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Effective pair potential between confined charged colloidal particles

Angeles Ramírez-Saito,[1] Martín Chávez-Páez,[1] Jesús Santana-Solano,[1] and José Luis Arauz-Lara[1,2]
[1]*Instituto de Física "Manuel Sandoval Vallarta," Universidad Autónoma de San Luis Potosí, Alvaro Obregón 64, 78000 San Luis Potosí, San Luis Potosí, Mexico*
[2]*Programa de Ingeniería Molecular, Instituto Mexicano del Petróleo, Eje Lázaro Cárdenas 152, 07730 Mexico DF, Mexico*

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The pair correlation function $g(r)$ between like-charged colloidal particles in quasi-two-dimensional geometries is measured by optical microscopy for a wide range of particle concentrations and various degrees of confinement. The effective pair potential $u(r)$ is obtained by deconvoluting $g(r)$ via Monte Carlo computer simulations. Our results confirm the existence of a long-range attractive component of $u(r)$ and the appearance of an extra attractive term under stringent confinement.

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A pair of colloidal particles carrying electric charge of the same sign, immersed in an electrolyte solution, repel each other at large distances but they can feel a strong attraction at very short distances in the presence of large electrolyte concentrations. According to the well established theory developed by Derjaguin, Landau, Verwey, and Overbeek (DLVO), the repulsive part is a screened Coulomb-type interaction, arising from the electrostatic interaction between the charged particles, with the screening being due to the small ionic species in the solution clouding around the particles. The strong attraction at contact, on the other hand, is due to (induced) dipole-dipole interactions and is referred to as van der Waals interaction. The interplay of these two components of the DLVO pair potential, and their relative strength compared with the thermal energy k_BT, is sufficient to account for most of the phenomena observed in colloidal dispersions in the bulk: stability, aggregation, phase transitions, static and dynamic structure, etc. [1–3]. However, at variance with this theory, colloidal particles can experience a long-range attractive interaction when they are confined. Observations of an attractive potential between polystyrene spheres of diameter $\sigma \sim 1\,\mu$m in deionized water confined between two parallel charged glass plates have been reported by different groups [4–8]. The attractive minimum of the potential, having a depth $\lesssim k_BT$, is located at a distance between particles around 1.5–2σ, which is large compared with the range of few nanometers of the van der Waals forces. This effective interparticle potential $u(r)$ was obtained by deconvoluting measured equilibrium properties such as the two-dimensional (2D) radial distribution function (rdf) $g(r)$, via computer simulations or integral equations theories [4,5,7,8]. Attractive interactions have also been reported to be observed in nonequilibrium measurements of dynamical properties of isolated pairs of particles close to a single wall [6]. In this case, however, the fluid flow created by one particle moving away from the wall can drag along the other nearby particle [9]. Thus, the determination of $u(r)$ in this case is a more complex matter since it is masked by hydrodynamic interactions (HI). Although the HI can account, at least partially, for the apparent attraction observed in the nonequilibrium measurements, they cannot explain such observation in measurements of equilibrium properties. The puzzling observation of attraction between like-charged particles has raised a controversy about its origin, and has led to a number of different theories attempting to explain its mechanism in some situations [10–15]. Although various mechanisms have been proposed, the actual driving force for the attraction between like-charged particles has not been completely identified or it has not been taken into account properly. Thus, the phenomenon has remained elusive to a theoretical explanation so far and its existence has been questioned as probably being an artifact (a projection effect) of the measuring method. On the other hand, there are also reports of equilibrium properties measured close to a single wall, where no attraction was observed [16]. Thus, the matter of the actual form and the origin of the effective potential between like-charged colloidal particles under confinement is still far to be settled, and more theoretical and experimental work is needed to establish the different mechanisms leading to the phenomena observed under confinement, such as the attraction, and the conditions for them to occur.

