Electric-Field Induced Capillary Interaction of Charged Particles at a Polar Interface

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We study the electric-field induced capillary interaction of charged particles at a polar interface. The algebraic tails of the electrostatic pressure of each charge results in a deformation of the interface $u \sim \rho^{-4}$. The resulting capillary interaction is repulsive and varies as ρ^{-6} with the particle distance. As a consequence, electric-field induced capillary forces cannot be at the origin of the secondary minimum observed recently for charged PMMA particles at on oil-water interface.

Electrostatic forces operating on charged particles determine to a large extent the properties of emulsions and foams, and stabilize colloidal aggregates [1,2]. Charged particles at interfaces or in thin films form 2D hexagonal crystals [3–7], while for bulk colloidal suspensions several 3D crystal phases have been reported [8]. At a typical lattice spacing of a few microns, the interparticle forces are of the order of picoNewton.

A charge at a polar interface and its counterion cloud carry a finite dipole moment perpendicular to the interface (Cf. Fig. 1.) The resulting electrostatic force acting on two neighboring particles is repulsive and varies with the inverse fourth power of their distance [3,9–12]. This law has been confirmed experimentally for charged polystyrene particles [6].

The pair potential of PMMA particles at an oil-water interface has been measured by recording the trajectories and evaluating distance correlations. Besides the dipolar repulsion at short distances, an attractive force has been found at larger distances, and a minimum in the potential energy has been shown to occur at about 5.7 μm [7]. As a possible explanation, these authors propose that the deformation of the interface by the particles gives rise to a capillary interaction that varies logarithmically with their distance [7].

Quite generally, a capillary or elastic interaction is obtained when equilibrating an external force acting on the particles with the surface tension or the bending rigidity. A variety of such models have been studied, both for spherical and anisotropic defects [13–19]; these works deal with forces that act on the particle only, such as gravity. A somewhat different pattern arises for forces that operate both on the particle and on the surrounding interface. For example, a polymer grafted on a membrane exerts a force at the point of attachment and an opposite entropic pressure on the interface [20].

In this Letter we study the deformation of a polar interface due to a charged colloidal particle, and we derive the resulting capillary interaction. The present work is confined to the case most relevant for micron size colloidal particles, where the distance is much larger than the Debye length. After a reminder of the free energy of a deformation field, we calculate the electrostatic pressure profile exerted by a charge and the associated counterions (as shown schematically in Fig. 1.) The electric-field induced capillary interaction is compared to experimental findings and to the case of δ-force that was proposed in [7].

FIG. 1. a) Pressure profile $\hat{\pi}(r)$ induced on the interface by a charged particle (filled grey circle); open circles are the counterions. b) The corresponding deformation field $\hat{u}(r)$.

We consider particles of charge Q trapped at an electrolyte-insulator interface. In the absence of forces, the interface S is flat and its energy reads γS, where γ is the surface tension. The charged particles and their counterions exert on the interface a pressure that is given by the normal component of the stress tensor and comprises entropic and electrostrictive contributions,

$$\pi(\mathbf{r}) = k_B T(n_+ + n_-) + \mathcal{T}_{zz}^{\text{ins}} - \mathcal{T}_{zz}^{\text{el}}. \tag{1}$$

The first term is the entropic pressure of the excess density of positive and negative ions, $n_\pm = n_s \left(e^{\mp e\phi(r)/k_B T} - 1 \right)$, induced by N surface charges. Electroneutrality requires $e \int dV (n_+ - n_-) = -NQ$. The remaining terms involve the Maxwell tensor

$$\mathcal{T}_{ij} = \varepsilon \left(E_i E_j - \frac{1}{2} \mathbf{E}^2 \delta_{ij} \right), \tag{2}$$

evaluated at the electrolyte and insulating side of the interface. Note that both the dielectric constant ε and the normal component E_z of the electric field vector are discontinuous across the interface. The corresponding jump of the normal component of the Mawell tensor describes an electrostrictive force that arises from the difference in the electric field density in the two media.

