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LETTER TO THE EDITOR

Attractions between charged colloids at water interfaces

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Abstract

The effective potential between charged colloids trapped at water interfaces is analysed. It consists of a repulsive electrostatic and an attractive capillary part which asymptotically both show dipole-like behaviour. For sufficiently large colloid charges, the capillary attraction dominates at large separations. The total effective potential exhibits a minimum at intermediate separations if the Debye screening length of water and the colloid radius are of comparable size.

In view of various basic and applied issues such as the study of two-dimensional melting [1], investigations of mesoscale structure formation [2] or engineering of colloidal crystals on spherical surfaces [3], the self-assembly of sub-micrometre colloidal particles at water–air or water–oil interfaces has gained much interest in recent years. These particles are trapped at the interface if water wets the colloid only partially. This configuration is stable against thermal fluctuations. It appears to be even the global equilibrium state, because it is observed experimentally that the colloids immersed in the bulk phases are attracted towards the interface [1]. For charge-stabilized colloids at interfaces, the *repulsive* part of their mutual interaction is well understood and resembles a dipole–dipole interaction at large separations. This asymptotic interaction is caused by charges at the colloid–water interface [4] or by isolated charges at the colloid–air (or oil) interface [5]. Nonetheless, charged colloids at interfaces also exhibit *attractions* far beyond the range of van der Waals forces. According to [6–11], polystyrene spheres (radii $R = 0.25\text{--}2.5\ \mu\text{m}$) on flat water–air interfaces using deionized water exhibit the spontaneous formation of complicated metastable mesostructures. They are consistent with the presence of an attractive, secondary minimum in the effective intercolloidal potential at separations $d/R \approx 3\text{--}20$ with a depth of a few $k_B T$. In [12], PMMA spheres with radius $R = 0.75\ \mu\text{m}$ were trapped at the interface of water droplets immersed in oil. Here, the secondary minimum has been detected at a separation $d/R = 7.6$ and is reported to

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be surprisingly steep. The tentative explanation of these findings given in [12] invokes an analogue of long-ranged flotation or capillary forces which decay $\propto 1/d$. This interpretation was criticized in [13, 14], both of which concluded that possible capillary forces in this system are much shorter ranged, i.e., $\propto d^{-7}$, but the authors of these articles disagree with respect to the sign of these shorter-ranged forces. Recently we have shown [15] quite generally that long-ranged flotation-like forces $\propto 1/d$ can only arise in mechanically non-isolated systems. For isolated systems the capillary force is indeed much shorter ranged, and within a superposition approximation the power law discussed in [14] is found. For the experiment involving the interface of a mesoscopic droplet [12], mechanical isolation may indeed be weakly violated and thus small flotation-like forces can appear. Their interplay with capillary forces arising from the droplet curvature is not yet clear, and is currently under scrutiny [16]. On the other hand, for experiments performed on flat interfaces [6–11], mechanical isolation holds if there is no external electric field present and thus for them flotation-like forces cannot give rise to the observed attractions. Out of other attempts to explain the nature of this colloidal pattern formation we mention [17], in which this is attributed to oil contaminations of the interface, and [10], in which colloidal roughness is proposed as a source of attractive capillary interactions. At present, these attempts to explain the observed colloidal patterns at interfaces are only of qualitative nature.

Thus a theoretically sound mechanism for the appearance of an attractive minimum in the intercolloidal potential at large separations has not yet been found. Here we analyse the interaction between colloids at interfaces within the approach developed in [15] for a mechanically isolated system and we provide conditions for an asymptotically attractive intercolloidal potential and for the appearance of such a minimum.

In going beyond the superposition approximation studied in [15], we derive the full capillary interaction potential between two colloids as a functional of a general stress field acting on the interface. This capillary potential is studied for two cases: (i) the Debye screening length of water, κ^{-1} , is much smaller than the colloid radius R , and (ii) R and κ^{-1} are of comparable size. For a sufficiently high charge on the colloids, in both cases the ensuing capillary attraction turns out to be asymptotically stronger than the direct repulsion. Moreover, in case (ii) a *minimum* in the total (repulsive plus capillary) intercolloidal potential is found at intermediate separation $\kappa d_{\min} \gtrsim 10$.

