Charge renormalization for effective interactions of colloids at water interfaces

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(Dated: February 1, 2008)

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 air–water interfaces with arbitrarily shaped colloids.

PACS numbers: 82.70.Dd

The effective interactions of colloids trapped at fluid interfaces reveal qualitatively new features when compared to the ones in colloidal bulk solutions. First, there is the possibility of long–ranged capillary attractions mediated by deformations of the interface. Second, many colloids carry a significant amount of charge (e.g. charge–stabilized polymeric colloids, mineralic disks, proteins) and the exponentially screened electrostatic interactions in ionic bulk solvents become longer–ranged at interfaces between water and a nonpolar medium (typically air or oil). At such interfaces the colloids exhibit effective dipole–like repulsions which lead to the stabilization of two–dimensional crystals even at low surface coverages. 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. Within a simple model (the only analytically tractable one) the colloids are approximated as equal point charges located in the interface plane and the water phase is treated as a linearly screening medium. To leading order the interaction between two charges $q$ in the interface plane at separation $d$ is given by

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

Here, $\epsilon_1$ and $\epsilon_2$ are the permittivities of the nonpolar medium and water, respectively, and $\epsilon_0$ 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, $e$ is the elementary charge, and $\beta^{-1} = k_B T$. On this basis one would expect the repulsion $U \propto \epsilon_0^{-1}$ to become significantly weaker upon adding electrolytes. Various studies of colloidal aggregation at interfaces have used the predictions of the linear model for quantitative analysis of experimental results (see, e.g., Refs. [3, 6]). In Ref. [6] $q$ in Eq. (1) was replaced by $q_{\text{eff}} \propto \kappa^{-1}$ to account for geometric effects of a charged spherical colloid, which leads to $U \propto \epsilon_0^{-2}$.

The high colloidal surface charge densities $\sigma_c$ on the water side of experimentally used colloids (easily up to 0.5 $e$/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 corresponding linear solution of the PB problem at distances $> \kappa^{-1}$ from the charges. There the electrostatic potential $\Phi$ is small and linear DH electrostatics holds: $\nabla^2 \Phi \approx \kappa^2 \Phi$. 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 affect only the prefactor. This prefactor leads to a renormalized, effective charge $\tilde{q}$. For non-spherical 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 at the far field. In the limit $\sigma_c \to \infty$ of the surface charge density the renormalized DH potential at the colloid surface levels off at a constant regardless of the geometry of the charged body.

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 renor-
nonpolar medium $\varepsilon_1$

water $\varepsilon_2$

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 $l_G = 2e_2\varepsilon_2/|3e\sigma_c|$. In many colloidal experiments, $l_G \approx 1\text{ nm} < \kappa^{-1} \approx 1\ldots300\text{ nm} < R(\approx 1\text{ \mu m})$.

renormalized dipole field can be described in terms of a single renormalized parameter given by the effective charge $q_{\text{eff}}$. We find that the ratio $q_{\text{eff}}/q$ 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. In contrast to the case of colloids in the bulk we find that $q_{\text{eff}}$ does not level off for highly charged particles. Also the functional dependence of $q_{\text{eff}}$ on $\kappa$ differs from the bulk case; nonetheless $q_{\text{eff}}$ remains an increasing function of $\kappa$ [6]. As a consequence, the effective repulsion given by Eq. (1) becomes only weakly dependent on the screening length.