In this paper, we report measurements of the effective pair potential $u(r)$ between charged colloidal particles in a quasi-two-dimensional geometry under various conditions of confinement. We study aqueous suspensions of sulfate-polystyrene spheres of diameter σ in the micrometer range. The suspension is confined between two charged glass plates separated a distance h. The 2D-rdf $g(r)$ of these systems is measured using digital video microscopy. Assisted by Monte Carlo computer simulations [7,17], we determine $u(r)$ for different values of $\ell = h/\sigma$ and various particle concentrations. As it is shown here, we found a long-ranged attractive component of $u(r)$ in all cases studied in this work, even in strongly confined systems where projection effects are negligible. Thus, we confirm experimentally the existence of the controversial attractive potential between like-charged particles. Furthermore, we report the appearance of an additional attractive region of $u(r)$ close to contact that becomes apparent under stringent confinement. We also found that the form of $u(r)$ is strongly dependent on the relative plates' separation.

The systems studied are prepared following a standard protocol [8]. Briefly, monodisperse water suspensions of sulfate-polystyrene spheres are extensively dialyzed against nanopure water to eliminate the surfactant added by the manufacturer. In a clean atmosphere of nitrogen gas, the sus-

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pension of particles of diameter σ is mixed with a small amount of larger particles of diameter h. A small volume of the mixture ($\approx 1\ \mu l$) is confined between two clean glass plates (a slide and a cover slip), which are uniformly pressed one against the other until the separation between the plates is h. Thus, the larger particles scattered across the sample serve as spacers. The system is then sealed with epoxy resin, and the species of mobile particles allowed to equilibrate in this confined geometry at room temperature ($25.0 \pm 0.1\,°\mathrm{C}$). In our case, the systems are not in contact with ion-exchange resins. Thus, the extension of the double layer in our case is much more shorter than in other works [16]. We used different combinations of σ and h, within range 1–3 μm, attaining values of ℓ between 1.3 and 2.3. The samples are observed from a top view (perpendicular to the walls plane), using an optical microscope coupled to standard video equipment. Since h is comparable to σ, there is only little room for the particles to move in the perpendicular direction and they remain mostly in the midplane between the glass plates, forming in this way an effective two-dimensional system [18]. For each sample sufficient data was gathered to yield smooth $g(r)$ curves. Normally, 10^4-10^5 images (with a resolution of 640×480 pixels) were digitized covering a total time 100–1000 times the time decay constant of the dynamic correlation function $G(r,t)$, which is of the order of few seconds [7,19]. Particles' x and y coordinates in each image were determined using the method devised by Crocker and Grier [20], which allows us to locate the centroid of each sphere within a precision of 1/5 pixel ($\sim 0.02\sigma$). The 2D-rdf $g(r)$ is then obtained from the particles positions in each frame using standard methods. One should note that the distance r measured in our experiment is the lateral projection of the actual interparticle distance R. These two quantities coincide only when the particles are in the same plane. Clearly, this condition is met by all particles in the field of view in the limit $\ell \rightarrow 1$. Since our systems are not strictly two-dimensional ($\ell > 1$), the rdf measured in our experiment might contain some projection effects. Here, we report measurements of $g(r)$ for different values of ℓ and particle concentration in order to assess such effects that have been pointed out as a possible source of misleading data interpretation [21,22]. Our results are presented in the next paragraphs. We show first the case of strong confinement and later on we present results for less confined systems similar to those reported in the literature.

