

Confinement-Induced Colloidal Attractions in Equilibrium

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The Poisson-Boltzmann theory for colloidal electrostatic interactions predicts that charged colloidal spheres dispersed in water should repel each other, even when confined by charged surfaces. Direct measurements on highly charged polystyrene spheres, however, reveal strong, long-ranged confinement-induced attractions that have yet to be explained. We demonstrate that anomalous attractions also characterize the equilibrium pair potential for more weakly charged colloidal silica spheres sedimented into a monolayer above a glass surface. This observation substantially expands the range of conditions for which mean-field theory incorrectly predicts the sign of macroions' interactions, and provides new insights into how confinement induces long-ranged like-charge attractions.

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Interactions among charged colloidal particles in water are incompletely understood despite more than a century of study. For example, Poisson-Boltzmann theory predicts that similarly charged colloidal spheres should repel each other with a screened-Coulomb potential [1]. This reasonable prediction was contradicted by Kepler and Fraden's experimental observation that highly charged microspheres attract each other, at least under some conditions [2]. Optical tweezer measurements [3,4] subsequently demonstrated that anomalous attractions appear only when charged spheres are confined to a plane by charged surfaces. Confinement-induced like-charge attractions also are inconsistent with mean-field theory [5]. How confinement modifies charged colloids' interactions has proven a durable mystery.

This problem's intractability reflects the complexity of the macroionic environment. Under equilibrium conditions, charge-stabilized colloidal particles' long-range interactions result from a combination of direct Coulomb repulsions and indirect interactions mediated by microscopic ions in solution. The spheres' effective pair potential, $u(r)$, is an average over the simple ions' degrees of freedom. The Poisson-Boltzmann formalism performs this average in the mean-field approximation and so cannot account for fluctuations or correlations in the simple ions' distributions. Thermodynamically self-consistent liquid structure calculations demonstrate that particle-ion and ion-ion correlations indeed can mediate long-ranged attractions [6] consistent with metastable phase separation in bulk suspensions [7]. This mechanism's relevance to pairs of spheres confined by charged walls remains to be determined, however.

The apparent subtlety of confinement-induced like-charge colloidal attractions has inspired a critical reassessment of the experimental evidence. For example, all previous observations of confinement-induced attractions [2,4,8,9] were performed on polystyrene (PS) microspheres with highly acidic surface groups [10]. The only related study on confined silica spheres found no devia-

tions from mean-field theory's predictions [10]. Anomalous interactions therefore might be peculiar to highly charged spheres in general, or to PS in particular, in which case the effect would be far less generally important than originally supposed. Concern also has been raised that hydrodynamic coupling [11,12] or other experimental artifacts [10] might explain the observed attractions, particularly because error estimates were not available for some of the measurements [2,8].

This Letter describes digital video microscopy measurements of the equilibrium pair potentials for charged colloidal spheres under varying degrees of confinement. These measurements reveal strong and long-ranged like-charge colloidal attractions not only between PS spheres confined to the midplane between parallel glass walls, but also between more weakly charged silica colloid sedimented into a monolayer above a glass wall. Even though the sedimented spheres' dynamics should be influenced principally by the nearest wall, we find that intersphere attractions arise only in the presence of a second parallel wall, and that its influence is remarkably long ranged. These effects cannot be ascribed to kinematic artifacts [11,12] because the measurements are performed on dispersions in equilibrium. We also demonstrate that sample inhomogeneities have far too small an effect to account for our observations. Instead, our results are consistent with a *pairwise* confinement-induced attraction between like-charged colloidal spheres.

Our experimental system, shown schematically in Fig. 1, is prepared according to the methods of Ref. [3]. A dilute deionized colloidal suspension is confined between the parallel surfaces of a glass microscope slide and a No. 1 glass coverslip. The edges of the glass surfaces are sealed with a high-purity UV-cured adhesive (Norland Products Type 88) to form a closed sample volume, with access provided by glass tubes bonded to holes drilled through the upper glass slide. The separation, H , between surfaces is measured by focusing a laser beam onto the glass-water interfaces using a piezoelectric motion

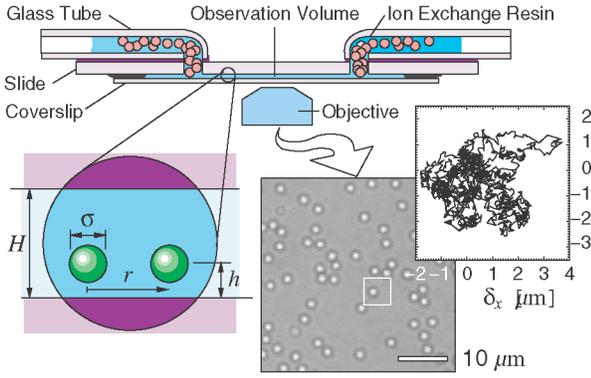


FIG. 1 (color online). Schematic of system used to measure interactions in a confined colloidal monolayer. Access tubes are sealed after colloid is introduced to maintain low ionic strength. The image is a detail from a video frame of $1.58 \mu\text{m}$ diameter silica spheres. The $6 \times 6 \mu\text{m}^2$ box contains the measured trajectory $\mathbf{r}_j(t)$ for one sphere sampled at $1/30$ s intervals over one minute.