The model. For a single spherical colloid of radius $R$ trapped at an interface as indicated in Fig. 1 we have solved the electrostatic problem given by the Poisson–Boltzmann equation in the water phase, $\nabla^2 \phi = \kappa^2 \sinh(\phi)$, and the Laplace equation in the oil phase, $\nabla^2 \phi = 0$. Here, $\phi = e\beta\Phi$, $\nabla^2 = \hat{R}\nabla$ and $\kappa = \kappa R$ are the dimensionless electrostatic potential, gradient operator and screening length, respectively. At the water–oil and the colloid–oil interface the tangential electric field and the normal electric displacement are continuous, while at the colloid–water interface the normal electric displacement has a jump $\sigma_c$. The differential equations with the appropriate boundary conditions are solved using the finite element method package FEMLAB [10]. In order to determine the potential at large distances from the particle we have chosen the computational space to be $8000 R$ so that the boundary conditions enclosing the box do not influence the data of interest. The nominal charge on the colloid is $q = \sigma_c 2\pi R^2(1 + \cos \theta)$. We have determined the effective charge 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: $q_{\text{eff}} = \lim_{\rho \to \infty}(2\pi e_0 \varepsilon_2^2/\varepsilon_1)(\rho^2/e\beta\kappa^{-2})\phi(\rho, z = 0)$. Finite box size effects become visible at a distance $\rho = 500 R$ from the colloid; thus all our data are taken within this range. The electrostatic interaction between two colloids at separation $d$ is indeed given by Eq. (1) to leading order in $d$, with $q$ replaced by $q_{\text{eff}}$. 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. For fixed permittivities, the ratio $q_{\text{eff}}/q = g(\kappa^*, \sigma_c^*; \theta)$ defines a renormalization function which depends on $\kappa^*$, the dimensionless charge density $\sigma_c^* = (e\beta R/(\epsilon_0\varepsilon_2))\sigma_c$ and $\theta$.

The linear Debye–Hückel regime. The linear regime holds if $\phi \ll 1$ everywhere and corresponds to $\sigma_c^*\kappa^{* - 1} \ll 1$. (The retrieval of the linear regime in this limit can be confirmed from the exact solution for the charged wall model.) In this regime, the renormalization function is independent of $\sigma_c^*$: $g \to g_{\text{lin}}(\kappa^*, \theta)$. The variation of $g_{\text{lin}}$ with $\kappa^*$ and $\theta$ is moderate and thus the renormalization function is of the order 1 (see Fig. 2). The variation of $g_{\text{lin}}$ resembles a weak effective power–law for a limited range of $\kappa^*$ but it is clearly inconsistent with the proposal in Ref. [6] that it should vary $\propto \kappa^{* - 1}$ in the range $1 < \kappa^{* - 1} < \infty$. The weak dependence of $g_{\text{lin}}$ on $\kappa^*$ reflects the fact that the electrostatic field originating from the surface charges “escapes” to the insulator phase both through the colloid and, to some extent, through the electrolyte. At large $\kappa^*$ the electrolyte “escape” route is blocked due to the thick counterion cloud surrounding the charged colloid and so the dependence of $g_{\text{lin}}$ on $\kappa^*$ disappears. The inadequate assumption of Ref. [6] is that the electrolyte “escape” route is the only one except for the field originating from the charges near the three–phase contact line.

The nonlinear regime. As inferred from the linear
regime the geometric contributions to the effective charge do not have a strong influence on \( g \) (\( g_{\text{lin}} \) is of the order of 1 for various contact angles as shown in Fig. 2). This encourages us to deduce some general properties of \( g \) without solving the full problem explicitly. In typical colloidal experiments \( R \) the radius of the colloid is of the order of 1 \( \mu \)m 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.

Since for a charged wall the potential outside the screening length levels off at large \( \sigma_c \) and the strength of the potential in the linear regime is \( \sigma_c^* \kappa^{-1} \), this implies that for fixed \( \kappa^{-1} \) and large \( \sigma_c^* \), \( \lim_{\sigma_c \to \infty} g \to 0 \) (in order to satisfy \( \sigma_c^* \kappa^{-1} = \text{const} \)), and that for fixed, large \( \sigma_c^* \), \( g \) must increase with \( \kappa \), i.e., \( g \) must increase upon adding electrolyte. Extrapolating these results for the charged wall to the present situation we find \( g \approx 4/(\sigma_c^* \kappa^{-1}) \), i.e., \( q_{\text{eff}} \) is proportional to the screening length. Thus the interaction potential between two colloids (Eq. 1 with \( q \to q_{\text{ef}} \)) is independent of the screening length and thus of the electrolyte concentration, at least within this crude “wall approximation”.

