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Charge Renormalization for Effective Interactions of Colloids at Water Interfaces

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We analyze theoretically the electrostatic interaction of surface-charged colloids at water interfaces with special attention to the experimentally relevant case of large charge densities on the colloid–water interface. Whereas linear theory predicts an effective dipole potential, the strength of which is proportional to the square of the product of charge density and screening length, nonlinear charge renormalization effects change this dependence to a weakly logarithmic one. These results appear to be particularly relevant for structure formation at fluid interfaces with arbitrarily shaped colloids.

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Charges are a ubiquitous and important component of soft matter systems underlying numerous phenomena observable at a macroscopic scale. It is therefore essential to have a proper understanding of electrostatics in its various manifestations and system types. As a paradigmatic case of soft matter systems, colloids are heavily charged, and the surrounding solvent contains highly mobile ions in a wide range of concentrations. Although in many cases it turns out that above the atomistic scale a mean-field description of the solvent is sufficient, the simplest approach of that type, the Poisson-Boltzmann (PB) equation, already leads to a highly nonlinear problem for the electrostatic potential distribution Φ,

$$\nabla^2 \phi(\mathbf{r}) = \kappa^2 \sinh \phi(\mathbf{r}),$$

where κ^{-1} is the Debye-Hückel screening length and $\phi = e\beta\Phi$ is the dimensionless electrostatic potential (e is the elementary charge and $\beta^{-1} = k_B T$ is the temperature). The PB equation poses a difficult problem and can be solved exactly only for a uniformly charged wall. Other geometries usually require numerical methods. Apart from studies relying mostly on numerical computations, more general, analytical insights have been obtained so far only for charged objects in bulk [1,2] and confined [3] solutions.

However, due to its complexity, there is lack of any insights into the nonlinear electrostatics for the emerging area of soft matter assembly at fluid interfaces. All efforts to understand the interfacial electrostatics have been limited to the linearized version of the PB equation [4,5]. Partially wetting colloids adsorb strongly and irreversibly at interfaces forming self-assembled structures which are important building blocks for manufacturing materials with specific properties, which in turn can be used in a variety of technological applications such as electro-optical devices, sensors, emulsion stabilization, etc. [6]. From a more fundamental viewpoint, particles at interfaces have proven to be useful model systems to tackle important questions in condensed matter physics, such as the phase behavior of two-dimensional crystals (see, e.g., Refs. [7–10]). Consequently, a full understanding of the *effective*, intercolloidal forces at interfaces (which are also quantitatively different from those in bulk solution) is indispensable for the interpretation of and control over self-assembly processes. *Strong* surface charges ubiquitous in such systems (e.g., charge-stabilized polymeric colloids, mineralic disks, proteins) complicate the concept of effective forces. At interfaces between water and a nonpolar medium (typically air or oil), the associated exponentially screened electrostatic interactions in ionic bulk solvents become longer-ranged, and the colloids exhibit effective dipolelike repulsions which lead to the stabilization of two-dimensional crystals even at low surface coverages [7]. These effective dipoles originate from colloidal surface charges on the water side and a cloud of screening ions in the water phase which is asymmetric with respect to the interface plane. The prototypical model [11], which is the only analytically tractable one, treats the colloids as equal point charges q located near the interface plane and the water phase as a linearly screening medium. Generalizations to slablike geometries are also possible [12]. With ϵ_1 and ϵ_2 denoting the permittivities of the nonpolar medium and water, respectively, and ϵ_0 the dielectric constant of vacuum, the interaction between two charges q in the interface plane at separation d is given to leading order by [13]

$$U(d) = q^2 \frac{\epsilon_1}{2\pi\epsilon_0\epsilon_2^2} \frac{\kappa^{-2}}{d^3}. \tag{1}$$

Here, ϵ_1 and ϵ_2 are the permittivities of the nonpolar medium and water, respectively, and ϵ_0 is the dielectric constant of vacuum. According to this linear model, the repulsion depends quadratically on the Debye screening length $\kappa^{-1} = [\epsilon_2\epsilon_0/(2\beta c_0 e^2)]^{1/2}$ where c_0 is the concentration of monovalent ions in bulk water. On this basis, one would expect the repulsion $U \propto c_0^{-1}$ to become significantly weaker upon adding electrolytes. Various experimental, theoretical, and simulation studies of colloidal aggregation at interfaces have used the predictions of the linear model for quantitative analysis of their results (see, e.g., Refs. [5,14,15]).

