Finite Ion-Size Effects Dominate the Interaction between Charged Colloidal Particles at an Oil-Water Interface

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The electrostatic interaction of charged spherical colloids trapped at an interface between a nonpolar medium and water is analyzed. Complementary experiments provide consistent values for the dipole-dipole interaction potential over a wide range of interparticle distances. After accounting for the contribution from the compact inner double layer arising from the finite size of the counterions, we demonstrate quantitative agreement between experiments and nonlinear Poisson-Boltzmann theory. We find that the inner layer contribution dominates the electrostatic interaction in the far field for particles pinned at the interface. This result is fundamentally different from screened electrostatic interactions in the bulk and could contribute to the further understanding of the structure of the compact counterion layer in highly charged systems.

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Since the pioneering work of Pieranski [1], it has been recognized that the electrostatic interaction between particles pinned at a water-oil interface exhibits a long-range dipole-dipole interaction, in addition to the screened Coulomb interaction present in bulk systems. The asymmetric counterion distribution between the polar and nonpolar phases results in a dipole normal to the interface. Hurd [2] calculated both the Coulombic and dipolar contributions, assuming a diffuse double layer and a linearization of the Poisson-Boltzmann equation. The potential as a function of center to center separation distance r between two particles is

$$U(r) = \frac{a_1 k_B T}{3r} e^{-\kappa r} + \frac{a_2 k_B T}{r^3}, \tag{1}$$

with a_1 and a_2 the prefactors that determine the order of magnitude of the screened Coulomb, diffuse double layer, and the dipole-dipole interaction, respectively. k_B is the Boltzmann constant, κ is the inverse Debye screening length, and T is the absolute temperature. At large enough particle separations ($\kappa r \gg 10$), the dipolar contribution dominates the interaction. A wide range of experiments confirm the dipolar nature of the interactions, as the interparticle potential decays as $\sim r^{-3}$. However, the predicted magnitude of the forces differs significantly from what is measured experimentally. Moreover, the dependence of the interactions on the ionic strength of the aqueous phase is observed to be $U \sim \kappa^{-0.43\pm0.04}$ [3], whereas Hurd's theory predicts $U \sim \kappa^{-2}$ [3,4].

To rationalize the discrepancy between the measured and predicted forces, Aveyard *et al.* [4] suggested that a small fraction of dissociated charges, present in the oil phase, dominates the long-range interaction. However, the experimentally observed dependence on electrolyte concentration ($\sim\kappa^{-0.43\pm0.04}$) is at odds with surface charge on the oil side [3]. The majority of the interactions hence must stem from charges on the water side interacting though the oil, as proposed by Hurd [2]. Because of the strong attraction of the counterion, crowding of ions and solvent molecules near the particle surface results in a condensed ion layer, as first described by Stern [5]. The presence of this steric layer screens the high surface charge density of the particle, which from a distance appears to have a lower, renormalized charge [6,7]. Moreover, a_2 is predicted to scale logarithmically with the effective surface charge. It has been suggested that this can explain the experimentally observed salt dependence. However, the magnitude of a_2 expected from the charge renormalization theory is still weaker by a factor of 10–50 compared to experiments, depending on the experimental method used [3].

In the present work, the difference between experiments and theory is investigated first, by using a range of complementary experiments. Polystyrene particles with a diameter of 3.1 μm were obtained from Interfacial

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Dynamics Corporation as aqueous dispersions containing 8 wt % of particles (white sulphate surfactant-free, with a reported charge density of 7.4 μC/cm^2). The suspensions were diluted by using isopropyl-alcohol-deionized water mixtures. An oil-water interface was created by using *n*-decane and deionized, bidistilled water. Polar components were removed from the decane by using adsorption onto aluminum oxide powder. Particle monolayers were prepared by spreading the diluted suspension on a water-decane interface. The three-phase contact angle was directly measured to be 90 ± 20° by using three independent direct measurement methods (for more details, see supplementary material [8]). For the water-air interface, the contact angle was found to be 40°, in agreement with the values reported recently by Horozov *et al.* [9].