controller. Mixed-bed ion exchange resin packed into the tubes helps to maintain total ionic strengths around 5×10^{-6} M in the $1 \times 4 \text{ cm}^2$ visible sample area. The tubes are sealed after a sample is introduced, and the suspension is allowed to equilibrate at ambient temperatures on the stage of a Zeiss S100TV Axiovert microscope. The particles in an $A = 136 \times 102 \mu\text{m}^2$ area are imaged with a $63\times$ objective lens and a $1\times$ video eyepiece onto a low-noise monochrome charge-coupled device camera. A detail from a typical video frame appears in Fig. 1.

We use high-resolution particle tracking algorithms [13] to locate the centroid $\mathbf{r}_j(t)$ of each particle in the plane at time t to within 30 nm. A typical trajectory appears in Fig. 1. The distribution,

$$\rho(\mathbf{r}, t) = \sum_{j=1}^{N(t)} \delta[\mathbf{r} - \mathbf{r}_j(t)], \quad (1)$$

of $N(t)$ particles in the field of view at time t provides detailed information on the particles' responses to random thermal forces and their mutual interactions.

To extract $u(r)$ from $\rho(\mathbf{r}, t)$, we adopt the approach pioneered by Kepler and Fraden [2] and Vondermassen *et al.* [14] by calculating the pair correlation function,

$$g(r) = \frac{1}{n^2} \langle \rho(\mathbf{r}' - \mathbf{r}, t) \rho(\mathbf{r}, t) \rangle, \quad (2)$$

where $n = N/A$ is the areal density in a field of view containing N particles on average, and the angle brackets denote averages over both angles and time. A typical example appears in the inset of Fig. 2(a).

The pair correlation function is related to the potential of mean force, $w(r)$, through the Boltzmann distribution,

$$w(r) \equiv -k_B T \ln g(r). \quad (3)$$

This reduces to the true pair potential in the dilute limit: $u(r) = \lim_{n \rightarrow 0} w(r)$. Because measurements must be made at finite concentrations, crowding may introduce additional structure into $g(r)$. The resulting minima in $w(r)$ are not evidence of pairwise attractions, but simply describe many-body structural correlations.

To distinguish like-charge attractions from crowding, Carbajal-Tinoco *et al.* [8] introduced the idea of analyzing $g(r)$ with the Ornstein-Zernike (OZ) integral equation [15], which describes the evolution of many-body correlations from a hierarchy of pairwise interactions. Truncating the hierarchy results in approximations that may be inverted to obtain expressions for $u(r)$. Among these, the hypernetted chain (HNC) is found to be accurate for “soft” potentials while the Percus-Yevick (PY) is more accurate for short-ranged interactions. The pair