As a consequence of the inhomogeneous pressure, the interface is no longer flat; the deformation $u(\mathbf{r})$ increases the total surface and thus the surface energy by the amount

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$$\gamma \int dS \left(\sqrt{1 + (\nabla u)^2} - 1 \right),$$

where ∇ is the 2D gradient in the interface plane. In the following, $\mathbf{r}$ denotes the in-plane coordinates, and z that normal to the interface. In the case of weak deformations, $|\nabla u| \ll 1$, we may expand the square root and retain the leading term only. Then the free energy functional reads

$$f[u(\mathbf{r})] = \frac{\gamma}{2} \int dS (\nabla u)^2 - \int dS \pi(\mathbf{r}) u(\mathbf{r}). \quad (3)$$

The actual deformation is determined by minimizing this functional. Linearizing the deformation about the equilibrium value $u(\mathbf{r})$ and integrating the first term by parts, one finds that the mimimum free energy f occurs for the deformation satisfying the Young-Laplace equation,

$$\gamma \nabla^2 u(\mathbf{r}) + \pi(\mathbf{r}) = 0, \quad (4)$$

and reads

$$f = -\frac{\gamma}{2} \int dS (\nabla u)^2. \quad (5)$$

As the most severe approximation of the present paper, we assume that the total pressure $\pi(\mathbf{r})$ is the linear superposition

$$\pi(\mathbf{r}) = \sum_\alpha \hat{\pi}(\mathbf{r} - \mathbf{r}_\alpha), \quad (6)$$

where $\hat{\pi}(\mathbf{r})$ is the pressure profile of a single charge at the origin. In Debye-Hückel approximation, the electrostatic potential is a linear superposition of single-particle terms $\phi = \sum_\alpha \varphi_\alpha$, and the total pressure is quadratic in the potential and its derivatives, $\pi(r) \sim \phi^2$. Besides the diagonal terms $\hat{\pi}_\alpha \sim \varphi_\alpha^2$, it comprises cross-terms $\varphi_\alpha \varphi_\beta$ that are significantly smaller and thus have been neglected in (6).

FIG. 2. The capillary interaction arises from the superposition of the deformation fields of nearby particles.

Because of the linearity of (4), a similar relation holds true for the deformation

$$u(\mathbf{r}) = \sum_\alpha \hat{u}(\mathbf{r} - \mathbf{r}_\alpha).$$

It is then sufficient to consider two particles at positions $\pm \frac{1}{2}\rho$. Discarding terms that do not depend on their distance ρ, one finds immediatly the pair potential

$$\Delta f(\rho) = -\gamma \int d^2 r \nabla \hat{u} \left(\mathbf{r} + \frac{1}{2}\rho \right) \cdot \nabla \hat{u} \left(\mathbf{r} - \frac{1}{2}\rho \right). \quad (7)$$

The single-charge pressure $\hat{\pi}(\mathbf{r})$ comprises the entropic pressure of the excess soluted ion density and the electric field energy. It is obvious from Fig. 1 that the force on the charge is directed towards the electrolyte, whereas the electrostrictive force on the surrounding interface is in the opposite direction. It is essential to note that the total force vanishes, i.e.,

$$\int dS \hat{\pi}(r) = 0. \quad (8)$$

In view of (5) we need to calculate the gradient of the deformation field. This is achieved most easily by applying Gauss' theorem on (4),

$$\gamma \oint_{\partial D} ds \mathbf{n} \cdot \nabla \hat{u} = -\int_D dS \hat{\pi}(r),$$

that relates the pressure integrated over the area D to the "flux" of the gradient field through the boundary ∂D. For a disk centered at the origin and polar coordinates r and θ, we have $ds = rd\theta$ and $\mathbf{n} = \mathbf{r}/r$. Using the condition (8) and the fact that $\hat{u}$ is isotropic, the integral over the disk is replaced by that over the infinite space outside,

$$\nabla \hat{u}(r) = \frac{1}{\gamma} \frac{\mathbf{r}}{r^2} \int_r^\infty dr' r' \hat{\pi}(r'). \quad (9)$$

Thus we have expressed the interaction free energy $\Delta f(\rho)$ by integrals over the single-charge electrostatic pressure $\hat{\pi}(r)$ that remains to be determined.