The high colloidal surface charge densities σ_c on the water side of experimentally used colloids (easily up to $0.5\ \mathrm{e/nm^2}$) invalidate the naive use of the linearized Debye-Hückel (DH) model with bare charges. Strong charge renormalization will occur due to the nonlinear contributions of the governing Poisson-Boltzmann equation (PB) in the water phase. The renormalization procedure (based on the separation of length scales) consists of the identification of the appropriate linear solution of the PB problem at distances $>\kappa^{-1}$ from the charges. There, the electrostatic potential Φ is small, and linear DH electrostatics holds: $\nabla^2\Phi \simeq \kappa^2\Phi$. For a uniformly charged wall or sphere, this solution has the same functional form as if the entire problem is solved within the linear theory and the nonlinear effects alter only the prefactor. This prefactor leads to a renormalized, effective charge [16]. For nonspherical charged bodies, the map between the DH solution and the PB solution in the linear region requires a selection of the appropriate boundary conditions at the charged object such that the DH and the PB solution match asymptotically [1]. For large surface charge densities in the bulk scenario, the asymptotic PB potential—and thus the effective DH potential everywhere—saturates, and only the potential close to the charged bodies, i.e., within the screening length, responds to changes of the surface charge.

The renormalization of charges at an interface is expected to differ from that in the bulk due to the proximity of a nonpolar phase which induces an algebraic decay of the electrostatic field near the interface; to a large extent, its strength is determined by the potential within the screening length. In order to study the effect of an interface on the renormalization, we have chosen the experimentally relevant system of a charge-stabilized colloidal sphere trapped at an interface with water. The renormalized dipole-field, which is isotropic in the interface plane, can be described in terms of a single renormalized parameter given by the effective charge q_{eff}. Surprisingly, this holds also for arbitrarily shaped and charged colloids [17], for which anisotropies in the interface plane only arise in higher orders of $1/d$. Thus, our results obtained for spheres will be generic for other objects. We find that the ratio q_{eff}/q factorizes into a geometric part (describable by a linear theory) which takes into account the geometry of a charged object, i.e., the charge distribution at the colloid-water interface, and a nonlinear part which is described by the analytically solvable case (within PB theory) of a charged wall, thus being independent of the colloid shape and the contact angle. The effective charge q_{eff} is an increasing function of κ (qualitatively similar to the bulk case [2]) and, as a consequence, the effective repulsion given by Eq. (1) becomes only weakly dependent on the screening length.

The model.—We have numerically solved the electrostatic problem for a single spherical colloid of radius R trapped at an interface (with charge density σ_c on the water side) as indicated in Fig. 1; the details will be given elsewhere. We have determined the effective charge q_{eff} through equating the asymptotics of the potential in the water-oil interfacial plane to the asymptotics of the potential for the point charge in Debye-Hückel approximation. This leads to a renormalization function $g(\kappa^*, \sigma_c^*; \theta) := q_{\mathrm{eff}}/q$ (depending on $\kappa^* = \kappa R$, the dimensionless charge density $\sigma_c^* = [e\beta R/(\epsilon_0\epsilon_2)]\sigma_c$ and θ for fixed permittivities) which is $\neq 1$ also for the linear regime. The electrostatic interaction between two colloids at separation d is indeed given by Eq. (1) to leading order in d, with q replaced by q_{eff}. This can be shown by a direct calculation of the force via a pressure tensor integration over the midplane (symmetry plane) between the two colloids.