We consider two spherical colloids $\alpha = 1, 2$ trapped at a deformed interface (meniscus) with vertical coordinate $z = \hat{u}(\mathbf{r} = (x, y))$. We denote \hat{h}_α as the vertical coordinate of the centre of colloid α and \mathbf{r}_α its lateral position so that $d = |\mathbf{r}_1 - \mathbf{r}_2|$. We define a reference configuration (with respect to which free energy differences are measured) by a flat interface $u = 0$ and $h_{\alpha,\text{ref}} = -R \cos \theta$. Here, θ is Young's angle and thus in the reference configuration the colloids are vertically positioned such that Young's law holds at the horizontal three-phase contact circle with radius $r_{0,\text{ref}} = R \sin \theta$. The corresponding free energy is given by [15]

$$\hat{\mathcal{F}} = \gamma \int_{S_{\text{men}}} d^2r \left[\frac{|\nabla \hat{u}|^2}{2} + \frac{\hat{u}^2}{2\lambda^2} - \frac{\hat{\Pi}}{\gamma} \hat{u} \right] + \sum_{\alpha=1,2} \left\{ \frac{\gamma}{2r_{0,\text{ref}}} \oint_{\partial S_\alpha} d\ell [\Delta \hat{h}_\alpha - \hat{u}]^2 - \hat{F}_\alpha \Delta \hat{h}_\alpha \right\}. \quad (1)$$

The first line of equation (1) comprises free energy differences associated with the change in meniscus area, in meniscus gravitational energy (γ is the water–air surface tension and λ is the capillary length) and with forces on the meniscus; the stress $\hat{\Pi}$ denotes the vertical force per unit area on the meniscus in the reference configuration. The first term in the second line takes into account the changes in water–colloid and air–colloid surface energies; $\Delta \hat{h}_\alpha$ is the difference in colloid centre position with respect to the reference configuration. The second term describes the energy difference if colloid α is shifted by the force \hat{F}_α (which is evaluated in the reference configuration). S_α is the circular disc of radius $r_{0,\text{ref}}$ delimited by the three-phase

contact line ∂S_α formed on the colloid α by the fluid interface in the reference configuration (traced counterclockwise), and $S_{\text{men}} = \mathbb{R}^2 \setminus (S_1 \cup S_2)$. This expression for the free energy is valid as long as the deviations from the reference configuration are small: $|\hat{u}|/r_{0,\text{ref}}, |\nabla \hat{u}| \ll 1$. A sufficient condition for this is $|\varepsilon_{\hat{F}}| \ll 1$, with $\varepsilon_{\hat{F}} := -\hat{F}_\alpha/2\pi\gamma r_{0,\text{ref}}$. Mechanical isolation implies $2\hat{F}_\alpha = -\int_{S_{\text{men}}} d^2r \hat{\Pi}$, i.e., the forces on the colloids are balanced by the force on the meniscus [15]. The meniscus-induced effective potential between the colloids is defined as $V_{\text{men}}(d) = \hat{\mathcal{F}}(\hat{u}, \hat{h}_\alpha|_{\text{eq}}; d) - \hat{\mathcal{F}}(\hat{u}, \hat{h}_\alpha|_{\text{eq}}; d \rightarrow \infty)$. The equilibrium free energy is found by minimizing equation (1) with respect to \hat{u} and \hat{h}_α . The equilibrium meniscus shape for the two colloids being infinitely apart is given by the superposition $\hat{u}(d \rightarrow \infty) = u_1 + u_2$ of the single colloid menisci, obtained in the presence of the stress field $\hat{\Pi}(d \rightarrow \infty) = \Pi_1 + \Pi_2$. Here, $u_\alpha = u(|\mathbf{r} - \mathbf{r}_\alpha|)$ is the equilibrium meniscus around *one* colloid and likewise $\Pi_\alpha = \Pi(|\mathbf{r} - \mathbf{r}_\alpha|)$ is the stress field on the interface caused by a *single* colloid. Furthermore we define the single-colloid quantity $\varepsilon_F = \int_{\mathbb{R}^2 \setminus S_1} d^2r \Pi/2\pi\gamma r_{0,\text{ref}}$. For finite d , the stress field can be written as $\hat{\Pi}(d) = \Pi_1 + \Pi_2 + 2\Pi_m$ and likewise we decompose $\hat{u}(d) = u_1 + u_2 + u_m$. Minimization of equation (1) yields

$$\nabla^2 u_m - \frac{u_m}{\lambda^2} = -\frac{2\Pi_m}{\gamma}, \quad (2)$$

with the boundary condition $u_m = 0$ for $\mathbf{r} \rightarrow \infty$, and at $\mathbf{r} \in \partial S_\alpha$ ($\beta \neq \alpha$):

