = 1/30 \) sec intervals and digitized as described in Sec. 2.1. Each pair of consecutive images, such as the examples in Fig. 2, provides one discrete sampling of the probability \( P(x, \tau|x', 0) \) that two spheres initially separated by \( x' \) will be separated by \( x \) a time \( \tau \) later. Repeatedly trapping and releasing the spheres over a range of initial separations enables us to sample \( P(x, \tau|x', 0) \) accurately. This probability density is the kernel of the master equation [29] for the pair distribution’s time evolution:
\[ \varrho(x, t + \tau) = \int P(x, \tau|x', 0) \, \varrho(x', t) \, dx'. \]  
(1.13)

Eq. (1.13) may be discretized and solved as an eigenvalue problem for the equilibrium distribution \( \varrho(x) \equiv \lim_{\bar{\rho} \to 0} g(x) \) whose logarithm provides a measurement of the pair potential through Eq. (1.11).

Data from reference [24] for three sizes of anionic polystyrene sulfate spheres all dispersed in the same strongly deionized 1:1 electrolyte are reproduced in Fig. 2. Solid curves passing through the data points result from nonlinear least squares fits to Eq. (1.10) for the spheres’ effective charges and the electrolyte’s screening length. As expected [14, 15, 16, 17, 18], the effective charges are one or two orders of magnitude smaller than the spheres’ titratable charges. The screening length of \( \kappa^{-1} = 310 \pm 20 \) nm is comparable to the spheres’ diameters and corresponds to a total ionic strength of \( 10^{-6} \) M, a reasonable value for deionized water at \( T = 25^\circ \)C. The apparent success of the screened-Coulomb functional form does not validate the Debye-Hückel approximation, however, since Kjellander’s analysis of the nonlinear mean-field theory also predicts a screened-Coulomb repulsion under experimental conditions [30].
Comparable results were obtained by Vondermassen et al. [21] from measurements on optical cross-sections of dilute suspensions at low ionic strength. Sugimoto et al. [20] studied pairs of spheres at higher ionic strength trapped in optical tweezers and were able to measure van der Waals attraction’s contribution to the interaction. In all cases, the measured pair potentials agree qualitatively and at least semi-quantitatively with predictions of the DLVO theory.

The observed pair repulsions at low ionic strength pose a challenge to theories predicting long-ranged pair-wise attractions. For example, Sogami and Ise [31, 32] proposed that the colloidal pair potential can develop an attractive tail in the grand canonical ensemble when the number $N$ of simple ions is allowed to vary:

$$U_{SI}(r) = \frac{Z^2e^2}{\epsilon} \left[ 1 + \kappa a \coth \kappa a - \frac{\kappa a}{2} \right] e^{-\kappa a r}. \quad (1.14)$$

This controversial theory has been quoted widely as a possible explanation for many anomalous colloidal phenomena. However, Eq. (1.14) fails to describe measured pair potentials such as those in Fig. 2, as can be seen from the overlaid nonlinear least squares fits. Since Eq. (1.14) fails for isolated pairs of spheres, it cannot be expected to describe the behavior of many spheres through superposition.

### 3.3. METASTABLE SUPERHEATED CRYSTALS

![Figure 3](image)

Figure 3  Electrohydrodynamic crystallization: (a) Initial fluid. (b) Oscillating electric field drives spheres back and forth in the plane and also drives them transversely to the walls (c) where they crystallize. (d) Removing the field allows the now-superheated crystals to melt. (e) Video microscope image of a layered metastable FCC colloidal crystal coexisting with a low density fluid. Superimposed traces indicate the trajectories of selected spheres and distinguish localized spheres in the crystal from freely diffusing spheres in the fluid. Some spheres, such as the one indicated with the arrow, collide with and temporarily bind to the crystal.
Suspensions of purely repulsive monodisperse spheres with pairwise additive interactions are believed to exist in three equilibrium phases: fluid, face-centered cubic (FCC) crystal or body-centered cubic (BCC) crystal. Experiments on charge-stabilized colloidal suspensions have revealed other states, however, including equilibrium liquid-vapor phase separation [33, 34], reentrant solid-liquid transitions [35], stable voids [34], and metastable superheated crystals [26, 36]. These additional states are most easily explained if the pair potential includes an attractive component [31, 32, 33, 34, 35, 37, 38] or if the system develops a many-body cohesion [39, 40].

Metastable crystals such as the example in Fig. 3.3 are made by forcing the spheres in a low density suspension against glass walls through an as-yet-unexplained electrohydrodynamic instability [36]. An oscillating electric field drives the spheres back and forth electrophoretically while simultaneously creating a surface-driven ion flux through electroosmosis. Under a very limited set of conditions, the interplay of hydrodynamic and electric forces drives spheres out of the bulk of the suspension and toward the walls. The volume fraction near the walls increases until several epitaxial layers of close-packed crystal form. The particular example in Fig. 3.3 consist of polystyrene sulfate spheres of radius $a = 0.326 \pm 0.003 \mu m$ (Catalog number 5065A, Duke Scientific, Palo Alto, CA) compressed by a 10 V peak-to-peak 60 Hz signal applied across a 1 mm gap in a cell 90 $\mu$m thick and 1 cm wide. Created in deionized water, such compression-generated crystals can have lattice constants extending to more than 3 $\mu$m. The crystals should melt in a matter of seconds once the compressing field is turned off, at a rate limited by diffusion. Indeed, this is what happens [36] for suspensions whose ionic strength is greater than $10^{-6}$ M. Crystallites in more strongly deionized suspensions, however, can persist for as long as an hour [26, 36], their facets and interfacial fluctuations attesting to a large stabilizing latent heat [26]. Such metastability is not possible in a system whose free energy results from the superposition of pair-wise repulsions [26].