Figure 1 shows $g(r)$ for different values of $\phi_a \equiv \pi N\sigma^2/4A$, the particles area fraction, where N is the average number of particles in the observed area A. In curves a–c, $\ell = 1.3$, realized with $\sigma = 1.53\ \mu$m and $h = 1.96\ \mu$m, and $\phi_a = 0.035$, 0.04, 0.043, respectively. In these cases, projection effects on $g(r)$ are negligible as one can see from a simple geometric analysis. For a given value of ℓ, the maximum deviation of r from R is $\epsilon \equiv 1 - r/R = 1 - (r^2/[r^2 + (\ell - 1)^2\sigma^2])^{1/2}$, obtained in the limiting case of one particle touching one wall is a distance R apart from another particle touching the opposite wall. Since particles are more likely to be around the midplane, the average deviation is in fact much less than ϵ. For systems a–c, we have $\epsilon \sim 0.04$ at $r = \sigma$, and decreases for larger r. In curve d, we have $\ell = 1.5$, realized with $\sigma = 2.04\ \mu$m and $h = 3.0\ \mu$m, and $\phi_a = 0.23$. Here too, projection, effects are negligible. The rdf's shown in Fig. 1 exhibit, as a function of ϕ_a, an overall increase of the structure and a similar general behavior, namely, one peak close to contact, a second peak at $r \sim 1.3 - 1.5\sigma$, and minor oscillations at larger distances. The first peak rises very sharply around $r = \sigma$ and its height increases with ϕ_a. The fact that particles are likely to be in contact, but do not aggregate, revels a strong interparticle repulsion rising rapidly as $r \rightarrow \sigma$. The second peak, located at a position closer than the lateral mean interparticle distance $d \equiv (\pi/4\phi_a)^{1/2}\sigma = 1.85 - 4.7\sigma$, is consistent with an effective interparticle attraction of longer range than the van der Waals attractive minimum of the DLVO theory.

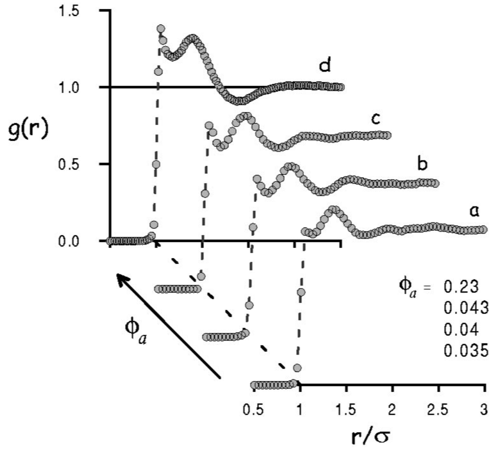

FIG. 1. Radial distribution function of quasi-two-dimensional colloidal suspensions measured by optical microscopy.

Clearly, the peculiar behavior of $g(r)$ shown in Fig. 1 cannot be explained only in terms of an interparticle interaction of the type given by the DLVO theory. In order to gain some insight on the functional form of the effective interaction leading to the equilibrium structure observed in our experiment, a Monte Carlo computer simulation algorithm for quasi-two-dimensional geometries, as the one in our experiment, was implemented to deconvolute the measured equilibrium properties. The interparticle potential is obtained as follows. A trial potential between particles $u_0(r) = -k_BT \ln g(r)$, with $g(r)$ being an experimental rdf at low concentration, is input in the simulation to get a computed rdf $g_{MC}(r)$. The wall-particle interaction is assumed to be only the excluded volume, which is not a restriction since a repulsive interaction would only renormalize ℓ. The trial pair potential is tuned up until the computed rdf coincides with the experimental one. The resulting potential is then taken as the effective pair potential $u(r)$ for the corresponding experimental system. We should emphasize that this method is less susceptible to projection errors on $u(r)$ than the strictly 2D deconvolution method used in other works [4,5]. Figure 2(a) shows the experimental and simulated rdf's for system c in Fig. 1, whereas Fig. 2(b) shows the pair potential $u(r)$ obtained in the way described above. As one can see here, $u(r)$ for this system has interesting features, namely, two attractive regions separated by barrier poten-