Our numerical results show, however, that, unlike in the bulk case, the effective charge does not level off but increases slowly: \( q_{\text{ef}} \propto \ln \sigma_c^* \). This can be understood in terms of a second, somewhat more refined “wall approximation”. 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 the charge renormalization function from the contact potential at the wall \( g_{\text{wall}} = \sigma_{c_{\text{wall}}}^*/\sigma_c^* \). The relation between the surface charge and the potential at contact \( \phi_{\text{wall}} \) for a charged wall is \( \sigma_c^* = 2\kappa^* \sin[\phi_{\text{wall}}^c/[2] \) in the linear limit (i.e., small \( \sigma_c^*/\kappa^* \) this reduces to \( \phi_{\text{wall}}^c = \sigma_c^* \kappa^{-1} \) and in the highly nonlinear limit (i.e., \( \sigma_c^*/\kappa^* \) large) \( \phi_{\text{wall}}^c = 2 \ln(\sigma_c^* \kappa^{-1}) \). The effective surface charge is obtained by equating the two limiting cases leading to \( g_{\text{wall}} = 2(\ln(\sigma_c^* \kappa^{-1}))/((\sigma_c^* \kappa^{-1}) \). 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, which we have shown in Fig. 2. \( g \approx g_{\text{wall}}(\sigma_c^*, \kappa^* \) \( g_{\text{lin}}(\kappa^*, \theta) \). In the strongly nonlinear regime this \( g_{\text{lin}} \) describes our full numerical data for \( g \) rather well (see Fig. 3). The wall model approximation of the renormalization function can be corroborated in an alternative, more involved determination of \( \sigma_{c_{\text{wall}}}^* \) 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 \( \kappa^* \). The failure of the \( g_{\text{lin}} \) for large \( \kappa^* \) reflects the disappearance of the nonlinear effects in this range.

Inserting \( q_{\text{eff}} \) (as obtained from the wall model) into Eq. 1 provides the interaction potential, exhibiting a weak dependence on the screening length:

\[
\beta U(d) \approx \frac{8\varepsilon_1}{\varepsilon_2 \lambda_B} \cos^4 \left( \frac{\theta}{2} \right) \frac{R^3}{d^3} \ln^2 \left( \frac{\sigma_c^*}{\kappa} \right) g_{\text{lin}}^2(\kappa^*, \theta), (2)
\]