The linear Debye-Hückel regime.—The linear regime holds if $\phi \ll 1$ everywhere; this corresponds to $\sigma_c^*\kappa^{*-1} \ll 1$ if the charge is large, or $\sigma_c^* \ll 1$ for any κ^*. (The limits of the linear regime can be determined from the DH solution for a charged sphere.) In this regime, the renormalization function g_{lin} is independent of σ_c^* and is a geometric DH correction to the point charge potential. The variation of g_{lin} with κ^* and θ is moderate, and thus the renormalization function is of the order 1 (see Fig. 2 top curve). We emphasize here that the variation of g_{lin} resembles a weak effective power law for a limited range of κ^*, but it is clearly inconsistent with the proposal in Ref. [5] that it should vary $\propto \kappa^{*-1}$ in the range $1 < \kappa^{*-1} < \infty$. The inadequate assumption of Ref. [5] is that the surface charge is completely immersed in the electrolyte (except at the three phase contact line) and the field, on route to "escape" to the nonpolar phase, is weakened by crossing the electrolyte. In the actual geometry, field lines may pass through

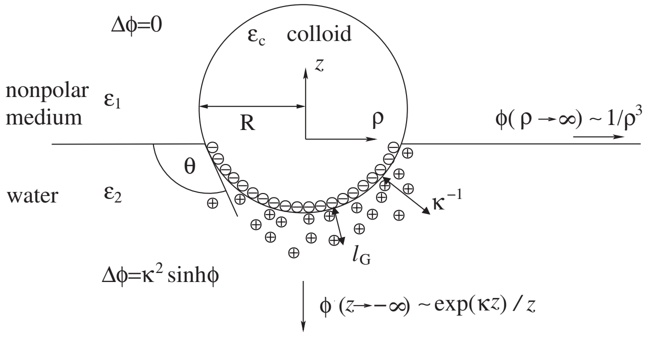

FIG. 1. Side view of a single colloid (homogeneously charged on the water side) trapped at the interface. Most of the counterions are confined in a layer close to the colloid surface with a width of the order of the Gouy-Chapman length $l_G = 2\epsilon_2\epsilon_0/(\beta e \sigma_c)$. In many colloidal experiments, $l_G(\approx 1\ \mathrm{nm}) < \kappa^{-1}(\approx 1\ldots300\ \mathrm{nm}) < R(\approx 1\ \mu\mathrm{m})$.

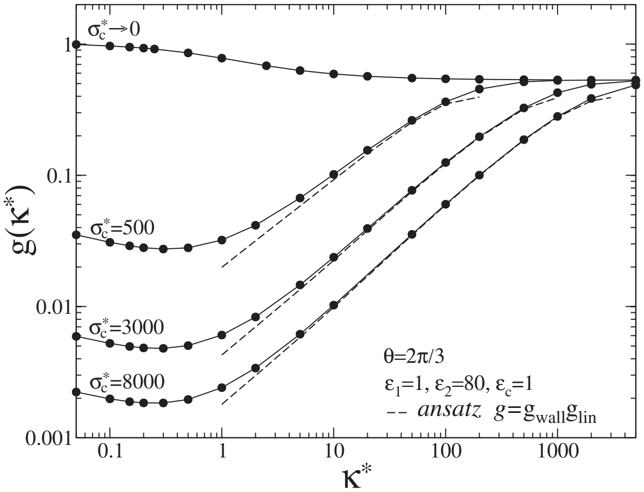

FIG. 2. The charge renormalization function in the nonlinear regime. For a colloid of radius $R = 1\ \mu$m, the two dimensionless charge densities $\sigma_c^* = 500$ and 8000 correspond to charge densities of 0.9 and 15 μC/cm^2 which approximately bracket the charge densities occurring on polymeric colloids.

the colloid and only a fraction of the field enters the top phase across the electrolyte, thus generating a weak κ^*-dependence in g_{lin}. At large κ^*, the field can no longer enter the nonpolar phase through electrolyte due to the thick layer of counterion cloud, and so the dependence of g_{lin} on κ^* disappears.