Van Roij, Dijkstra and Hansen [39, 40] have proposed an explanation based on a density functional expansion for the suspension’s free energy. Accounting for simple ions’ mutual interactions to lowest non-trivial order, they obtain a free energy which includes not only a superposition of DLVO-like repulsions but also additional volume terms which may be interpreted as many-body corrections to the free energy. Failing to account for the simple ions’ exclusion from the spheres’ volume in this expansion yields the Sogami-Ise result. Van Roij, Dijkstra and Hansen use their free energy functional to map out the macroions’ phase dia-
gram and, under conditions similar to those reported in [26] and [36], predict crystal-fluid coexistence with an exceptionally large volume fraction contrast. Comparisons with other experiments suggest comparable explanations for void formation and other anomalous bulk phenomena. Despite its apparent success, the density functional theory is still the subject of heated debate, in part because of concerns regarding the convergence of the expansions involved, and in part because it may not explain all of the anomalous observations.

3.4. CONFINED PAIR ATTRACTIONS

Figure 4 Confinement-induced attraction between pairs of colloidal spheres. Pair potential for spheres of radius 0.327 µm confined between parallel glass walls. For large separations, spheres are free to move in all three dimensions and their pair potential resembles that for unconfined spheres. Once the spheres are confined to the mid-plane by electrostatic interactions with the walls, the pair potential has a minimum, indicating long-ranged attractions. At very small wall spacings, spheres also experience an unscreened repulsion mediated by the glass walls.

The same spheres which repel each other in isolation and form metastable crystals when compressed also can develop a strong and long-ranged pair attraction when confined by one or two glass walls. Such attractions were first observed by Kepler and Fraden [22] who measured \( g(r) \) directly by tracking particles in dilute suspensions sandwiched between parallel glass plates and applied Eq. (1.11) to obtain \( U(r) \). Carbajal-Tinoco, Castro-Román and Arauz-Lara reproduced this result, further applying liquid structure theory to demonstrate that many-body correlations could not account for the apparent pair attraction [23]. This interpretation was supported by Rajagopalan and Rao’s analysis of the experimental data with a predictor-corrector algorithm [41].

Optical tweezer measurements [24] such as the middle two examples in Fig. 3.4 confirmed the walls’ role by demonstrating their influence on
two otherwise isolated spheres. Spheres between widely separated walls (Fig. 3.4 top) move freely in three dimensions; their pair potential is described accurately by the DLVO theory. As the walls move closer, the spheres become confined to the midplane by their electrostatic interaction with the glass’ negative charge. At the same time, a long-ranged attractive component becomes evident in the pair potential, yielding an overall minimum roughly $0.5 k_B T$ deep at a separation of about 3 diameters. The challenge is to explain how nearby walls induce attractions between otherwise repulsive spheres and to ascertain whether or not the same mechanism accounts for the observed many-body cohesion in the metastable crystallites.

Neu [42] and Sader and Chan [43] (NSC) have proved that the nonlinear Poisson-Boltzmann equation can only yield repulsions in confined geometries. The NSC proof holds for constant potential boundary conditions, at least some variants of constant charge boundary conditions, and for confining pores of arbitrary cross-section. This important result suggests that confinement-induced like-charge attractions are qualitatively inconsistent with the Poisson-Boltzmann formulation. Trizac recently has extended this proof to exclude steric effects based on the the small ions’ finite size as an explanation [44].

These proofs also appear to contradict recent perturbative calculations [45] which find wall-induced attractions for constant charge boundary conditions. The disagreement might hinge on details of the boundary conditions [45], in which case wall-induced attractions would seem to be a rather specialized phenomenon. The variety of experiments exhibiting like-charge attractions, however, points to a broader context for like-charged colloidal attractions and thus a more general mechanism outside of mean-field theory.

As a further complication, still closer confinement appears to induce a long-ranged repulsion in the pair potential, as in the bottom trace of Fig. 3.4. Stillinger [46] and Hurd [47] analyzed the related problem of charged colloid interacting near an air-water interface. Their results imply a leading-order repulsion of the form

$$\beta U_I(r) = \frac{Z^* 2 \lambda B}{\epsilon g r}$$

mediated by the glass, whose dielectric constant $\epsilon_g$ sets the scale for the effect. The effective image charges, $Z^*$ are reduced below the sphere’s bare charges by screening in the electrolyte, additional screening by the Helmoholtz double layer at the glass-water interface, and by the dielectric mismatch at the interface. The magnitude of this charge renormal-
ization has not been established, so meaningful comparison with experiment is not yet possible.

3.5. DISCUSSION

No consensus has yet emerged regarding which of the DLVO theory’s approximations fails in strongly interacting charge-stabilized colloid, or why this failure leads to qualitatively new phenomena. Although it is far from complete, the existing body of experimental evidence allows us to place constraints on the evolving theory.

So far, no interaction measurement on isolated pairs of spheres has found anomalous attractions. And yet evidence for many-body attractions abounds when the number density of the same spheres is increased. On this basis, we provisionally rule out theories which predict pairwise attractions for isolated spheres.

Image charges in the confining walls, or sphere-induced changes in the walls’ charge state could conceivably lead to attractions. The additional repulsion observed for tightly confined spheres [see, for example, the lowest curve in Fig. 2] provides one counterindication, however. Bulk phenomena such as the observed metastability of superheated colloidal crystallites further indicates that glass surfaces are not necessary to engender many-body colloidal attractions.

Fluctuations in ion density around the spheres seem another likely candidate. Existing calculations suggest that such fluctuations do indeed lead to attractions, but that they are doubly-screened and thus short-ranged [48, 49]. Similarly, careful handling of the kinetics of ion adsorption onto colloidal surfaces leads to short-ranged attraction [50]. The experimentally observed attractions, on the other hand, are longer-ranged than the singly-screened pair repulsion. If ionic fluctuations are responsible, the mechanism must involve modes of fluctuation not yet considered.

Finally, anomalous attractions are observed on length scales extending to several micrometers. It seems unlikely, therefore, that the discrete structure of the solvent or the discrete size of the simple ions can play a role in mediating the attraction. In other words, the primitive model should suffice. However, the solvent can have another influence on the suspended spheres’ dynamics.

Very recently, Squires and Brenner [51] proposed that at least some anomalous colloidal attractions may result from a surprising interplay of electrostatic and hydrodynamic interactions. Exploring this suggestion invites a more thorough discussion of colloidal hydrodynamics, another area in which long-established theories at last can be tested through a
combination of digital video microscopy and optical tweezer manipulation.