Here \( \lambda_B = \beta \varepsilon_2/(4\pi \varepsilon_2 \varepsilon_0) \approx 0.7 \) nm is the Bjerrum length for water. As discussed before \( g_{\text{lin}} \) becomes a constant of the order of 1 for large \( \kappa \) and the \( \kappa \)-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 a number of publications concerning the aggregation and compression behavior of colloidal monolayers. However, direct or indirect measurements of pair potentials are rather limited. Reference 11 reports results for two batches of polystyrene (PS) particles: (a) charged sulfate groups, \( R = 0.55 \) \( \mu \)m, \( \sigma_c = 12.5 \) \( \mu \)C/cm\(^2\) and (b) charged carboxyl groups, \( R = 0.5 \) \( \mu \)m, \( \sigma_c = 2.8 \) \( \mu \)C/cm\(^2\), both investigated at an interface between air and ultrapure water (\( \kappa^* \approx 1 \)). The tail of the repulsive potential (obtained by inverting pair correlation functions) was fitted to a dipole form (see Tab. 1). Comparison with the present renormalized theory (Eq. 2) requires knowledge of \( \theta \). Two different visual methods applied to sulfonated PS particles at the air–water interface \( 5, 12 \) yield quite different results which also affects the theoretical result (see Tab. 1).
The comparison between experimental and theoretical values reveals that for the air–water interface the renormalized charges on the water side seem to be sufficient to explain the observed repulsions. In this case charge renormalization is essential because the straightforward application of the linear theory (Eq. (1)) with the bare charge gives \( U \sim 10^7 \times (R/d)^3 \), which is orders of magnitude off. For the oil–water interface, Ref. [6] reports tweezer measurement data for the effective pair potential (PS spheres with sulfate groups, \( R = 1.35 \mu \text{m}, \sigma_c = 8.9 \mu \text{C/cm}^2 \)) for two electrolyte concentrations (\( \kappa^* \approx 2 \) and 130). Both data sets could be fitted to one and the same pair potential. Although the uncertainty in the contact angle translates into a considerable spread of the theoretical predictions, the renormalized theory yields a potential which is too small by at least a factor of 20. Therefore, the experimental results of Ref. [6] point to still another source of repulsion between the colloids. In Ref. [6] this other source was argued to be colloidal surface charges on the oil side, inferred only from the lack of a strong \( \kappa \)-dependence in the repulsion as predicted by the linear theory. This argument is insufficient since the renormalized interaction weakens the \( \kappa \)-dependence considerably; the hypothesis of possible extra charges on the oil side is rather supported by the insufficient magnitude of the renormalized potential. Asymptotically the charges on the oil side together with their image charges in the water create a net dipole in the nonpolar phase \( \rho_{\text{oil}} \approx 2q_{\text{oil}} h \), where \( h \) is their average distance from the bottom of the particle. Due to the high dielectric constant of water, \( \rho_{\text{oil}} \) will be rather independent of the electrolyte concentration [13]. The total effective dipole moment of the colloid is then given by \( \rho_{\text{oil}} + \rho_{\text{water}} \) where \( \rho_{\text{water}} = (2e_1/e_2)qk^{-1}g(\sigma^*, \kappa^*, \theta) \) is the dipole moment caused by the charges on the water side. The asymptotic interaction between two colloids is then dominated by true dipole-dipole interactions given by

\[
U(d) \approx \frac{1}{8\pi \epsilon_0 \epsilon_1} \left( \rho_{\text{oil}}^2 + 2 \rho_{\text{oil}} \rho_{\text{water}} \right) \frac{1}{d^3},
\]

which in addition to the interaction given in Eq. (1). The results in Tab. I suggest that \( \rho_{\text{oil}} \) is at least \( \sqrt{20} \) times larger than \( \rho_{\text{water}} \) (for pure water). Even then, a certain electrolyte concentration dependence of the interaction potential can be expected through the ensuing cross term \( \propto \rho_{\text{oil}} \rho_{\text{water}}(\kappa^*) \) which has not been discussed in Ref. [6]. We note that recent, more extensive tweezer measurements at an oil–water interface show indeed a marked dependence on the electrolyte concentration [13].

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 \( \sigma_c \) and the screening length \( \kappa^{-1} \) from

\[
U \propto \sigma_c^2 \kappa^{-2} \quad \text{(linear theory)}
\]

to

\[
U \propto \ln^2 \left( \epsilon_1 / (\epsilon_0 \epsilon_2 \sigma_c \kappa^{-1}) \right).
\]

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 \( \kappa^{-1} \) is smaller than the linear size of the colloid. For colloids at an air–water interface, available experimental results compare well with the renormalized theory, while for colloids at an oil–water interface the renormalized theory underestimates the observed effective potential, pointing to an additional source of repulsion such as possible residual charges on the oil side.

Acknowledgment: M. O. acknowledges financial support from the DFG through the Collaborative Research Centre “Colloids in External Fields” SFB-TR6.

| \( \sigma_c^* \) | \( \kappa^* \) | \( \beta U/(R/d)^3 \times 10^4 \) | \( \theta \) |
|-----------|-----------|-----------------|------|
| \text{air–water} \ (Ref. [1]) | | | |
| 3900 | 1 | 8.06 | 1.8 . . . 4.6 | 30° . . . 80° |
| 800 | 1 | 2.16 | 1.1 . . . 2.8 | 30° . . . 80° |
| \text{oil/water} \ (Ref. [6]) | | | |
| 6800 | 2 | 220 | 1.2 . . . 10 | 75° . . . 124° |
| 6800 | 135 | 220 | 0.3 . . . 2.3 | 75° . . . 124° |

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

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