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Pair correlations of a dilute charged colloidal fluid near a glass wall

Carl Franck, Michael Covelli, and Richard V. Durand*
Laboratory of Atomic and Solid State Physics and Center for Materials Research, Cornell University, Ithaca, New York 14853-2501

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Using confocal microscopy we examine the static structure of low density, highly charged colloidal suspensions near a repulsive glass boundary. We find no sign of an interparticle attraction of the magnitude noted previously.

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Liquid suspensions of colloidal particles have long been of technological interest: whether they be dispersions of paint ready for application or biosensitive particles for use in immunoprecipitation assays [1]. Attention has recently been directed to such systems near boundaries for the purpose of assembling mesoscopic structures that might serve as optical devices [2] as well as in fundamental studies of the liquid-solid transitions in reduced dimensions [3]. Over the past several years, experimentalists have reported an attractive component between like-charged colloidal particles of diameters of the order of a micron in water suspensions confined between pairs of glass boundaries [4–6] and near a single boundary [7]. The effect has been enough to exhibit an attractive well in the interparticle potential [$U(r)$, r being the center-to-center separation] of as much as k_BT [5] at room temperature, a striking contrast to the Derjaguin-Landau-Verwey-Overbeek theory [8] for forces between such particles in the bulk, where the attractive component provided by the dispersion force is insignificant at the separations cited.

Inspired by these experiments, a strong effort has been made to understand the basis for an equilibrium wall-mediated attraction between like-charged particles. Confounding an earlier prediction, Neu [9] has shown that solutions of the mean field Poisson-Boltzmann equation for such particles in a tube cannot yield an attraction. Ma *et al.* [10] using a two-dimensional model with a particular non-Coulombic potential argued that a boundary can promote attraction if fluctuations are included. Larsen and Grier [7] have suggested that a wall-mediated attraction might be closely related to the metastability of crystallites in dense systems. Their idea is that in a confined system, the wall plays the same role as surrounding particles in a crystallite. Roij and Hansen [11] have argued that metastability is not a sign of an attraction, but rather a feature of two-phase coexistence due to formerly neglected aspects of the energetics of the counterion cloud surrounding each macroion. Finally, Allahyarov *et al.* [12] have hinted that the theory of the well-established attraction of rodlike colloidal objects that are similarly charged, e.g., complementary strands of DNA, might be used to understand attraction of objects in unexpected geometries such as the spheres of the present work.

Meanwhile, concerns have been raised as to the possible sources for the observed behavior beyond an equilibrium wall-mediated attraction. Considering the video microscopy work [4,6], Rao and Rajagopalan [13] have noted that a relatively large depth of field may lead to an apparent attractive well. We look forward to further work on this concern. Recently, we have shown [15] that confocal microscopy, the method employed in the present work, can readily overcome these optical projection artifacts by virtue of its high depth resolution.

Squires and Brenner [14] have also raised the concern that a transient nonequilibrium interaction needs to be added to the purely equilibrium interpretation provided in the single-wall experiment of Larsen and Grier, Ref. [7]. They argue that upon release from optical tweezers near the electrostatically repulsive boundary, the particle pairs experience a hydrodynamic attraction due to the motion of surrounding water. They go as far as presenting quantitative agreement with the original experimental results. However, modeling concerns prevent this interpretation from being definitive. Assuming the equilibrium electrostatic interaction between the particles as given by the original experimental interpretation of the experiment, the authors are required to fit the degree of wall charging. Even granting that their wall charge density is correct, the fact that the pair interaction they employ was provided by the original experimental work means that their analysis is not self-consistent and therefore problematic. How can one trust the originally claimed equilibrium interaction provided by an experiment that is being argued to be severely subject to nonequilibrium effects? We need direct insight into the equilibrium interaction between particles near a boundary. As we have shown in Ref. [15] even our understanding of the equilibrium interaction far from a boundary is unsettled. Specifically, the observed interaction length is widely variable, a fact well known from the experimental literature we quote and augment. In that work, we concluded nevertheless that the interaction range between highly charged colloidal particles is surprisingly shorter than one would expect, even generously allowing for ionic impurities. In contrast with works of Refs. [7,14], the work we present here is unambiguously in equilibrium: we are immune to forcing. And in contrast to the difficult and non–self-consistent arguments provided in the earlier work, we present an analysis that is simple and direct in order to make comparison with other experiments. Furthermore, we bypass the modeling of the kinetic drag effect which requires attention to the experimental protocols for particle release that were followed.