4. HYDRODYNAMIC INTERACTIONS

Particles immersed in a fluid excite long-ranged flows as they move, and similarly move in response to passing flows. By generating and reacting to a fluid’s local velocity, colloidal particles experience hydrodynamic interactions with each other and with the walls of their container. Despite its long-recognized ubiquity, such hydrodynamic coupling is incompletely understood. This Section addresses the hydrodynamically coupled dynamics of well-separated particles moving slowly through a viscous fluid, a comparatively simple limiting case of considerable practical importance. In particular, it applies the method of singularities [52], also known as stokeslet analysis, to the hydrodynamics of small colloidal systems and compares the results to recent measurements. The favorable outcome suggests that stokeslet analysis offers a tractable, general, and scalable framework for describing many-body colloidal hydrodynamics.

4.1. STOKESLET ANALYSIS

In general, the local flow velocity \( \vec{u} \) in an incompressible fluid is described by the Navier-Stokes equation

\[
\eta \nabla^2 \vec{u} = \vec{\nabla} p + \rho \left[ \frac{\partial \vec{u}}{\partial t} + (\vec{u} \cdot \vec{\nabla}) \vec{u} \right],
\]

(1.16)

where \( \rho \) is the fluid’s mass density, \( \eta \) is its kinematic viscosity, and \( p \) is the local pressure. In an incompressible fluid with no sources or sinks,

\[
\vec{\nabla} \cdot \vec{u} = 0
\]

(1.17)

completes the description.

If inertial contributions to the flow are damped out by viscous drag, the first term on the left-hand side of Eq. (1.16) dominates the second, and the equation of motion reduces to the Stokes form

\[
\eta \nabla^2 \vec{u} = \vec{\nabla} p.
\]

(1.18)

Eq. (1.18) becomes a good approximation when the characteristic flow speed \( U \) over a characteristic length scale \( L \) is sufficiently small, a relationship codified by the Reynolds’ number \( \text{Re} \):

\[
\text{Re} = \frac{\rho U L}{\eta} \ll 1.
\]

(1.19)
For a neutrally buoyant colloidal particle a micron in diameter moving through water at less than 100 \( \mu \text{m/sec} \), \( Re < 10^{-4} \) and the Stokes approximation seems well justified. The Reynold’s number’s nebulous definition can lead to confusion when small particles (with correspondingly small Re) excite long-ranged flows in comparatively large systems. The present discussion focuses on small numbers of spheres in confined geometries, and so side-steps this issue.

Flows vanish on solid surfaces thus setting boundary conditions for solutions to Eqs. (1.17) and (1.18). Once these boundary conditions are satisfied, we can calculate the viscous drag on a particle by integrating the pressure tensor

\[
\Pi_{\alpha\beta} = -p \delta_{\alpha\beta} + \eta (\nabla_\alpha u_\beta + \nabla_\beta u_\alpha)
\]

over its surface:

\[
F_\alpha = \int_S \Pi_{\alpha\beta} dS_\beta.
\]

**A sphere in an unbounded fluid.** Stokes used this approach in 1851 to obtain the force needed to translate a sphere of radius \( a \) through an otherwise quiescent fluid of viscosity \( \eta \) at a constant velocity \( \vec{v} = v \hat{z} \). The flow past the sphere has the form

\[
\frac{u_\alpha(\vec{r})}{v} = \frac{3}{4} a \left( \frac{\delta_{az}}{r} + \frac{z r_\alpha}{r^3} \right) + \frac{1}{4} a^3 \left( \frac{\delta_{az}}{r^3} - \frac{3 z r_\alpha}{r^5} \right),
\]

where \( \vec{r} \) is the distance from the sphere’s center and \( z \) the displacement along the direction of motion. The flow’s contribution to the pressure is

\[
p(\vec{r}) = \frac{3}{2} \eta a \frac{\vec{r} \cdot \vec{v}}{r^3}.
\]

Substituting these into Eqs. (1.20) and (1.21) yields

\[
\vec{F} = \gamma_0 \vec{v},
\]

for the drag, where the sphere’s drag coefficient is

\[
\gamma_0 = 6 \pi \eta a.
\]

The same drag coefficient parameterizes the force needed to hold the sphere stationary in a uniform fluid flow \( \vec{u} \). Conversely, a constant force \( \vec{F} \) applied to the sphere causes it to attain a steady-state velocity

\[
\vec{v} = b_0 \vec{F},
\]
where \( b_0 = 1/\gamma_0 \) is the sphere’s mobility.

Similar calculations for more complicated systems can be acutely difficult; very few have analytic solutions. For this reason, a daunting variety of approximation schemes have been devised for hydrodynamic problems, most specialized to particular geometries and flow conditions. Progress for many-body systems such as colloidal suspensions has been steady, but slow.

**Faxén’s Law.** The foundation for the analysis which follows is provided by Faxén’s first law [53], introduced in 1922. It relates the force experienced by a sphere at \( \vec{r} \) moving with velocity \( \vec{v} \) through a fluid to characteristics of the flow field \( \vec{u}(\vec{r}) \) around it:

\[
\frac{\vec{F}}{6\pi\eta a} = [\vec{u}(\vec{r}) - \vec{v}] + \frac{a^2}{6} \nabla^2 \vec{u}(\vec{r}).
\]  

(1.27)

If pressure gradients are small over the sphere’s diameter, then the second term on the right-hand side of Eq. (1.27) may be ignored. In this approximation, the sphere is simply advected by the external flow.