Starting from the screened potential $\varphi(r, z)$ of a single interfacial charge at the origin, we evaluate the pressure profile according to Eqs. (1) and (2). Expanding the ion densities to quadratic order, $n_+ + n_- = n_s (e\varphi/k_B T)^2$, and noting $\kappa^2 = (2n_s e^2/\varepsilon_{el} k_B T)$, we find the entropic pressure

$$k_B T(n_+ + n_-) = \frac{\varepsilon_{el}}{2} \kappa^2 \varphi(r, z)^2.$$

The relevant component $\mathcal{T}_{zz} = \frac{\varepsilon}{2}(E_z^2 - E_r^2)$ of the Maxwell tensor depends on both normal and in-plane derivatives of the potential. The latter one, $E_r = \partial_r \varphi$, being continuous at the interface, the electrostrictive force simplifies to

$$\mathcal{T}_{zz}^{ins} - \mathcal{T}_{zz}^{el} = \frac{\varepsilon_{el} - \varepsilon_{ins}}{2} E_r^2 - \frac{\varepsilon_{el}}{2} E_z^2 \Big|_{el} + \frac{\varepsilon_{ins}}{2} E_z^2 \Big|_{ins}$$

In Debye-Hückel approximation (DHA), the 2D Fourier transform of φ is known, and explicit forms of the potential at the interface can be given in the domains separated by the Bjerrum length ℓ_B and the Debye screening length κ^{-1}. Here we confine ourselves to the case of large distances well beyond κ^{-1} and the particle size a, where the potential in the electrolyte reads [9–12]

$$\varphi_{el}(r, z) = (Q\varepsilon_{ins}/2\pi\kappa^2 \varepsilon_{el}^2) e^{-\kappa z} r^{-3} \quad (r \gg \kappa^{-1}).$$

(High charge densities may result in a renormalized value for Q.) The in-plane electric field $E_r \sim r^{-4}$ is negligible at large r; for the normal component one finds $E_z|_{el} = \partial_z \varphi_{el} = -\kappa \varphi_{el}$. Its value at the insulating side

of the interface is obtained from the continuity condition $\varepsilon_{\text{ins}}E_z|_{\text{ins}} = \varepsilon_{\text{el}}E_z|_{\text{el}}$. Thus the first term in $\mathcal{T}_{zz}^{\text{ins}} - \mathcal{T}_{zz}^{\text{el}}$ cancels the entropic pressure, the second one is negligible, and the third one gives

$$\hat{\pi}(r) = \frac{\varepsilon_{\text{ins}}}{2}\left(\frac{\varepsilon_{\text{el}}}{\varepsilon_{\text{ins}}}\kappa\varphi_{\text{el}}(r,0)\right)^2. \tag{10}$$

Now it is straightforward to calculate the gradient of the interface deformation,

$$\nabla\hat{u}(r) = \frac{1}{32\pi^2}\frac{\varepsilon_{\text{ins}}Q^2}{\gamma\varepsilon_{\text{el}}^2\kappa^2}\frac{\mathbf{r}}{r^6}, \tag{11}$$

This remarkable result, $\nabla\hat{u} \sim r^{-5}$, relies only on the asymptotic form of the potential $\varphi_{\text{el}} \sim r^{-3}$ and the fact that the net force (8) on the interface vanishes. As a consequence, the deformation field is negative and varies as $\hat{u} \sim (-1/r^4)$.

Now we discuss the behavior of $\hat{\pi}(r)$ and $\nabla\hat{u}(r)$ at small distances. The singularities for $r \to 0$ are clearly unphysical and would cause the deformation free energy Δf to diverge. The above screened potential φ_{el} and electrostatic pressure $\hat{\pi}$ are valid at large distances $r \gg \kappa^{-1}, a$. At intermediate distances $a < r < \kappa^{-1}$ screening is irrelevant; evaluating the stress tensor with the bare electrostatic potential $\varphi_{\text{el}} \sim r^{-1}$, one finds a modified power law $\hat{\pi}(r) \sim r^{-4}$ [21]. For micrometer size charged colloids, however, the particle radius a provides the most relevant physical cutoff. For this reason, it will be referred to in the remainder of this paper, although one should keep in mind that the actual situation may be more complex, especially for small molecules.

Thus the power laws of both $\hat{\pi}(r)$ and $\nabla\hat{u}(r)$ cease to be valid at distances smaller than a. Moreover, Eq. (8) requires a strong negative force operating on the particle at $r = 0$. An important conclusion can be drawn directly from the relation (8): $\nabla\hat{u}$ is positive everywhere and tends towards zero at $r = 0$.