$$\frac{\partial(u_m + u_\beta)}{\partial n_\alpha} = \varepsilon_{\hat{F}} - \varepsilon_F + \frac{u_m + u_\beta - \langle u_m + u_\beta \rangle_\alpha}{r_{0,\text{ref}}}, \quad (3)$$

with $2\pi r_{0,\text{ref}} \langle \cdot \rangle_\alpha \equiv \int_{\partial S_\alpha} (\cdot) d\ell$. The superposition approximation entails $\Pi_m = u_m = 0$ for all d (i.e., $\varepsilon_{\hat{F}} = \varepsilon_F$), and was analysed in [15]. To identify the corrections to it, we write $V_{\text{men}} = V_{\text{sup}}[\Pi] + V_m[\hat{\Pi}]$ and obtain after some algebra (in the following we consider $\lambda \rightarrow \infty$; this limit can be safely taken in the case of mechanical isolation [15])

$$\begin{aligned} V_{\text{sup}} &= \int_{S_1} d^2r \Pi_2 u_2 - \int_{S_{\text{men}}} d^2r \Pi_1 u_2 + 2\pi\gamma r_{0,\text{ref}} \varepsilon_F \langle u_2 \rangle_1, \\ V_m &= - \int_{S_{\text{men}}} d^2r (\Pi_2 u_m + 2\Pi_m u_2 + \Pi_m u_m) + 2\pi\gamma r_{0,\text{ref}}^2 \\ &\quad \times \left[(\varepsilon_F^2 - \varepsilon_{\hat{F}}^2) + \varepsilon_{\hat{F}} \frac{\langle u_m \rangle_1}{r_{0,\text{ref}}} - (\varepsilon_F - \varepsilon_{\hat{F}}) \frac{\langle u_1 + u_2 \rangle_1}{r_{0,\text{ref}}} \right]. \end{aligned} \quad (4)$$

In the following, we apply this general expression for the capillary potential within two electrostatic models which provide explicit expressions for Π and Π_m . Generically, the water phase contains screening ions which lead to a finite Debye screening length $\kappa^{-1} = (\varepsilon_2/8\pi\beta c_0 e^2)^{1/2}$, where c_0 is the concentration of monovalent ions, e is the elementary charge, and $\beta^{-1} = k_B T$. We denote by $\varepsilon_1, \varepsilon_2, \varepsilon_c$ the permittivities of air, water, and the colloid, respectively, using Gauss units.

(1) $\kappa r_{0,\text{ref}} \gg 1$. The electrostatics of the single-colloid configuration has been analysed in [18] with the result that only charges at the colloid–air interface generate a stress on the interface. The potential Φ_0 at the air–water interface is small so that the interface resembles a perfect conductor. According to [18], $\Pi \approx (\varepsilon_1/8\pi) E_{z,0^+}^2$, where $E_{z,0^+}$ denotes the z -component of the electric field right above the interface, leading to the following robust parametrization of the corresponding numerical results:

$$\Pi(r) = \frac{\gamma \varepsilon_F}{r_{0,\text{ref}}} b(\mu) \left(\frac{r}{r_{0,\text{ref}}} - 1 \right)^{\mu-1} \left(\frac{r}{r_{0,\text{ref}}} \right)^{-\mu-5}, \quad (5)$$

where $\varepsilon_F > 0$, $b = \mu(\mu+1)(\mu+2)(\mu+3)/6$ and $\mu \in (0, 1)$ is a fitting parameter depending on ε_c and the contact angle θ . Π has an integrable divergence as $r \rightarrow r_{0,\text{ref}}$ and rapidly

(i.e., $r \gtrsim 2r_{0,\text{ref}}$) reaches its asymptotic dipole behaviour $\propto r^{-6}$. The dipole asymptotics renders the repulsive part of the intercolloidal potential V_{rep} for large d ,

$$V_{\text{rep}} = 4\pi\gamma r_{0,\text{ref}}^2 \varepsilon_F b(\mu) \left(\frac{r_{0,\text{ref}}}{d} \right)^3, \quad (6)$$

and $\Pi_m = (\Pi_1 \Pi_2)^{1/2}$ because the electric field of the two-colloid configuration is the superposition of the electric fields in the single-colloid configurations. This stress is strongly peaked around the colloid centres and the main contribution in equations (4) stems from the regions around the colloids as $d \rightarrow \infty$. Therefore, in order to obtain V_{men} to leading order in $1/d$ one can employ the approximation $\Pi_m \approx \Pi^{1/2}(d)(\Pi_1^{1/2} + \Pi_2^{1/2})$ to solve equations (2) and (3) and to evaluate the integrals in equation (4):

$$V_{\text{men}}(d) \approx -2\pi\gamma r_{0,\text{ref}}^2 \varepsilon_F^2 \left(\frac{r_{0,\text{ref}}}{d} \right)^3 \frac{8b(\mu)}{\mu + 1} [1 + M(\mu)]. \quad (7)$$