**The mobility tensor.** This observation immediately suggests a simplified approach to colloidal hydrodynamic coupling. Consider a sphere labelled \( j \), located at \( \vec{r}_j \) within a suspension. A force \( \vec{f}(\vec{r}_j) \) applied to this sphere excites a flow \( \vec{u}(\vec{r} - \vec{r}_j) = H(\vec{r} - \vec{r}_j) \vec{f}(\vec{r}_j) \) at displacement \( \vec{r} \). This linear relationship is guaranteed by the form of the Stokes equation, and the constant of proportionality, \( H \), is known as the Oseen tensor and is obtained from Eqs. (1.22), (1.24) and (1.25). At large enough distances, \( \vec{u} \) appears sufficiently uniform that a sphere at \( \vec{r}_i \) is simply advected according to Faxén’s law:

\[
v_\alpha(\vec{r}_i) = u_\alpha(\vec{r}_i) = b_{i\alpha,j\beta} f_\beta(\vec{r}_j),
\]  

(1.28)

(1.29)

where \( b_{i\alpha,j\beta} \) is a component of a mobility tensor describing sphere \( i \)'s motion in the \( \alpha \) direction due to a force applied to sphere \( j \) in the \( \beta \) direction. More to the point, \( b_{i\alpha,j\beta} = H_{i\alpha,j\beta}(\vec{r}_i - \vec{r}_j) \). Similarly, \( b_{i\alpha,i\alpha} = b_0 \) describes the sphere’s own response to an external force.

Any number of sources may contribute to the flow past sphere \( i \), with each of their contributions adding linearly in the Stokes approximation. The mobility tensor therefore may be factored into a self-mobility and a mobility due to all external sources,

\[
b_{i\alpha,j\beta} = \delta_{i\alpha,j\beta} \frac{\delta_{i\alpha,j\beta}}{6\pi\eta a} + b^e_{i\alpha,j\beta}.
\]  

(1.30)
All of the results we will obtain follow from this equation, once the necessary flow fields have been calculated. In particular, we will consider contributions from two sources: (1) neighboring spheres and (2) bounding planar surfaces.

The stokeslet approximation. The flow field generated by a moving sphere is essentially independent of the sphere’s radius when viewed at sufficiently large distances. Consequently, we may approximate the flow field around a sphere driven through an unbounded fluid by the flow due to a unit force on a point within the fluid. The corresponding Oseen tensor is the Green’s function for the system:

\[
G^S_{\alpha\beta}(\vec{r}) = \frac{1}{8\pi\eta} \left( \frac{\delta_{\alpha\beta}}{r} + \frac{r_{\alpha}r_{\beta}}{r^3} \right). 
\]

This Green’s function plays an important role in many hydrodynamic problems and is known as a stokeslet. Comparison with Eq. (1.22) shows that \(G^S\) is indeed a good approximation for \(H\) when \(r > a\).

4.2. PAIR DIFFUSION [54]

As a first application of the stokeslet approximation to colloidal hydrodynamics, we calculate two colloidal spheres’ hydrodynamic coupling in an unbounded fluid. Each sphere moves in the flow field \(G^S\) due to its neighbor. The corresponding mobility tensor is

\[
b_{i\alpha,j\beta} = \delta_{ij}\delta_{\alpha\beta} \frac{6}{6\pi\eta a} + (1 - \delta_{ij}) G^S_{\alpha\beta}(\vec{r}_i - \vec{r}_j) 
\]

with \(i, j = 1, 2\). This result describes the spheres’ hydrodynamic interactions at separations large compared with their diameters. It is not in the most convenient form for comparison with optical tweezer measurements, however. For those purposes, we relate spheres’ mobility to their more easily measured diffusivity.

Mobility and diffusivity. A sphere suspended in a fluid follows a random thermally-driven trajectory \(\vec{r}(t)\) satisfying

\[
\langle |r_\alpha(t) - r_\alpha(0)|^2 \rangle = 2D_\alpha t, 
\]

where the angle brackets indicate an ensemble average, and \(D_\alpha\) is the sphere’s diffusion coefficient in the \(\alpha\) direction. In 1905, Einstein demonstrated that a sphere’s diffusivity at temperature \(T\) is simply related to its mobility through the now-familiar Stokes-Einstein relation

\[
D_0 = \frac{k_B T}{6\pi\eta a}. 
\]
where $k_B$ is Boltzmann’s constant. This was the first statement of the more general fluctuation-dissipation theorem which plays an important role in statistical mechanics. Batchelor generalized Einstein’s derivation to systems of $N$ particles: The probability to find $N$ particles at equilibrium in a particular configuration $\{\vec{r}_1, \ldots, \vec{r}_N\}$ depends on their interaction $\Phi(\vec{r}_1, \ldots, \vec{r}_N)$ through Boltzmann’s distribution, $P(\vec{r}_1, \ldots, \vec{r}_N) = \exp \left[ -\frac{\Phi}{k_B T} \right]$. The corresponding force $-\vec{\nabla} \Phi = k_B T \vec{\nabla} P / P$ drives a probability flux $k_B T b \vec{\nabla} P$, where $b(\vec{r}_1, \ldots, \vec{r}_N)$ is the particles’ mobility tensor. The system reaches equilibrium when this interaction-driven flux is balanced by a diffusive flux $-D \vec{\nabla} P$. It follows that the $N$-particle diffusivity is

$$D = k_B T b.$$ (1.35)

Elements of $D$ parameterize generalized diffusion relations [55]

$$\langle \Delta r_{i\alpha}(\tau) \Delta r_{j\beta}(\tau) \rangle = 2 D_{i\alpha,j\beta} \tau.$$ (1.36)

describing how particle $i$’s motion in the $\alpha$ direction couples to particle $j$’s in the $\beta$ direction. Off-diagonal terms in $D$ thus encode hydrodynamic interactions and lead to coupling of the spheres’ motions.

$D$ can be diagonalized by changing variables to a basis of coordinates $\psi$ consisting of linear combinations of the $\vec{r}_i$. These linear combinations are normal modes of the system in that they evolve without mixing; they offer natural experimental probes of the particles’ dynamics.