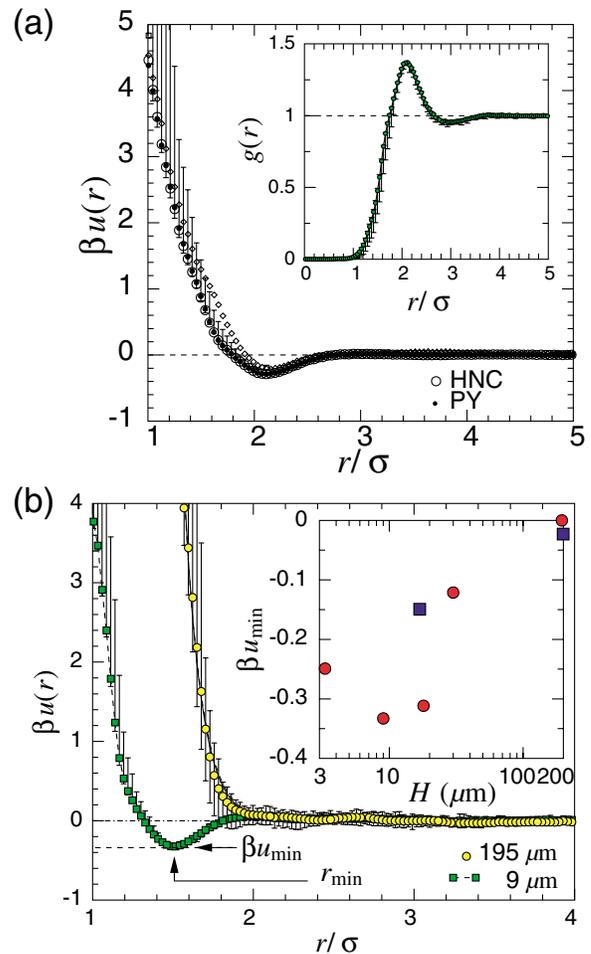


FIG. 2 (color online). Colloidal pair potentials. (a) PS spheres $\sigma = 0.652 \mu\text{m}$ diameter at $H = 1.3 \pm 0.1 \mu\text{m}$ and $h = H/2$. Circles: $n\sigma^2 = 0.056$, diamonds: $n\sigma^2 = 0.020$. Inset: Pair correlation function at $n\sigma^2 = 0.056$. (b) Silica spheres $\sigma = 1.58 \mu\text{m}$ diameter at $H = 195 \mu\text{m}$ (circles) and $9 \mu\text{m}$ (squares). The solid curve is a fit to Eq. (6). Inset: The minimum's dependence on H for $\sigma = 1.58 \mu\text{m}$ (circles) and $2.2 \mu\text{m}$ (squares).

potential can be evaluated in these approximations as [16]

$$u(r) = w(r) + \begin{cases} k_B T n I(r) & \text{(HNC)} \\ k_B T \ln[1 + n I(r)] & \text{(PY)}, \end{cases} \quad (4)$$

where the convolution integral,

$$I(r) = \int_A [g(r') - 1 - n I(r)] [g(|\mathbf{r}' - \mathbf{r}|) - 1] d^2 r', \quad (5)$$

is solved iteratively, starting with $I(r) = 0$. Evaluating $I(r)$ directly rather than with numerical Fourier transforms reduces sensitivity to errors in $g(r)$ [10].

Figure 2(a) shows a typical pair potential obtained with Eqs. (1)–(5) for a suspension of $\sigma = 0.652 \mu\text{m}$ diameter polystyrene sulfate spheres (Duke Scientific Lot 22998, density 1.05 g/cm^3) at areal density $n\sigma^2 = 0.056$ confined to the midplane ($h = H/2$) between charged glass surfaces [17] separated by $H = 1.3 \pm 0.1 \mu\text{m}$. These spheres' acidic surface groups dissociate almost completely in water, endowing them with a surface charge density of roughly one 1 electron equivalent per 3 nm^2 [3,4,13]. As in previous studies [2,4,8,9], $u(r)$ displays a minimum $0.3k_B T$ deep at a range of 2σ .

Excellent agreement between the HNC and PY approximations implies that the OZ formalism is reliable at the experimental areal density. Differences between the two constitute one contribution to the estimated error in $u(r)$.

The diamonds in Fig. 2(a) show HNC results for a similar suspension at one-third the areal density, $n\sigma^2 = 0.020$. Their agreement with the higher-density data demonstrates the pairwise additivity of $u(r)$ in this range of areal densities, and is consistent with optical tweezer measurements [4] that found comparable confinement-induced attractions even at vanishing areal densities. This differs from density-dependent effects observed in more concentrated suspensions [18].

The data in Fig. 2(b) were obtained for silica spheres $\sigma = 1.58 \mu\text{m}$ in diameter (Duke Scientific Lot 24169). These differ from PS spheres in two respects: They carry one-fifth the surface charge density [17] and are twice as dense (2.0 g/cm^3). Consequently, they sediment into a monolayer roughly $h = 0.9 \mu\text{m}$ above the lower wall, with out-of-plane fluctuations smaller than $\delta h = 300 \text{ nm}$ [10,17]. This height does not vary perceptibly with wall separation for $H \geq 4 \mu\text{m}$.

Previous measurements of these spheres' interactions in sedimented monolayers at $H = 200 \mu\text{m}$ showed no sign of interparticle attractions [10]. The pair potential in Fig. 2(b) at $H = 195 \pm 5 \mu\text{m}$ similarly is monotonically repulsive. The mean-field prediction [1],

$$\beta u(r) = Z^2 \lambda_B \frac{\exp(\kappa\sigma)}{(1 + \frac{\kappa\sigma}{2})^2} \frac{\exp(-\kappa r)}{r}, \quad (6)$$

yields good agreement for an effective charge number $Z = 6500 \pm 1000$ on each sphere, and Debye-Hückel screening length $\kappa^{-1} = 180 \pm 10 \text{ nm}$, consistent with a

total concentration of $5 \mu\text{M}$ of monovalent ions at the experimental temperature of $297 \pm 1 \text{ K}$. These results agree both with previous measurements on comparable systems [10] and also with the charge regulation theory for interacting silica surfaces [17].