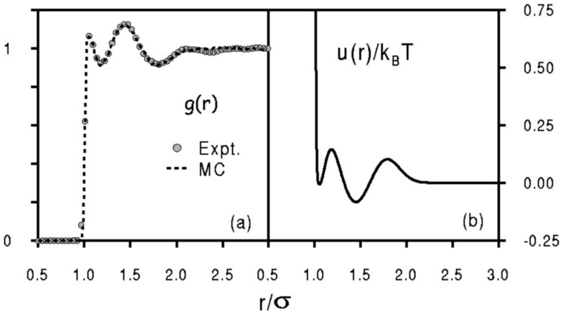

FIG. 2. (a) Measured and computed radial distribution functions for system *c* in Fig. 1. (b) Effective pair potential.

tials. The attractive region close to contact is responsible for the peak at $r\approx\sigma$ for dilute systems, and the other attractive region for the peak at $r\sim 1.4\sigma$. The latter is the long-range attractive potential previously reported by different groups and the origin of the controversy mentioned in the introduction.

A relevant question at this point is whether this $u(r)$ provides a realistic representation of the actual effective interparticle interaction, and therefore it can predict the structure of other systems under similar conditions. To answer this question, $u(r)$ in Fig. 2(b) was used in the MC algorithm to compute the structure of a set of systems at fixed $\ell=1.3$ and different values of the particles area fraction ϕ_a. Our results are shown in Fig. 3(a). As one can see here, the computed rdf's exhibit the same characteristics of the experimental systems shown in Fig. 1, namely, they have a peak close to contact whose height increases with ϕ_a, and a second peak at $r\sim 1.4\sigma$. The former becomes the dominant peak at large ϕ_a. This qualitative prediction provides already an indication that the form of $u(r)$ is physically meaningful. However, a more direct test of the predictive capability of $u(r)$ is shown in Figs. 3(b) and 3(c). Here, experimental (circles) and computed (dotted lines) correlation functions are compared for two concentrated systems similar to sample *c* in Fig. 1, but with $\sigma=2.04$ μm and $h=3.0$ μm ($\ell\sim 1.5$). Actually, one of them is sample *d* in Fig. 1. From these figures, we see that $u(r)$ is in fact capable of predicting correctly the trends and the shape of the structure of systems prepared in a different regime of concentrations and for different values of σ and h, but similar ℓ. The excellent agreement between measured and computed rdf's shows that the predictions of this pair potential are both qualitatively and quantitatively accurate. Then, these results indicate that $u(r)$ contains the essential features of the real pair potential for these experimental conditions. The functional form used to fit the potential used in the simulations was

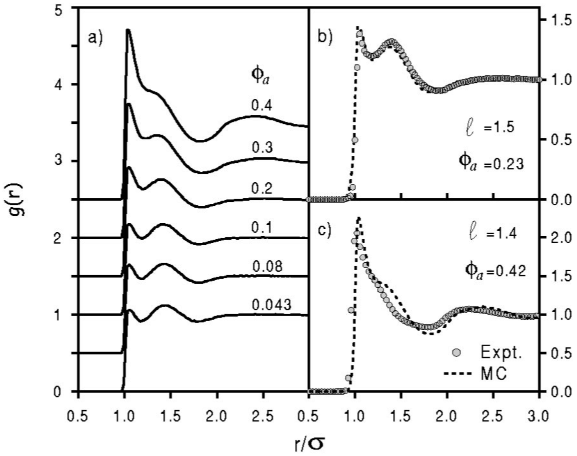

FIG. 3. (a) $g_{MC}(r)$ vs ϕ_a, computed using $u(r)$ in Fig. 2(b). (b) and (c) Comparison of computed $g(r)$ with measured $g(r)$.

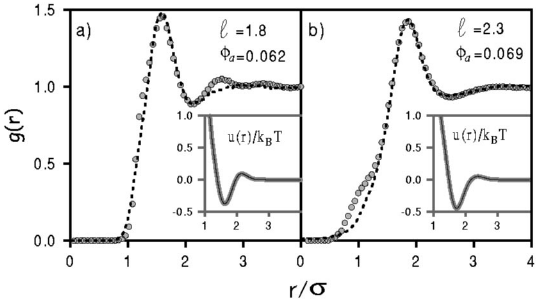

FIG. 4. Measured and computed rdf's for $\ell=1.8$ (a) and $\ell=2.3$ (b). The insets show the corresponding pair potentials.