The nonlinear regime.—In typical colloidal experiments [14], the radius of the colloid is of the order of 1 μm and thus is much larger than the screening length for electrolyte concentrations $c_0 > 10^{-5}$ M ($\kappa^{-1} < 0.1\ \mu$m). Therefore, close to the colloid surface at the water side, the electrostatic problem is similar to that for a charged wall in electrolyte as curvature corrections tend to zero [18]. As already mentioned, in the bulk, the strength of the far field potential saturates for large σ_c. Our numerical results show, however, that, unlike in the bulk case, the effective charge does not level off but increases slowly: $q_{\text{eff}} \propto \ln\sigma_c^*$. The logarithmic behavior reflects the behavior of the contact potential for large σ_c. This can be understood as follows. At the interface, the asymptotic behavior of the potential is determined by the electric field which "escapes" to the oil phase. The escaping field strength is proportional to the potential right at the colloid surface on the water side because the escaping field lines originate there. Thereby, we can approximate $\sigma_{c,\text{eff}}^*$ in the charge renormalization function, $g = \sigma_{c,\text{eff}}^*/\sigma_c^*$, by the charge density which gives the correct contact potential ϕ_c^{wall} at the wall in linear theory. Within PB theory, $\sigma_c^* = 2\kappa^* \sinh[\phi_{\text{wall}}^c/2]$ [16]; in the linear limit (i.e., small σ_c^*/κ^*), this reduces to $\phi_{\text{wall}}^c = \sigma_c^*\kappa^{*-1}$ and in the highly nonlinear limit (i.e., σ_c^*/κ^* large), $\phi_{\text{wall}}^c = 2\ln(\sigma_c^*\kappa^{*-1})$. By equating the two limiting cases, we obtain $g_{\text{wall}} = 2[\ln(\sigma_c^*\kappa^{*-1})]/(\sigma_c^*\kappa^{*-1})$. However, the full renormalization function g contains in addition the geometric contributions unaccounted for by the wall approximation. We augment the nonlinear "wall" part by the linear "geometry" part, $g \approx g_{\text{wall}}(\sigma_c^*, \kappa^*)g_{\text{lin}}(\kappa^*, \theta)$. In the strongly nonlinear regime, this *ansatz* describes our full numerical data for g rather well (see Fig. 2). The wall model approximation of the renormalization function can be corroborated in an alternative, more involved determination of $\sigma_{c,\text{eff}}^*$ by calculating the effective dipole generated by the surface charges and the counterion cloud. The latter approach gives rise to corrections $O(\kappa^{*-1})$ which explain the behavior of g for small κ^*. The failure of the *ansatz* for large κ^* reflects the disappearance of the nonlinear effects in this range.

The separability of the renormalization function into a wall and a geometry part allows us to propose an interaction potential valid for two like, but arbitrarily shaped colloids with characteristic spatial extensions and radii of curvature larger than κ^{-1}:

$$\beta U(d) \approx \frac{1}{2\pi^2}\frac{\epsilon_1}{\epsilon_2}\frac{A^2}{\lambda_B d^3}\ln^2\left(\frac{\sigma_c^*}{\kappa^*}\right)g_{\text{lin}}^2(\kappa^*, \theta). \tag{2}$$

Here, $\lambda_B = \beta e^2/(4\pi\epsilon_2\epsilon_0) \approx 0.7$ nm is the Bjerrum length for water, and A is the area of the charged surface exposed to water. For a sphere, $A = 2\pi R^2(1 + \cos\theta)$. As discussed before, g_{lin} becomes a constant of the order of 1 for large κ, and the κ-dependence of U is contained only in the wall term $U \propto \ln^2[\sigma_c^*\kappa^{*-1}]$. The comparison with the predictions of the linear theory, $U \propto (\sigma_c^*\kappa^{*-1})^2$, shows that the nonlinear PB theory yields a drastically changed dependence on both the charge density and the screening length.

Comparison with experiment.—There are numerous publications concerning the aggregation and compression behavior of colloidal monolayers. The number of studies concerned with a quantitative determination of the pair potential is limited; nevertheless, all of them consistently yield $U(d) \propto d^{-3}$. This dipolar asymptotic behavior is shared by both electrostatic repulsions and capillary attractions [19]. The magnitude of the latter is affected by a factor ε_F which is the ratio between the total electrostatic

TABLE I. Comparison between available experimental data and Eq. (2) for the amplitude of the interaction potential. For simplicity, here $g_{\text{lin}} = 1$.