Here, the function $M(\mu)$ is given by a lengthy analytical expression; it increases almost linearly for $\mu \in (0, 1)$ with $M(0) = 0$ and $M(1) = 1/5$. The leading asymptotic behaviour $\propto d^{-3}$ stems from V_m (the superposition approximation predicts $V_{\text{sup}} \propto d^{-6}$ [15]). The repulsive and capillary forces decay with the same power but with opposite signs of the amplitudes. Hence, the total intercolloidal potential will be attractive if $\varepsilon_F > \varepsilon_{F,\text{crit}} = (\mu + 1)/4[1 + M(\mu)]$ with $1/4 < \varepsilon_{F,\text{crit}} < 5/12$ for $0 < \mu < 1$. The appearance of capillary attractions thus depends sensitively on the colloidal charge via ε_F . These critical values for ε_F are at the limit the maximum deviation for the meniscus occur at the three-phase contact line and are given to leading order in $1/d$ by the single-colloid solution: $|\nabla \hat{u}| \approx \varepsilon_F$, $\hat{u}/r_{0,\text{ref}} \approx -\mu\varepsilon_F/4$. Experiments which are performed in the limit $\kappa r_{0,\text{ref}} \gg 1$ [5, 18] estimate charge densities on the colloid–air surface compatible with $0 < \varepsilon_F \ll 1$ and thus the electrostatic repulsion would always be stronger than the capillary attraction. Even if ε_F were large enough such that the capillary attraction would dominate, equations (6) and (7) would not render a minimum in the total potential at *intermediate* separations. However, the possibility for the occurrence of such a minimum arises outside the regime $\kappa r_{0,\text{ref}} \gg 1$.

(2) $\kappa r_{0,\text{ref}} \lesssim 1$. In this regime, κ^{-1} provides an additional length scale which leads to interesting crossover phenomena, and the charges on the colloid–water surface are not completely screened in the range of separations of interest. The stress is given by

$$\Pi = \frac{\varepsilon_1}{8\pi} \left(1 - \frac{\varepsilon_1}{\varepsilon_2} \right) \left[E_{z,0^+}^2 + \frac{\varepsilon_2}{\varepsilon_1} E_{\parallel,0}^2 \right] + p_{\text{osm}}. \quad (8)$$

Here, $E_{z,0^+}$ and $E_{\parallel,0}$ are the perpendicular and the parallel component of the electric field at the interface on the air side. The osmotic pressure $p_{\text{osm}} = \beta^{-1} \Delta n$ is generated by the excess ion number density Δn at the interface on the water side. In order to solve the electrostatic problem, we introduce two simplifications: the Debye–Hückel approximation, and the point-charge approximation, by which the total charge q of the colloid is concentrated at the centre of S_α . Then the osmotic pressure is given by $p_{\text{osm}} = (\varepsilon_2/8\pi)\kappa^2\Phi_0^2$ and the electrostatic repulsion between two colloids by $V_{\text{rep}}(d) = q\Phi_0(d)$, where Φ_0 is the electrostatic potential at the interface. V_{rep} exhibits a crossover from a screened Coulomb repulsion to a dipole repulsion at $\kappa d_c \approx 8\text{--}10$ [4]. The single-colloid stress, equation (8), is dominated by $E_{\parallel,0}$ and p_{osm} for $\kappa r < 6\text{--}8$, yielding $\Pi(r) \propto \exp(-2\kappa r)/r^4$. For larger distances, it is dominated by $E_{z,0^+}$ and the familiar dipole form arises, $\Pi(r) \propto r^{-6}$. The stress $\hat{\Pi}$ exerted by two colloids can again be determined by superimposing the electric fields and potentials of the single-colloid solution, leading to

$$\Pi_m = \frac{\varepsilon_1}{8\pi} \left(1 - \frac{\varepsilon_1}{\varepsilon_2} \right) (E_{z,0^+})_1 (E_{z,0^+})_2 + \frac{\varepsilon_2 - \varepsilon_1}{8\pi} (E_{\parallel,0})_1 (E_{\parallel,0})_2 \cos \phi + \frac{\varepsilon_2}{8\pi} \kappa^2 (\Phi_0)_1 (\Phi_0)_2. \quad (9)$$