**Normal mode diffusivity.** In the particular case of two identical spheres, diagonalizing the diffusivity tensor yields diffusion coefficients for collective (C) motion of the center-of-mass coordinate $\vec{R} = \vec{r}_1 + \vec{r}_2$ and relative (R) motion $\vec{r} = \vec{r}_1 - \vec{r}_2$, with one set of normal modes directed perpendicular ($\perp$) to the initial separation, and the other parallel ($\parallel$):

$$D_{\perp}^{C,R}(r) = \frac{D_0}{2} \left[ 1 \pm \frac{a^3}{r^3} + O \left( \frac{a^3}{r^3} \right) \right],$$ (1.37)

$$D_{\parallel}^{C,R}(r) = \frac{D_0}{2} \left[ 1 \pm \frac{a^3}{r^3} + O \left( \frac{a^3}{r^3} \right) \right].$$ (1.38)

Positive corrections apply to collective modes and negative to relative. The collective diffusion coefficients $D_{\perp}^{C}$ and $D_{\parallel}^{C}$ are enhanced by hydrodynamic coupling because fluid displaced by one sphere entrains the other. Relative diffusion coefficients $D_{\perp}^{R}$ and $D_{\parallel}^{R}$ are suppressed, on the other hand, by the need to transport fluid into and out of the space between the spheres.
Batchelor [56] obtained comparable results in 1976 by solving the Stokes equations in bispherical coordinates. In so doing, he also obtained additional terms up to $O(a^6/r^6)$. This observation highlights both the weakness and the strength of stokeslet analysis. The stokeslet $G^S$ depends only on a sphere’s position and not on its radius. Consequently, Eq. (1.32) contains information only to linear order in $a$. On the other hand, Eq. (1.32) can be generalized readily to any number of spheres, and the associated diffusivity tensor diagonalized to obtain the independent collective modes in any configuration. Stokeslet analysis trades accuracy for efficacy.

Having applied so many approximations in deriving Eqs. (1.37) and (1.38) the reader might be concerned about the results’ accuracy. Figure 5 shows the four normal modes’ measured diffusion coefficients for silica spheres of radius $a = 0.495 \pm 0.025$ µm (Lot 21024, Duke Scientific, Palo Alto, CA) suspended in water. Electrostatic interactions were minimized by adding 2 mM NaCl to the suspension, and the temperature was stabilized at $T = 29.00 \pm 0.05$°C. Under these conditions, the viscosity of water is $\eta = 0.817$ cP, so that a single sphere’s free-diffusion coefficient should be $D_0 = 0.550 \pm 0.028$ µm²/sec.

An isolated pair of spheres was captured with optical tweezers, raised to 25 µm above the nearest surface and released, their motions being tracked through digital video microscopy for 5/30 sec thereafter. Repeatedly positioning and releasing the spheres over a range of initial separation yielded statistically large samples of the spheres’ hydrodynamically coupled motions in the plane. These were binned in $r$ and analyzed according to Eq. (1.36) to extract the plotted diffusivities. In the absence of hydrodynamic coupling, the spheres’ pair diffusivities would be $2D_0$, shown as a dashed line in Fig. 5. Indeed, this is the limiting behavior for large separations, as might be expected. The dashed curves resulting from Eqs. (1.37) and (1.38) agree well with the measurements, with no adjustable parameters.

Crocker [57] reported a larger data set for two polystyrene microspheres in the space between two widely separated glass surfaces. Although the experimental data were correspondingly cleaner, they agreed less well with Eqs. (1.37) and (1.38). Crocker surmised that the spheres’ hydrodynamic coupling to the nearer wall reduced their diffusivities, and that this affected collective diffusion more than relative. However, a quantitative analysis of a wall’s influence was not available and the correction was treated semi-empirically. The data in Fig. 5 were obtained far enough from bounding surfaces that wall-induced drag could be neglected.
The same experimental technique used to acquire diffusion data far from bounding surfaces also can be used to probe diffusion as a function of distance from a wall. Optical tweezers can be used to position spheres reproducibly at any height above the surface, thereby permitting efficient data collection as a function of height. Coupling to bounding surfaces is another area where stokeslet analysis can provide quantitative predictions for colloidal dynamics. It also is an area where previous efforts have provided accurate results for a few configurations against which we can test stokeslet analysis’ efficacy.

4.3. HYDRODYNAMIC COUPLING TO A WALL

The flow field around a moving sphere, like a stokeslet, spans an unbounded system. A wall’s no-flow boundary condition modifies the flow field, breaking its symmetry and increasing the drag. Faxén addressed this problem in 1927 with his method of reflections. He obtained the diffusivity for a sphere at height $h$ above a wall moving parallel (||) to the surface:

$$D_{||}(h) = D_0 \left[ 1 - \frac{9}{16} \frac{a}{h} + \frac{1}{8} \frac{a^3}{h^3} - \frac{45}{256} \frac{a^4}{h^4} - \frac{1}{16} \frac{a^5}{h^5} + O \left( \frac{a^6}{h^6} \right) \right].$$  \hspace{1cm} (1.39)

The method of reflections is challenging even for this configuration and cannot be generalized to many-body systems.

As early as 1906, Lorentz reported the Green’s function for flow near a flat surface. Seventy years later, Blake [58] recognized that Lorentz’s
result could be reinterpreted by analogy to electrostatics. He suggested that the flow due to a stokeslet could be canceled on a bounding surface by conceptually placing its hydrodynamic image on the opposite side. Solutions to the Stokes equations being unique, the resulting flow must be Lorentz’s Green’s function for bounded flow.

In electrostatics, the image needed to cancel a charge distribution’s field on a surface is just an appropriately scaled duplicate of the initial source. In hydrodynamics, the image of a stokeslet is not simply another stokeslet, but rather a more complicated combination including sources which Blake dubbed a stokeslet doublet (D) and a source doublet (SD). This combination is depicted schematically in Fig. 6. The flow due to the entire image system is described by the Green’s function [58]

\[
G^W_{\alpha\beta}(\vec{r} - \vec{R}) = -G^S_{\alpha\beta}(\vec{r} - \vec{R}) + 2h^2 G^D_{\alpha\beta}(\vec{r} - \vec{R}) - 2h G^{SD}_{\alpha\beta}(\vec{r} - \vec{R}),
\]

(1.40)

where \(\vec{R} = \vec{r} - 2h\hat{z}\) is the position of the image and

\[
G^D_{\alpha\beta}(\vec{x}) = \frac{1 - 2\delta_{\beta z}}{8\pi\eta} \frac{\partial}{\partial x_\beta} \left( \frac{x_\alpha}{x^3} \right)
\]

(1.41)

\[
G^{SD}_{\alpha\beta}(\vec{x}) = (1 - 2\delta_{\beta z}) \frac{\partial}{\partial x_\beta} G^S_{\alpha\beta}(\vec{x})
\]

(1.42)
are Green’s functions for a source doublet and a stokeslet doublet, respectively.