Direct and indirect measurements of the interparticle interaction forces are performed in order to evaluate possible inconsistencies between different experimental approaches. First, monolayers of micrometer polystyrene particles at a water-decane interface are visualized by using bright field microscopy (Olympus BX51WI) at low surface fraction ϕ_s and used to obtain the pair correlation function $g(r)$. The pair correlation was calculated by image analysis counting 10^6 particles, averaging over 1000 images (see [8] for the raw data). The pair interaction potential $U(r)$ is then obtained from fitting the Boltzmann distribution $U(r) = -k_B T \ln g(r)$ to these curves, and the resulting potential is included in Fig. 1 for interparticle spacings between 20 and 40 μm. The dependency of the averaged potential on interparticle spacing is consistent with the dipolar interaction, and an average value for $a_2 = 1 \times 10^{-13}$ m^3 is obtained. As the potential calculation by inversion of $g(r)$ is particularly sensitive to the particles that are closest to each other, a lower bound for the potential was estimated by fitting an envelope to the data points and calculating the potential from this curve. A lower bound of $a_2 = 5 \times 10^{-14}$ m^3 is thus obtained.

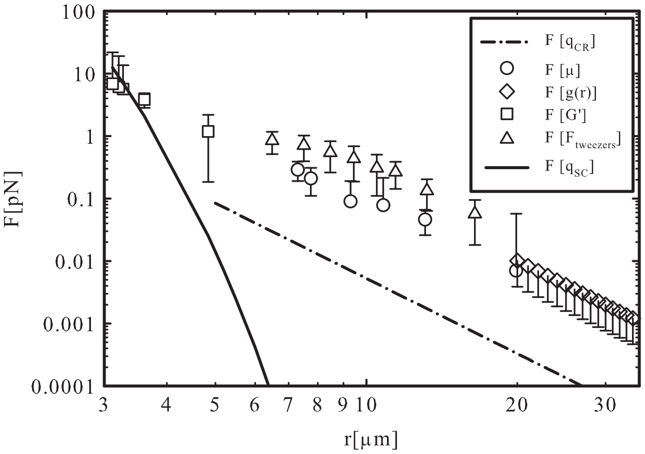

FIG. 1. Experimental measurements of the interaction forces (F) as a function of separation distance (r) between 3.1 μm polystyrene colloids at the water-decane interface, obtained from inversion of $g(r)$, (◇), by using optical tweezers $F[F_{\text{tweezers}}]$ (△), derived from macroscopic rheological measurements $F[G']$ (□), and strain fluctuations $F[\mu]$ (○). Predictions of the screened Coulomb $F[q_{\text{SC}}]$ and the long-range dipolar interactions $F[q_{\text{CR}}]$, based on charge renormalization theory [7], are given for comparison.

Laser tweezers provide direct measurements of particle pair interactions at interfaces for smaller separation distances [3,4]. Particles are held in a time-shared optical trap, and the force is measured as the separation is decreased. The optical tweezer setup is described in detail by Park *et al.* [3]. Averaging over several tens of particle pairs is found to be necessary as the pair interactions show a significant degree of scatter. While the majority of the particle pairs exhibit purely repulsive interactions to separations as close as $r = 5$ μm, the degree of repulsion varies significantly. Some of the measurements even exhibit a near-field attraction, in which the particles suddenly "jump in" to a closer separation, due to attractive interactions. For the repulsive part, an average value of $a_2 = (1.3 \pm 0.5) \times 10^{-13}$ m^3 is obtained.

As a third, indirect characterization of the particle interactions, the interaction potential is calculated from the dependence of macroscopic shear modulus on surface coverage. At sufficiently high surface fractions ($\phi_s \geq 0.2$), a 2D colloidal crystal is obtained and there exists a simple relation between the interparticle distance and the surface coverage. Assuming pairwise additivity of the interaction potential, the dependency of the high-frequency shear modulus ($G'_{\infty,2\text{D}}$) of a 2D colloidal crystal on surface coverage (and hence on interparticle distance) can be related to the pair interaction potential [10,11]. Experimentally, the shear modulus is determined here by two methods: via the thermal strain fluctuations of the lattice by using a microrheological method [12] and by measuring the interfacial linear shear rheology. The latter was performed by using a magnetic rod rheometer [13] and a double wall ring device mounted onto a sensitive rotational device [14]. The relation between the concentration-dependent high-frequency shear modulus ($G'_{\infty,2\text{D}}[\phi_s]$) of a 2D colloidal crystal and the pair interaction potential is given by the Zwanzig-Mountain equation [10]:

$$G'_{\infty,2\text{D}}[\phi_s] = \frac{8\phi_m^{2\text{D}} n}{9\pi^2} \frac{\partial^2 U}{\partial r^2}, \qquad (2)$$

where $\phi_m^{2\text{D}}$ is the maximum packing in 2D ($\phi_m^{2\text{D}} = 0.906$), n is the number of nearest neighbors ($n = 6$), and U is the pair interaction potential. The measured moduli, for different surface coverages, yield results as a function of the average interparticle spacing r, as obtained by using different concentrations, are given in Ref. [8]. The interactions deduced from these experiments yield a lower limit (Fig. 1), as both hydrodynamic interactions and the presence of defects in the crystal may affect the measurement of the interaction force. The results of all three measurements are shown in Fig. 1 as the force $F = -dU/dr$.