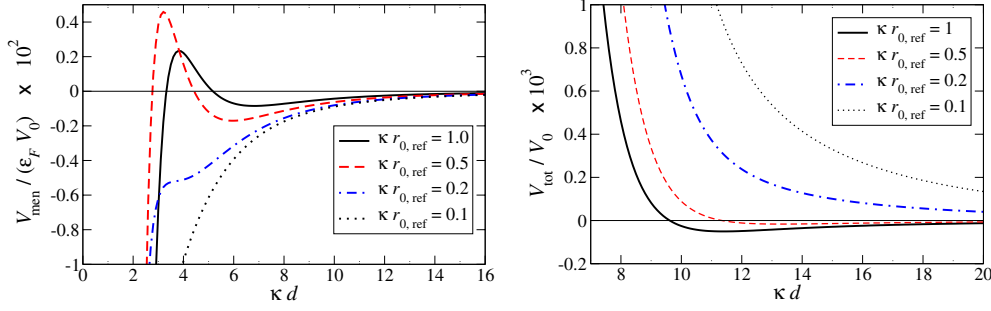


Figure 1. The capillary potential (left panel) obtained from the full numerical solution in units of $V_0 = q^2 \kappa^2 r_{0,\text{ref}} / 2\pi \epsilon_2$ for $\kappa r_{0,\text{ref}} = 0.1$ – 1.0 and the parameters $\epsilon_2/\epsilon_1 = 81$ and $\kappa\lambda = 100$. The peak approximation fails for $\kappa d \lesssim 8$. The total intercolloidal potential $V_{\text{tot}} = V_{\text{men}} + V_{\text{rep}}$ (right panel) for $\epsilon_F = 0.6$ and the same parameters and units.

(This figure is in colour only in the electronic version)

As before, the subscript $\alpha = 1, 2$ denotes evaluation of the single-colloid function at $|\mathbf{r} - \mathbf{r}_\alpha|$ and $\cos \phi = (\mathbf{r} - \mathbf{r}_1) \cdot (\mathbf{r} - \mathbf{r}_2) / |\mathbf{r} - \mathbf{r}_1| |\mathbf{r} - \mathbf{r}_2|$. In the limit $d \gg d_c$, u_m and V_{men} can be estimated via an expansion in $1/d$ using a peak approximation for Π_m as before. This yields an asymptotically attractive capillary potential which again decays $\propto d^{-3}$. For intermediate separations d , we have compared these results with a full numerical solution to equations (2) and (3) without any approximation for Π_m or V_{men} . In figure 1 (left panel) we show the results for V_{men} . For $d > d_c$ the $1/d$ -expansion and the numerical results agree with each other, both exhibiting the dipole-like asymptotic behaviour. For smaller d the extrapolated $1/d$ -expansion predicts a repulsive capillary potential which is borne out by the numerical results only partly as $\kappa r_{0,\text{ref}} \rightarrow 1$. The superposition contribution V_{sup} is again negligible in the expression for V_{men} . The total intercolloidal potential $V_{\text{tot}} = V_{\text{men}} + V_{\text{rep}}$ is depicted in figure 1 (right panel) for the exemplary value $\epsilon_F = 0.6$. Asymptotically V_{tot} is attractive for $\epsilon_F > \epsilon_{F,c} \approx 0.34[1 + 0.30/(\kappa r_{0,\text{ref}})^2]^{1/2}$, obtained from a fit to numerical results for $\kappa r_{0,\text{ref}} \in [0.1, 2.0]$.