Applying Faxén’s first law and identifying \( b'_{\alpha\beta} = G^W_{\alpha\beta} \) leads, after some calculation, to

\[
D^S_{\parallel}(h) = D_0 \left[ 1 - \frac{9}{16} \frac{a}{h} + \mathcal{O} \left( \frac{a^3}{h^3} \right) \right],
\]

(1.43)

where the \( S \) superscript distinguishes this result from Eq. (1.39). As before, we are left wondering whether or not the higher-order terms in the more specialized analysis are important.

Figure 6 shows typical data obtained with optical tweezers and digital video microscopy for a silica sphere’s diffusion above a wall. The particular sphere for this data set was one of the pair studied in the previous section, and was probed under the same conditions. The sphere’s height above the wall was repeatedly reset by the optical tweezer at \( \tau = 83 \) msec intervals. During this period of free motion, it could diffuse no more than \( \Delta z = \sqrt{2D_0\tau} = 0.3 \) \( \mu \)m out of plane. Advancing the microscope’s focus in intervals of \( 1.0 \pm 0.3 \) \( \mu \)m allowed us to sample the dynamics’ dependence on height above the wall. Comparison with Eqs. (1.39) and (1.43) reveal that the first order stokeslet result agrees well with measurements, with no free parameters.

4.4. PAIR DIFFUSION NEAR A WALL

\[ D^C(r, h) \]
\[ D^R(r, h) \]

Figure 7 Measured in-plane pair diffusion coefficients for two silica spheres 1 \( \mu \)m in diameter suspended in water at \( T = 29^\circ \)C a height \( h = 1.55 \pm 0.06 \) \( \mu \)m above a glass wall.

In his 1927 treatise, Oseen suggested that Faxén’s results might be applied to more complicated systems even if his methods could not. Oseen
pointed out that the drag on a sphere near a wall can be factored into the sphere’s drag in an unbounded system and an additional contribution due to the wall:

$$\gamma_\alpha(h) = \gamma_0 + \gamma^w_\alpha(h). \quad (1.44)$$

He proposed that the drag coefficient for motion in a given direction might be approximated by linearly superposing individual contributions $\gamma_i$ from all bounding surfaces and neighboring particles:

$$\gamma(\vec{r}) \approx \gamma_0 + \sum_{i=1}^{N} \gamma_i(\vec{r} - \vec{r}_i). \quad (1.45)$$

Oseen himself emphasized that this cannot be rigorously correct because it violates boundary conditions on all surfaces. Even so, if the surfaces are well-separated, the errors may yet be acceptably small. Largely on the basis of this hope, Oseen’s linear superposition approximation has been widely adopted.

The data in Fig. 7 show measured in-plane pair diffusion coefficients for 1 $\mu$m diameter spheres positioned by optical tweezers at $h = 1.55 \pm 0.66 \mu$m above a glass wall. These are the same spheres as were studied in the previous two sections. Naively adding the drag coefficients [53] due to sphere-sphere and sphere-wall interactions yields $D^{-1}_\psi(r, h) = D^{-1}_\psi(r) + [D^{-1}_\parallel(h) - D^{-1}_0]/2$. Results of this linear superposition approximation appear as dashed curves in Fig. 7. While adequate for spheres more than 50 radii from the wall, linear superposition underestimates the wall’s influence for smaller separations.

A more complete treatment not only resolves these quantitative discrepancies but also reveals an additional influence of the bounding surface on the spheres’ dynamics: the highly symmetric and experimentally accessible modes parallel to the wall are no longer independent. As shown in Fig. 8, each sphere interacts with its own image, its neighbor, and its neighbor’s image. These influences contribute $b^{e_{\alpha,j\beta}}_{i\alpha,j\beta} = (1 - \delta_{ij}) G^S_{\alpha\beta}(\vec{r}_i - \vec{r}_j) + G^W_{\alpha\beta}(\vec{r}_i - \vec{R}_j)$ to the mobility of sphere $i$ in the $\alpha$ direction. Eigenvectors of the corresponding diffusivity tensor appear in Fig. 8. The independent modes of motion are rotated with respect to the bounding wall by an amount which depends strongly on both $r$ and $h$. Even though the experimentally measured in-plane motions are not independent, they still satisfy Eq. (1.36) with pair-diffusion coefficients $D^C_{\alpha,R}(r, h) = D_{1\alpha,1\alpha}(r, h) \pm D_{1\alpha,2\alpha}(r, h)$, where the positive sign corresponds to collective motion, the negative to relative motion, and $\alpha$ indicates directions either perpendicular or parallel to the line connect-
ing the spheres’ centers. Explicitly, we obtain

\[
\frac{D_{\perp}^{C,R}(r,h)}{2D_0} = 1 - \frac{9}{16} \frac{a}{h} \pm \frac{3}{4} \frac{a}{r} \left[ 1 - \frac{1 + \frac{3}{2} \xi}{(1 + \xi)^{3/2}} \right]
\]

and

\[
\frac{D_{\parallel}^{C,R}(r,h)}{2D_0} = 1 - \frac{9}{16} \frac{a}{h} \pm \frac{3}{2} \frac{a}{r} \left[ 1 - \frac{1 + \xi + \frac{3}{2} \xi^2}{(1 + \xi)^{5/2}} \right]
\]

up to \(O(a^3/r^3)\) and \(O(a^3/h^3)\), where \(\xi = 4h^2/r^2\). These results appear as solid curves in Figs. 6 and 7. Not only does the stokeslet approximation perform better than linear superposition for spheres close to a wall, it performs equally well at all separations we have examined.