The consistent set of experimental data for the interaction potential can now be compared to the theoretical predictions based on the nonlinear solutions of the Poisson-Boltzmann (PB) equation, decomposing the contributions to the interactions potential as in Eq. (1). For the particles used in the present work, the renormalized charge q_{eff} was calculated to be 5×10^{-15} C by following Ref. [7] starting from the surface charge density of the bare particle and using a contact angle of 90°, $\kappa^{-1} = 300$ nm, and ϵ_1 and ϵ_2 equal to 2 and 80, respectively. The predicted screened Coulomb interaction and the dipolar contributions using the renormalized charge model are shown in Fig. 1 and yield values of $a_1 \sim 235$ m and the dominant dipolar contribution in the far field with $a_2 \sim 4.5 \times 10^{-15}$ m^3. When comparing the predictions of the charge renormalization for the dipolar part [7] with the experimental data at separations larger than twice the particle diameter in Fig. 1, the experimentally measured dipolar interaction is underestimated by more than an order of magnitude. Vice versa, in order to obtain the 10–50 times higher value of a_2 from the charge renormalization theory, unrealistic values of the surface charge and surface potentials are obtained. The dipolar contribution cannot be explained within the framework of the PB theory, even taking into account nonlinear charge renormalization effects.

In this Letter, we propose that the discrepancy between the experimental and theoretical magnitudes of the far-field electrostatic repulsion is due to the assumptions of diluteness in the PB theory; i.e., we consider the effect of neglecting the finite size of ions and solvent molecules. It is suggested that there is a large dipole moment stemming from this asymmetric dense counterion ("Stern") layer surrounding the particles, as is shown schematically in Fig. 2(a). Although the steric layer is thin, the dipoles resulting from the finite-sized counterions give rise to a contribution which is of the right order of magnitude to explain the more than an order of magnitude difference between experiments and the renormalization theory. A detailed calculation of the ion-size effects on the electric field lines and the resulting interactions is beyond the scope of the present Letter. This can still be calculated by using a continuum approach and the Poisson-Boltzmann formalism, by using Bikerman's model or its variations [15–17]. The resulting electrostatic fields can be calculated and will depend on the dielectric properties of the two liquids and the particle, the surface charge, and the three-phase contact angle. However, in the present Letter we establish first if a finite ion-size effect can provide us with the right order of magnitude of the strength of the interactions.

To estimate the strength of the dipoles arising from the asymmetry in the dense counterion layers, a simplified approach following the one employed by Hurd [2] is used. The starting point is the integral expression for the electrostatic interactions between point charges, derived by Stillinger [18]. The dielectric properties of the particle are hence neglected, and we consider only the effects of charges located in the dense counterion layer at a distance $d_{\mathrm{ST}}/2$ from the surface of the particle. The calculation then proceeds identically to the one by Hurd [2], but the Debye length now needs to be replaced by $d_{\mathrm{ST}}/2$, and the relevant dielectric constant is the one pertaining to the steric layer ϵ_{ST}. The resulting strength of the dipole p normal to the interface for a particle also depends on the amount of charge in this steric layer q_{ST} and the dielectric constant of the nonpolar solvent ϵ_1 through which the interactions predominantly take place, leading to