Reducing the interwall separation qualitatively changes $u(r)$, introducing a minimum consistent with a long-ranged attraction. As for the PS data in Fig. 2(a), the confined silica spheres' interactions are independent of sphere concentration, and consistent results are obtained with both HNC and PY approximations. The example at $H = 9.0 \pm 0.2 \mu\text{m}$ in Fig. 2(b) displays a minimum $u_{\min} = -0.3k_B T$ deep at $r_{\min} = 1.5\sigma$. The inset of Fig. 2(b) reveals clearly resolved minima in $u(r)$ for plate separations as large as $H = 30 \mu\text{m}$. Such a long-ranged influence, extending to more than 100 screening lengths, is not likely to result from electrostatic coupling between the spheres and the distant charged wall. Instead, it might reflect the walls' contribution to the local salt concentration [13] or their influence on the silica spheres' effective charges [17]. The nonmonotonic dependence of the potential well's depth on plate separation may also reflect variations in such factors as temperature and salt concentration from run to run. Comparable results are obtained for slightly larger silica spheres ($\sigma = 2.22 \pm 0.01 \mu\text{m}$, Bangs Laboratories Lot No. 4186).

The accuracy with which wall-mediated attractions are resolved in Fig. 2 can be quantified by considering sources of error in the measurement technique. Whereas accurate methods for measuring $\rho(\mathbf{r}, t)$ from particles' images are well established [13], those for estimating $g(r)$ from $\rho(\mathbf{r}, t)$ involve subtleties which only recently have been explored in detail [10,19]. In particular, the number $N = \mathcal{O}(100)$ of particles in the field of view is insufficient to accurately assess $g(r)$ at small separations. Instead, $M = (\Delta \pi \sigma N n dr)^{-1}$ statistically independent snapshots are required to $g(r)$ to within Δ at $r = \sigma$ with spatial resolution dr [10]. If $g(r)$ were undersampled in this sense, density fluctuations could distort $u(r)$.

The interval between statistically independent configurations is set by the time $\tau = (4Dn)^{-1}$ a particle of diffusivity D needs to diffuse the mean interparticle distance. Thus, the total time required to measure $g(r)$ scales as $M\tau \propto n^{-3}$ [10,19]. For this reason, using the densest possible suspension consistent with reliable many-body corrections is highly desirable.

We estimate D and thus τ by calculating the probability $P(\delta_k, t) = \exp[-(\delta_k - v_k t)^2 / (2D_k t)]$ for a particle to travel a distance δ_k in the k th direction over time t . Based on fit values for D_k , the sampling periods $M\tau$ needed to attain accuracy better than $\Delta = 0.01$ with spatial resolution $dr = 40 \text{ nm}$ range from 20 s in our most dense PS sample to 47 min in our least dense silica sample, and were exceeded in all measurements. Variations in $g(r)$ among subsamples of the full data sets are consistent with expected equilibrium fluctuations.

Even statistically accurate measurements can yield misleading results if external forces induce correlations that mimic attractive interactions. Two-dimensional histograms of $\rho(\mathbf{r}, t)$ averaged over each experiment's duration reveal that the glass surfaces establish featureless potential energy landscapes to within $0.05k_B T$ for $r \geq \sigma$. Typical drift speeds of $v_k < 0.2 \mu\text{m/s}$ are far too small to mediate measurable in-plane hydrodynamic coupling [12]. Consistency between fit values of D_k further confirms the samples' isotropy.

In light of the preceding consistency checks, the reproducible absence of attractions in silica samples at $H = 195 \mu\text{m}$ [17] rules out explanations for attractions in more confined samples based on variations in the spheres' properties. Nevertheless, such variations contribute to errors in $g(r)$ and $u(r)$. In particular, a small population ($< 2\%$) of dimers increases measured correlations near contact. This is exacerbated in our silica data by a small ($< 1\%$) population of undersize particles whose height, h , and out-of-plane fluctuations, δh , are larger than average and lead to projection errors at small separations [20]. Such particles are easily identified by analyzing their apparent size and brightness [13]. We recalculate $g(r)$ without these outliers, deconvolve the result with the suspensions' 2.5% dispersion in diameters [21], and subtract the statistical error to set a lower bound on $g(r)$. Recomputing $u(r)$ and adding the difference between HNC and PY approximations in quadrature yields the upper estimates for $u(r)$ in Fig. 2. Applying statistical and liquid structure corrections to the unmodified $u(r)$ yields the lower limits.

Contrary to the predictions of mean-field theory, our measurements demonstrate that confinement by parallel glass walls induces long-ranged pairwise-additive attractions between similarly charged colloidal spheres in equilibrium. Quantitative error estimates ensure that these anomalous interactions are indeed clearly resolved. Explanations based on kinematic effects such as hydrodynamic coupling similarly are excluded. Confinement-induced like-charge attractions are evident at surprisingly large plate separations in Fig. 2(b). Their appearance for comparatively weakly charged silica spheres suggests that such qualitative failures of the mean-field theory for macroionic interactions may indeed be quite common.

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