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*Present address: Stark Investments, St. Francis, WI 53235-3716.

Thus, in the present work, we use an equilibrium sampling technique based on confocal microscopy to examine pair correlations near a single flat glass boundary. Our samples were as described in Ref. [15]. They were composed of highly negatively charged latex spheres ($\approx 10^6$ dissociable groups per particle) of 1 μm diameter [16]. The samples featured here were at least five days old at the time of measurement. Setting aside uncertainty over the location of the boundary (discussed below), a pilot study with a year old sample gave similar results. Tumbling the samples prior to measurement ensured that they were well equilibrated to the ion exchange resin used to control ionicity. When it was monitored, the ambient temperature during measurement was found to be between 22 °C and 23 °C. Following the supplier's quoted volume fraction, the samples were prepared with bulk particle densities of 2.5, 7.5, and $25\times10^{-3}\ \mu\text{m}^{-3}$ in nearly density matched water media of ordinary and deuterated water. The cell wall of interest was borosilicate glass. It is expected to be negatively charged by the same aqueous chemical dissociation mechanism that charges the particles [18]. Reference [15] has additional details. The optical system was a Bio-Rad MRC600 laser scanning confocal attachment on a Zeiss Axiovert 10 inverted microscope. We used the same statistical analysis of images in Ref. [15]: A series of optical slices perpendicular to the optic axis were treated as independent samples of particle positions. The slices were 10 s apart to ensure statistical independence of the images. We collected data in sets (referred to as "stacks") of 50 successive images taken at a fixed z value. For the work plotted here, we analyzed over 1800 images. The particles' coordinate perpendicular to the glass-water boundary has been corrected for the refractive index of the heavy and light water mixture.

In our preliminary work, we were faced with ambiguity as to the location of the wall itself. However, in the data featured here, we fortunately found a few immobile particles which we recognized as being stuck by dispersion forces to the wall [19], which would have otherwise been repulsive at greater distances due to electrostatics since the wall is charged negatively as are the particles. These stuck particles not only served to locate the wall with high precision (0.07 μm), but also gave a convenient means of calibrating the depth of field of our confocal slices. The latter quantity depends on both the microscope optics and the settings of the algorithm used to recognize particles in the digital images.

In choosing the number density of samples in this work, we were guided by our finding [15] that in the bulk for preparations with densities between 0.24 and $7.5\times10^{-3}\ \mu\text{m}^{-3}$, there was insignificant change in the measured pair distribution function with density. This indicates that samples were all in the low density limit, for which the simple connection between the pair distribution function $g(r)$ and the pair interaction potential $U(r)$, $\ln[g(r)] = -[U(r)/k_BT]$ [20] holds. For this paper's near wall study, we repeated the test that we were operating in the low density regime by using prepared sample densities from the middle of the range used in our bulk study, $2.5\times10^{-3}\ \mu\text{m}^{-3}$, through higher density by a factor of 10. With the exception of our measurement for the z position closest to the wall, where we used the lowest density only, we will show that the measured pair distribution function does not vary significantly with the prepared sample density. This result is especially important in light of our finding that the particle density derived from images (using the depth of field derived by z scanning a stuck particle) was frequently much greater than we had expected: by as much as a factor of 5 beyond the bulk density we had prepared according to the manufacturer's stated volume fraction. We did however find instances where the image-derived densities had the expected value. In addition, density fluctuations were noticed of as much as a factor of 2 when we compared the average density of stacks of images taken by returning to the same z value within periods of time as long as hours. On the other hand, in systematic sampling of the fluctuations in the density over several stacks including examples of ones for which the density was much greater than expected as well as randomly chosen runs, in only one case did we find excessive variation in density within the stack. Similarly, rapid z sectioning (one image per z position) gave comparatively smooth density vs z position profiles.

Due to our uncertainty in the sample density based on images, we have taken care to examine $g(r)$ vs z over a broad range of expected density. In speculating over the cause for these fluctuations, our attention is drawn to the gathering of particles that we notice around ion exchange resin when we first survey our specimens before each confocal run with ordinary bright field imaging under mercury lamp illumination. Due to this gathering effect we were careful to choose sample regions for confocal scans that were not near ion exchange resin beads and their concentrations of particles. In any case, work is needed to ascertain the origins of these density fluctuations.