5. ELECTROHYDRODYNAMIC COUPLING

5.1. THE SQUIRES-BRENNER THEORY

In the ongoing quest to explain charged colloid’s anomalous interactions in confined geometries, Squires and Brenner [51] applied results from the previous section to a new analysis of nonequilibrium optical tweezer measurements. Their result is a previously unsuspected electrohydrodynamic mechanism for like-charge attractions. Two spheres pulled close to a repulsive wall by optical tweezers will retreat from the wall when released. Such concerted motion leads to no hydrodynamic coupling for spheres in an unbounded fluid [53]. Symmetry considerations had been invoked to preclude the possibility of lateral coupling for
bounded spheres, too. However, Fig. 8 demonstrates that normal and lateral motions are coupled. The retreating pair consequently experiences a hydrodynamic attraction to each other driven by the electrostatic repulsion from the wall. This electrohydrodynamic interaction is long-ranged and could explain the wall-induced attractions measured in [26]. It is difficult to decide, however, if the observed particle affinity is due to this electrohydrodynamic coupling alone, since experimental parameters like the charge density of the glass are not known with sufficient accuracy. Furthermore, it is unclear whether a similar analysis for spheres bounded by two walls would lead to similar results, although work along these lines is ongoing [59].

5.2. EQUILIBRIUM INTERACTIONS NEAR A SINGLE WALL

![Figure 9](image)

Figure 9  Pair correlation function for sedimented monolayer of silica spheres at two different areal densities together with effective pair potential extracted from the HNC equation. The same pair potential characterizes the structure of both monolayers.

While the Squires-Brenner mechanism may explain like-charge attractions observed with optical tweezers, it cannot explain equilibrium attractions; no net lateral coupling can result from random motions toward and away from a bounding wall. And yet, equilibrium attractions have been observed in doubly-confined monolayers. It would be interesting to learn, therefore, whether confinement by a single wall can induce equilibrium like-charge attractions. We have addressed this question by performing equilibrium measurements of particle interactions near a wall. In discussing its results, we also take the opportunity to point out some requirements and common pitfalls in the determination of pair interaction energies from measured radial distribution functions.
We studied monolayers of silica spheres (1.58 \( \mu \text{m} \) diameter, Catalog # 8150, Duke Scientific, Palo Alto, CA) sedimented in deionized water (Barnstead Nanopure) onto the bottom surface of the glass sample cell shown schematically in Fig. 2. The particles are small enough to undergo Brownian motion, yet heavy enough to sediment into a well-defined monolayer a matter of minutes. Their equilibrium height is set by balancing gravitation against electrostatic repulsion from the glass. For low particle concentrations, all the particles subsequently stayed within a thin layer of fluid, their diffusion essentially restricted to two dimensions. The sample cell’s thickness of 200 \( \mu \text{m} \) ensured that coupling to the upper wall could be neglected.

The suspension was maintained at low ionic strength by diffusive contact with mixed bed ion exchange resin in the sealed access tubes, and its temperature was maintained at 29.0 \( \pm \) 0.1 \( ^\circ \text{C} \) with a transparent temperature controller attached to the top surface. Typically, 25 spheres were visible in the 70 \( \times \) 52 \( \mu \text{m}^2 \) field of view at any time.

Variations in the spheres’ height above the wall due to thermal fluctuations were not measured, but should be no larger than \( \Delta h = 0.1 \mu \text{m} \). This is consistent with the observed absence of fluctuations in their appearance despite our microscope’s limited \( \pm 0.1 \mu \text{m} \) depth of focus. The neglected antagonistic effects of electrostatic sphere-wall repulsion (softening the hard wall potential) and van der Waals attraction (augmenting the gravitational restoring force) should not alter this value dramatically. We conclude that it will be legitimate to treat the equilibrium motion of these sedimented spheres as two-dimensional.

Imaging and binning pair separations yields a measurement of \( g(r) \) for a given areal density \( n \) of spheres. If \( n \) is sufficiently low, the potential \( U(r) \) emerges from Boltzmann’s relation:

\[
U(r) = -k_B T \ln g(r),
\]

so that structure in \( g(r) \) reflects structure in the pair potential. This simple relation has been used for direct evaluations of the pair interaction in very dilute suspensions [21]. For finite \( n \), the radial distribution function also reflects the interaction of a pair of particles with other nearby particles, and generally

\[
W(r) = -k_B T \ln g(r)
\]

is the potential of mean force, a distinct quantity from \( U(r) \). There is no simple exact expression relating \( U(r) \) to either \( W(r) \) or \( g(r) \), but unless the concentration is very high, reliable approximations can be expected from integral equations. For colloidal systems, the Ornstein-
Zernike equation for the direct correlation function

\[ c(r) = g(r) - 1 - n \int c(r') \left[ g(|r' - r|) - 1 \right] d^2r' \]  

(1.50)

(here in its two-dimensional form) in conjunction with an appropriate closure relation has proven particularly useful [60]. Good results for “soft” potentials are typically obtained with the hypernetted chain closure

\[ c(r) = -U(r)/k_B T + g(r) - 1 - \ln g(r). \]  

(1.51)

Carbajal-Tinoco et al. used this approach to analyze the structure of polystyrene spheres confined by two walls and concluded that the pair interaction included a long-ranged attraction [23].

A trustworthy statistical evaluation of pair interactions obviously requires adequate sampling of all the particle separations considered. The implied practical constraints are less obvious, however, and, to our knowledge, no quantitative criterion for “adequate sampling” has so far been proposed.

The presented measurements rely on the detection of systematic deviations from a perfectly random particle distribution. It is essential, therefore, to choose the amount of experimental data large enough that particle separations in the range of interest would occur at least once in the reference system of non-interacting particles.

Let \( A_r \) be the area for which a pair separation \( \leq r \) between randomly distributed spheres would be realized exactly once on average. If the concentration \( n \) is low, then \( A_r \) will be larger than the experimentally available viewing area \( A_{exp} \), and thus a number \( N_r = A_r/A_{exp} > 1 \) of uncorrelated images will be necessary in order to sample this range of separations. We will consider a set of frames to be statistically independent if they were recorded at time intervals of at least the time

\[ \tau = (4Dn)^{-1} \]  

(1.52)

that it typically takes particles with diffusion constant \( D \) to move across the average inter-particle distance \( n^{-1/2} \). Then the time required to sample separations of \( r \) or smaller is given by \( T(r) = N(r)\tau \).