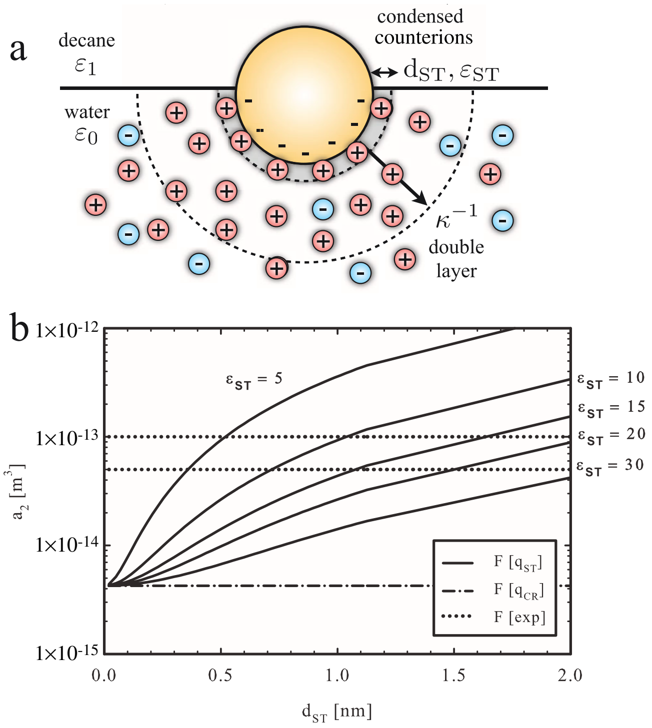

FIG. 2 (color online). (a) Cartoon of the particle at the water-decane interface with all relevant parameters. (b) Prefactor a_2 as a function of the dielectric constant ϵ_{ST} and the thickness of the condensed shell d_{ST} for a particle with $q_{\mathrm{ST}} = 10^{-12}$ C. The range of a_2 values from experiments $F[\mathrm{exp}]$ are given by the dotted lines; the predictions from the renormalization (PB) theory $F[q_{\mathrm{CR}}]$ are given by the dash-dotted line.

$$p = \frac{2\epsilon_1}{\epsilon_{\mathrm{ST}}} q_{\mathrm{ST}} d_{\mathrm{ST}}. \tag{3}$$

For highly charged particles, most of the counterions are located in this steric shell with a thickness $d_{\mathrm{ST}} = 2d$, the thickness of which depends on surface charge [15,16]. A lower bound estimate for d_{ST} is the order of the effective solvated size of the ions (see Ref. [17] for a detailed discussion). For the case of sodium ions, the hydrated radius equals approximately $a = 0.35$ nm [17]. When ion-ion correlations are considered, realistic values for

d_{ST} can go up to 1 nm [19]. The charge in the counterion layer q_{ST} is determined by the concentration of the counterions, which reaches a constant concentration in the condensed layer which scales as $1/a^3$ [15]. To obtain a reasonable estimate for q_{ST}, we use the difference between the bare particle charge and the remainder of the charge in the diffuse double layer as estimated from the charge renormalization theory. Note that most of the counterions reside in the dense counterion layer anyway. Finally, it should be noted that the dielectric constant in the dense layer will be lower near the particle surface compared to the bulk water, due to the locally high electric field [20]. By estimating the electric field strength on the order of 0.1 V/Å for the surface charges involved, the dielectric constant ϵ_{ST} has been reported to be in the range of 6–20 [21]. Given this estimate of the dipole from the condensed layer, the force as a function of interparticle distance can then be calculated from

$$F = \frac{3p^2}{8\pi\epsilon_0\epsilon_1 r^4}, \tag{4}$$

from which a_2 can be calculated to be

$$a_2 = \frac{3\epsilon_1 q_{ST}^2 d_{ST}^2}{2\pi\epsilon_0\epsilon_{ST}^2 k_B T}. \tag{5}$$

In Fig. 2(b), calculations of the surface ion layer contribution to the interaction prefactor a_2 are plotted for a range of realistic values for the dielectric constant (ϵ_{CL} ~5–30) and sizes of the steric layer, as inferred from the ion sizes. The dotted lines indicate the range of the experimental data, obtained from Fig. 1. The order of magnitude of the experimentally observed a_2 is more in the range of the predictions using realistic estimates of the parameters of the steric layer.

In summary, the colloidal interactions for charged particles at the oil-water interface, where the oil has a low dielectric constant, can be quantitatively described by considering charge dissociation on the water side alone. The magnitude of the screened Coulomb part and the parameters that control a_1 will be very similar to the case of particles in bulk [7], and finite size ion effects are negligible. However, the manner in which the dipolar interaction depends on the parameters such as surface charge, electrolyte concentration, and contact angle differs. The predictions of the PB theory, even in its nonlinear versions, cannot explain the experimental values obtained for a_2 performed by using a range of different and complementary techniques. Using a relatively simple model, we showed that the magnitude of the dipolar interaction a_2 can be rationalized by considering the finite size of the ions. The dipolar interaction for particles at interfaces is dominated by the dipole over asymmetric condensed ion layer. A full detailed calculation of the dipole interaction requires solving models that account for the structure of the dense layer, such as the Bikerman model [17]. A point that merits further investigation is if more detailed calculations can capture the experimentally observed rather weak dependence on electrolyte concentration for highly charged systems ($\sim\kappa^{-0.43\pm0.04}$). This requires a detailed calculation of the competing effects of electrolyte on the overall charge in the dense layer and the shell thickness [16,22,23], and the dependence of ϵ on the local electric field strength will weaken the electrolyte dependence.

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