In producing our plots of the pair correlation function $g(r)$ as a function of z, the distance along the optic axis, which is perpendicular to the wall ($z=0$ corresponding to the wall-suspension interface) we studied the effect of varying the depth of field digitally. A feature in an image was identified as a particle if the integrated pixel strength divided by the square of the radius of gyration was greater than a threshold value. This cut served to filter out the images that were too weak to be included in the depth of field or too large to be judged as single particles (instead of the aggregates that we have rarely noted). We therefore effectively controlled the depth of the field by changing this threshold. Focusing our attention on a wall stuck particle, we found that we could vary the depth of field from 0.6 to over 3.2 μm thickness. While all our results were consistent within statistical uncertainty, we chose to display the results here for a depth of field of 1.5 μm since that is comparable to the diameter of a particle and hence quite thin but nevertheless thick enough to provide good statistics. In fact, considering our earlier bulk findings [15], we expect there to be no significant projection effect that would cause our results to deviate from the three dimensional $g(r)$ (the fact that one happens to study a flat observation volume in no way complicated the analysis). In fact as discussed in the text accompanying Fig. 2 of Ref. [15], we explicitly showed by simulating the effect of projection that it was inconsequential

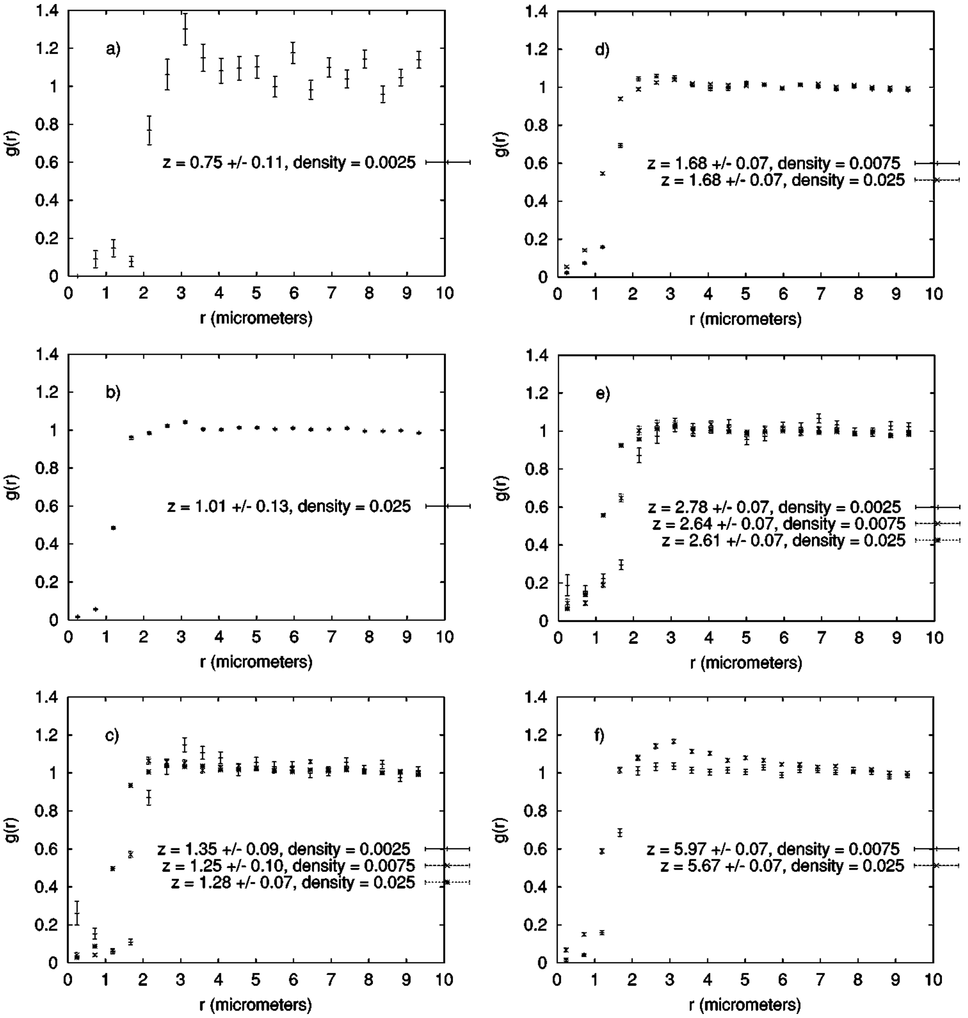

FIG. 1. Colloidal pair distribution function g vs r, center-to-center particle separation (in micrometers), as a function of z, the distance from the glass boundary to the center of the particles (in micrometers) and number density as indicated (in particles per inverse cubic micrometers). The plots are for different ranges of z as follows: (a) 0.6–0.9, (b) 0.9–1.1, (c) 1.2–1.4, (d) 1.6–1.8, (e) 2.5–2.9, and (f) 5.6–6.0.

for a system with comparable depth of field. In Fig. 1 here, we show results at z between 0.8 and 6.0 μm (distances corrected for the refractive index of the suspension) for various densities. Except for the first observation, the one closest to the wall, we selected these plots because they offered different densities for similar z values. In a few cases, our results were statistically limited. We see that with respect to variation in the prepared density, we find little change in $g(r)$ except for a tendency to lower the effective diameter from 1.9 ± 0.2 μm to 1.25 ± 0.1 μm (over all z values) as we pass from the lowest to the highest density. Note that our results are consistent with our earlier bulk studies [15] where we pointed out that the effective diameter in the dilute limit is shorter than expected. There is easily enough information in the present results for discussion in light of previous work. Our smallest z value is considerably shorter that reported by Vondermassen *et al.* [17] for chemically similar particles of roughly the same diameter. Our concerns about this later work, which is limited by its use of conventional microscopy are expressed in Ref. [15]. Due to ambiguity in close particle identification as discussed in Ref. [15], we ignore data for separations below 1 μm.