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\begin{aligned}
u(r)=&A_1\exp[-A_2(r-1)]+B_1\exp[-B_2(r-1)]/r\\
&-C_1\exp[-(r-1)^2/C_2]-D_1\exp[-(r-D_2)^2/D_3]\\
&+E_1\exp[-(r-E_2)^2/E_3].
\end{aligned}
$$

The first term of this potential mimics the hard-core interaction. The second term is a repulsive DLVO-type contribution. The third term allows us to reproduce the sharp peak exhibited by the experimental $g(r)$ close to contact. The fourth and fifth terms were used to adjust the positions and shapes of the main peak and its following minimum, respectively.

A complementary picture emerges when the plates' separation is varied. In this case, $u(r)$ in Fig. 2(b) is unable to reproduce the trends of the structure as a function of ℓ (data not shown). This indicates that the effective pair potential between particles is modified when ℓ is varied. To quantify the extent of such changes, we measured $g(r)$ for several systems at different separations and concentrations. Afterwards, the effective pair potential for each of those systems was obtained by MC simulations, using the functional form proposed above. The results for two systems at similar concentrations but different values of ℓ are shown in Fig. 4. Symbols represent the experimental data and lines the simulations. One should note that, in these cases, we recover the shape of $g(r)$ [and $u(r)$] already reported in the literature [4,5,7,8] since $g(r)$ smooths around $r=\sigma$ as ℓ increases. The insets show the corresponding effective potentials required to reproduce the experimental rdf's. Comparing $u(r)$ in Figs. 2 and 4, one can see that the effective pair potential is highly sensitive to the relative plates' separation ℓ.

From our experimental results for $g(r)$, which cover a wide range of concentrations and confining conditions, it is possible to extract some physical characteristics of the effective interparticle potential in quasi-two-dimensional geometries. First of all, we stress the fact that in all cases reported here, and others not shown, $g(r)$ was found to exhibit consistently a peak located at a distance closer than the mean interparticle distance. This confirms the existence of a long-ranged attractive component of the effective pair potential between like-charged particles with a depth of the order of the thermal energy. In extreme confining conditions an additional feature appears, namely, an attractive component close to contact. The plausibility of such effective interparticle interaction was tested by comparing its predictions with experimental results obtained in different experimental regimes. Comparison of $u(r)$ in Figs. 2 and 4 shows that the interparticle interaction can be quite sensitive to the confining conditions. Although our experimental system does not allow us to vary ℓ continuously, Figs. 2 and 4 clearly illustrate the trends and the magnitude of the changes in $u(r)$ as ℓ is varied in the range of interest. At low ℓ, there are two attractive regions. The one close to contact, which is reported here, is probably diminished as the relative plates separation gets longer. When ℓ is large (~ 2), projection effects increase around $r=\sigma$, and mask the actual form of $u(r)$ in that region. Thus, we cannot follow correctly the evolution of $u(r)$ close to contact for large ℓ. On the other hand, the effect of increasing ℓ on the long-range attractive component is that it gets deeper and its location shifted toward larger values of r. One should note that the functional form of $u(r)$ used in the MC simulations is just a working function. The only component with known physical meaning is the Yukawa term, which represents the repulsive term of the DLVO pair potential. The attraction close to contact could be a modified van der Waals interaction. The other terms are modeled by Gaussian functions for convenience, but they could be modeled in other ways. We do not provide here an explanation of the physical grounds of $u(r)$ and its different components. This is still an open question. However, we provide a systematic experimental study of the behavior of $u(r)$ in quasi-two-dimensional geometries which can guide future theoretical developments.

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