σ_c^*	κ^*	$\beta U/(R/d)^3 \times 10^{-3}$		θ
		Expt.	theory	(Refs. [14,20])
air-water—Ref. [21]				
3900	1	8.06	1.8–4.6	30^o–80^o
800	1	2.16	1.1–2.8	30^o–80^o
oil-water—Ref. [10]				
3900	2	2.36	0.8–6.5	75^o–124^o
oil-water—Ref. [5]				
6800	2	220	1.2–10	75^o–124^o
6800	135	220	0.3–2.3	75^o–124^o

force on the colloid perpendicular to the interface and the surface tension force scale $2\pi\gamma R$ [19]. For the studies analyzed below, we found $\varepsilon_F < 0.1$, and thus we may neglect capillary effects. Comparison with the present renormalized theory [Eq. (2)] requires knowledge of θ. Two different visual methods [14,20] differ significantly which also affects the theoretical result (see Table I). (a) Inversion of pair correlation functions: Reference [21] reports results for two batches of polystyrene (PS) particles ($R = 0.55$ μm and 0.5 μm) at the interface between air and ultrapure water. Reference [10] reports corresponding results for PS particles ($R = 1.0$ μm) at the interface between oil and ultrapure water. The comparison between the experimental and the theoretical values reveals that the renormalized charges on the water side seem to suffice in order to explain the observed repulsions. Charge renormalization is essential because the straightforward application of the linear theory [Eq. (1)] with the bare charge gives $\beta U \sim 10^7 (R/d)^3$, which is orders of magnitude off. (b) Pair force measurements with optical tweezers: Reference [5] reports data for the effective pair potential between PS spheres ($R = 1.35$ μm) at the oil-water interface for two electrolyte concentrations. The independence of the magnitude of the dipole potential on the electrolyte concentration could not be explained by linear theory, and thus residual surface charges on the colloid-oil surface were postulated as the main source of repulsion [22]. This picture is now frequently invoked in the literature; however, its validity is strongly doubtful for the following reasons. As shown, linear theory is invalid and cannot be used for the physical interpretation; for the repulsive potential, renormalized theory predicts the lack of a strong dependence on κ. We note that recent, more extensive tweezer measurements at an oil-water interface show indeed a weak dependence on the electrolyte concentration [23], fully consistent with our model. On the other hand, the *magnitude* of the repulsive potential obtained with the laser-tweezer method is larger by a factor >20, thus pointing to still another source of repulsion between the colloids. Yet in this respect, the results from the laser-tweezer experiments are inconsistent with the ones from Ref. [10] discussed under (a) above. An independent check of the tweezer results by using inversion of the pair correlation function for the same experimental system seems to be necessary.

In summary, within Poisson-Boltzmann theory, we have discussed the electrostatic interaction of charged spherical colloids trapped at an interface between a nonpolar medium and water. For charges on the water side only, we have found a strong renormalization of the effective repulsion U, changing the dependence on the surface charge density σ_c and the screening length κ^{-1} from $U \propto \sigma_c^2 \kappa^{-2}$ (linear theory) to $U \propto \ln^2[e\beta/(\epsilon_0\epsilon_2)\sigma_c\kappa^{-1}]$. For very large charge densities, there is a possibility of a near independence of the effective interactions on the salt concentration. Geometric effects induced by the shape of the colloid are not expected to alter this result significantly as long as κ^{-1} is smaller than the diameter of the colloid. Available experimental results appear to be inconsistent with each other. Potentials determined from pair correlation function data compare well with the renormalized theory, and thus the existence of residual charges on the colloid-oil surface can be questioned. Potentials determined from tweezer measurements are significantly larger; their salt dependence but not their strength is captured by the renormalized model. Thus, resolving the experimental inconsistencies is clearly necessary to advance a quantitative description.

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