The required number of frames \( N_f \) can be found by considering a circular sampling area of radius \( r \). The average number of randomly distributed particles contained in this area at any given time is \( n \pi r^2 \), and the average number of pairs is \( N_r = (n \pi r^2)^2 / 2 \). Thus, \( 1/N_r \) is the factor by which the original area \( \pi r^2 \) has to be multiplied in order to obtain the area \( A_r = N_f A_{exp} \) accommodating an average of one pair of
particles with a separation smaller or equal to $r$. In summary, the time required to sample all particle separations down to some value $r$ just once is

$$T(r) = N_t \tau = [2\pi r^2 D \exp n^3]^{-1}. \tag{1.53}$$

Correspondingly larger sampling times will be chosen to get the desired statistical accuracy.

Although the above arguments are by no means rigorous and some of the thresholds involved could have been chosen differently, we do expect Eq. (1.53) to show the correct scaling behavior. In particular, it is important to note the rapid increase of the required sampling time with decreasing particle concentration. Because of the difficulties to keep parameters like the concentration, temperature, and the ionic strength constant over long periods of time, statistical accuracy strongly favors larger particle concentrations. On the other hand, interpreting the measured correlations becomes increasingly difficult at larger concentrations, and above a certain concentration the available schemes to account for many-body effects no longer converge. The chosen particle concentrations represent a subtle compromise between statistical and interpretive considerations.

**The radial distribution function.** Figure 9 shows pair correlation functions measured for our spheres at two different areal densities. Both curves indicate a repulsive interaction causing particle depletion from a zone about twice as large as the particle diameter $\sigma = 2a$. Beyond this “effective diameter”, both curves indicate a preferred center-to-center separation between two and three diameters. The curve for higher particle concentration clearly shows the onset of the oscillatory behavior that is typical of a structured fluid, and the height of the corresponding maximum in $g(r)$ is seen to depend strongly on the concentration. Interestingly, no such dependence was found in a similar study on spheres in a thin slit, where very similar rescaled concentrations $n^* = n\sigma^2$ were used [61].

**The interaction energy.** Oscillations in $g(r)$ correspond to minima in the potential of mean force. Applying Eqs. (1.50) and (1.51) to these data, however, remove all traces of these oscillations, as shown in Fig. 9. The dip in the potential of mean force, which might have been mistaken for an attractive component of the pair potential is due entirely to many-particle interaction.

In contrast to the radial distribution function from which it was calculated, our result for the pair potential $u_{HNC}(r)$ should be independent
of the concentration. In order to check this, we have used the pair potential $u_{\text{HNC}}(r)$ computed from data for $n^*=0.05$ as the input for a forward HNC calculation predicting the radial distribution function at $n^*=0.08$. The observed agreement with the experimental curve at that concentration demonstrates that our implementation of the HNC is self-consistent.

With thus reinforced confidence in the accuracy of the extracted pair potential, we have compared our result to the DLVO theory’s predictions, Eq. (1.10). The two-parameter fit represented graphically in Fig. 9 yields $Z=4400$ and $\kappa^{-1}=0.3 \, \mu\text{m}$. These parameters correspond to a reasonable value for the ionic strength of $10^{-6}$ M, and a very low charge density of the silica surfaces consistent with the low degree of silanol dissociation under these solution conditions.

The observed good agreement with a pure screened Coulomb expression is not an obvious result, even from a classical point of view. For particles so close to a dielectric wall, one might have expected signs of an unscreened and thus longer ranged interaction mediated by the wall [46, 47].

**Discussion**

The observed absence of any long range attraction calls for a comment on previous studies with different results. Anomalous attraction has been reported for systems of sulfate latex particles, which have a much higher surface charge density in pure water than silica particles, although both types of particles are quite similar in many other respects. Our observations could therefore indicate a correlation of high particle charge and long range attraction at low ionic strength.

On the other hand, it should be kept in mind that the evaluation of interaction energies from recorded two-dimensional particle positions is a nontrivial task; more than once have published experimental data been reinterpreted in an entirely different way [51, 62]. The only other measurement of long range attraction induced by a single wall used two particles trapped periodically in optical tweezers [26], and as mentioned before, it cannot be ruled out that the observed effect was due entirely to nonequilibrium electro-hydrodynamic coupling rather than attractive pair interaction.

Equilibrium measurements face different problems. As outlined in the previous section, good statistics and time constraints require the simultaneous observation of many particles, which introduces the need to discern the many-body contributions to the measured distribution functions. This can be done, as we have seen, by employing two-dimensional
integral equations from liquid structure theory, but the methods rely on a high degree of monodispersity of the particles and a (very nearly) two-dimensional configuration. Earlier studies reported radial distribution functions with nonzero values below one sphere diameter [22, 23, 61], which clearly hints at particle displacements from the image plane. As pointed out by Rao and Rajagopalan [62], even small displacements can lead to projection errors that skew the observed $g(r)$ sufficiently to introduce an spurious attraction in $u(r)$. A simple way to account for projection effects has been proposed for the case where all out-of-plane displacements within a viewing volume of finite thickness are equally likely [63], but cannot be expected to give reliable results for particles interacting with two nearby walls.

Lateral heterogeneity of these walls could also be a source of error. Although the relative affinity of several spheres to a favorable zone within the plane might provide all the apparent marks of an inter-particle attraction, no effort has been reported to exclude this mechanism as the origin of the observed attraction. In Ref. [23], where $U(r)$ for particles in a narrow slit was calculated from $g(r)$ in a similar way as in our study, the reported pair potentials show a suspiciously oscillatory behavior and qualitatively resemble the potential of mean force. As long as the role that potential error sources might have played in the measurements of like-charge pair attraction is unclear, a rest of doubt seems in order.
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References