We have included measurements in Fig. 1 close to the wall distance ($z=2.5$ μm), where Larsen and Grier [7] using optical tweezers observed an attractive well of about $0.7k_BT$ (at room temperature) for 0.65 μm diameter highly charged particles at center-to-center separations between particles of 3–4 μm. Considering the low density relation $\ln[g(r)]=-[U(r)/k_BT]$ [20], a Larsen and Grier effect should give rise to $g(r)$ as large as 2.0 at the quoted separations. As we will point out, this is clearly inconsistent with our measurements. Scanning the range of r between 3 and 4 μm for the attraction noted in a previous work, and recalling that our earlier bulk work detected no sign of enhancement of $g(r)$ due to liquid structure at comparable densities (note that near the repulsive wall, the density is expected to be even smaller than in the bulk), we find the following: for $z\approx0.75$ [Fig. 1(a)], $g(r)$ remains below 1.4; for $z\approx1.0$ [Fig. 1(b)], $g(r)<1.06$; for z between 1.3 and 2.8 [Figs. 1(c)–(e)], $g(r)<1.09$; and for $z\approx6$. [Fig. 1(f)], $g(r)<1.2$. Note that these limits are good for the variety of densities presented (for the smallest z, we have only one density, but it is well within the low density regime established by our bulk studies). We conclude that we have safely set limits on a possible long-range attraction by taking the dilute limit of the pair distribution function for an interesting range of distance from the wall. Besides casting doubt on the original interpretation of the single-wall optical tweezer study [7], we note that in experiments where particles were confined between a parallel pair of glass boundaries, the contrast with the present result is similarly striking: For a confined colloidal pair between plates spaced by $3.0 \pm 0.5\ \mu$m, Crocker and Grier [5] found an interaction strength comparable to $k_B T$. At half this distance from a single wall, we see no such effect since this would imply a peak in $g(r)$ of ≈ 2.7. The question of whether a long-range attractive interaction exists is still open. The point we are making here is that nothing comparable to earlier reports is of evidence in our measurements.

To summarize, in contrast to previous experiments and resultant theory, we have set limits on wall-mediated attraction between colloidal particles of high surface charge in low ionicity water suspensions. This supports possible concerns that diminished the resolution of particle position along the optic axis in all geometries and hydrodynamic interaction in the case of a single wall may have heavily influenced earlier observations. Future work could usefully examine the importance of confinement between pairs of walls vs the single repulsive wall geometry used here. Despite the success we have had in measuring the pair distribution function in the low density limit, further work could require one to overcome the density fluctuations we have noted. Finally, higher statistics measurements could carry the search for new interactions beyond the limits we have set.

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