A quantitative comparison with experiments is difficult because the three important quantities q , θ , and κ^{-1} which enter into ϵ_F and the scale of V_{men} have not been determined separately for the same system. Therefore, we can only estimate whether a minimum as obtained in figure 1 can occur in actual experiments. For almost all experiments pure water is claimed to have been used, for which $\kappa^{-1} \approx 1 \mu\text{m}$. The total charge is given by $q = 2\pi\sigma R^2(1 + \cos \theta)$ where σ is the charge density. Thus, for colloids with $R = 0.5 \mu\text{m}$ and $\theta = \pi/2$ at pure water–air interfaces ($\gamma = 0.07 \text{ N m}^{-1}$), we obtain numerically $\epsilon_F \approx 45(\sigma \text{ nm}^2/e)^2$. The potential scale at $T = 300 \text{ K}$ is given by $V_0 = q^2 \kappa^2 r_{0,\text{ref}} / (2\pi \epsilon_2) \approx 1.4 \times 10^8 k_B T (\sigma \text{ nm}^2/e)^2$. The value $\epsilon_F = 0.6$ used in figure 1 corresponds to a charge density $\sigma = 0.12 e \text{ nm}^{-2}$ (literature estimates for the actual charge density vary between 0.07 [6] and 0.53 [10] $e \text{ nm}^{-2}$), in which case $V_0 = 2 \times 10^6 k_B T$. For $\kappa r_{0,\text{ref}} = 0.5$, the minimum in the total potential (see figure 1) occurs at $\kappa d_{\text{min}} \approx 13$ with $V_{\text{min}} \approx -1.6 \times 10^{-5} V_0 = 32 k_B T$. This minimum is shallow enough that thermal movements of the colloids around the minimum position should be visible, similar to reports in the literature.

Such large charge densities actually call for solving the Poisson–Boltzmann equation near the colloids. Incorporating the correct geometry, this is a very involved numerical task and will be considered in future work. From that we expect the following modifications: the screening ions will concentrate near the colloid in a layer with thickness of a few nanometres (as given

by the Gouy–Chapman length $l_G = 8\pi\epsilon_2/(\beta e\sigma)$. Outside this layer, the colloids appear as heavily screened objects with an effective charge q_{eff} and the Debye–Hückel approximation is valid. This charge q_{eff} enters both the electrostatic repulsion and the capillary attraction such that asymptotically $V_{\text{rep}} \propto q_{\text{eff}}^2(r_{0,\text{ref}}/d)^3$ and $V_{\text{men}} \propto \epsilon_F q_{\text{eff}}^2(r_{0,\text{ref}}/d)^3$. The total force on one colloid (as expressed by ϵ_F) is not determined by q_{eff} , but rather by the interfacial stress in the screening layer (dominated by p_{os} and $E_{\parallel,0}$). Since this layer is thin compared to the colloid radius, near the three-phase contact line the problem appears to be similar to that of a charged plate half-immersed in water. For an order of magnitude estimate of ϵ_F we have used the analytical solution for a fully immersed plate and obtain $\epsilon_F \sim \epsilon_2/(\pi\gamma\beta^2 e^2 l_G) = 1.2(\sigma \text{ nm}^2/e)$ for the parameters discussed above. Thus, $\epsilon_F = 0.6$ (as used in figure 1) is obtained for $\sigma = 0.5 e \text{ nm}^{-2}$, not too far from the Debye–Hückel result. We emphasize that the occurrence of a potential minimum for $\epsilon_F > \epsilon_{F,c}$ (i.e., for a sufficiently large charge q) is a consequence of the *intermediate distance* crossover in Π from being pressure dominated (by $E_{\parallel,0}$ and p_{osm}) to tension dominated (by $E_{z,0^+}$). This mechanism is captured correctly by the presently employed approximations (point charge and Debye–Hückel treatment).

To summarize, we have calculated the effective intercolloidal potential for charged colloids floating on a water interface. We have derived a general expression for the capillary potential as an explicit functional of the stress on the interface. We have quantitatively studied the capillary potential when the stress is due to the electrostatic field of charged colloids in the cases that the radius R of the colloid compared with the Debye screening length κ^{-1} of water is either very large or of about the same size. In both cases the asymptotic behaviour of the capillary potential and of the direct electrostatic repulsion is equal, $\propto d^{-3}$, but different in sign. The superposition approximation, predicting a capillary potential $\propto d^{-6}$, is insufficient because it takes into account only the energy change as the subsystem ‘one colloid + surrounding meniscus’ is shifted vertically in its own (single-colloid) force field. The correction to the superposition approximation, embodied in Π_m , considers the additional force by the second colloid. The capillary attraction only dominates for a sufficiently large charge and the total intercolloidal potential exhibits an attractive minimum only if $\kappa^{-1} \sim R$. This minimum can be understood as a consequence of the pressure-to-tension crossover in the stress acting on the interface. The depth of the potential minimum is significantly reduced compared to the natural energy scale γR^2 of capillary interactions and is of the order of several $k_B T$ for parameters relevant for actual experimental conditions.

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