In order to regularize the surface integral in Eq. (7), we explicitly introduce a cut-off a and replace (11) with

$$\nabla\hat{u}(r) = \frac{1}{32\pi^2}\frac{\varepsilon_{\text{ins}}Q^2}{\gamma\varepsilon_{\text{el}}^2\kappa^2}\frac{\mathbf{r}}{(r^2+a^2)^3}. \tag{12}$$

Although the precise form of this cut-off function is somewhat arbitrary, it satisfies the limit $\nabla\hat{u} = 0$ for $r \to 0$ as imposed by Eq. (9). For $r \gg a$, it shows the long-range behavior that has been obtained rigorously from (8) and (10).

Inserting $\nabla\hat{u}(\mathbf{r}\pm\frac{1}{2}\rho)$ in (7), one finds that the capillary interaction

$$\Delta f(\rho) = -(\varepsilon_{\text{ins}}Q^2/32\pi^2\gamma\varepsilon_{\text{el}}^2\kappa^2)^2 I$$

depends on particle distance and size through the integral

$$I = \int_0^\infty dr\, r\int_0^{2\pi}d\theta\frac{r^2-\frac{1}{4}\rho^2}{\left(\left(r^2+\frac{1}{4}\rho^2+a^2\right)^2-r^2\rho^2\cos^2\theta\right)^3}.$$

This definite integral can be performed analytically. Since in all applications, the particle distance ρ exceeds significantly the size a, we retain only the leading term in powers of (a/ρ) and thus have

$$I = -\frac{2\pi}{a^2\rho^6}\left(1+\mathcal{O}\left(a^2/\rho^2\right)\right).$$

The variation with the particle radius $\sim a^{-2}$ does not depend on the precise form of the cut-off function chosen above. Thus we obtain the capillary interaction

$$\Delta f(\rho) = \frac{1}{2^9\pi^3}\frac{\varepsilon_{\text{ins}}^2Q^4}{\varepsilon_{\text{el}}^4\kappa^4}\frac{1}{\gamma a^2\rho^6} \tag{13}$$

that is repulsive and varies with the inverse sixth power of the distance. Note that Δf depends on the particle charge, its size, and the Debye length.

We compare our result for the capillary interaction with experimental findings and previous work. In Ref. [7], a minimum in the interaction potential of PMMA particles was reported to occur at a distance of 5.7 microns. As a possible explanation, these authors considered the competing electrostatic and capillary interactions. Interfacial charges are subject to the well-known repulsive potential

$$V = \frac{\varepsilon_{\text{ins}}}{2\pi\varepsilon_{\text{el}}^2}\frac{p^2}{\rho^3},$$

where p is dipole moment formed by the charge and its screening cloud [10]. On the other hand, assuming an electric-field induced δ-force $\hat{\pi}(\mathbf{r}) = -\pi_0\delta(\mathbf{r})$, one obtains an attractive capillary interaction $\Delta f_\delta(\rho) = (\pi_0^2/2\pi)\ln\rho$. The sum of V and Δf_δ shows a minimum at finite distance that has been considered in Ref. [7]. Note, however, that this force does not satisfy the condition (8).

As shown schematically in Fig. 1 and discussed below (11), the electrostatic pressure profile induced by a screened surface charge comprises a long-range contribution and a δ-force,

$$\hat{\pi}(\mathbf{r}) = g(r)r^{-6} - \pi_0\delta(\mathbf{r}),$$

with a cut-off function g that is constant for $r \gg a$, vanishes at the origin, and satisfies Eq. (8). By now it should be clear that the long-range contribution to the pressure completely changes the capillary forces: While that of a pure δ-force is attractive and depends logarithmically on distance, the capillary interaction of interfacial charges is repulsive and varies as $\Delta f(\rho) \sim \rho^{-6}$. We conclude that the mimimum in the interaction potential reported in [7] cannot arise from $V + \Delta f$.

Finally we compare the relative magnitude of the forces arising from V and Δf. If the particle's charge Q is located at the interface, the dipole moment reads $p = Q/\kappa$, and the capillary interaction can be expressed in terms of the dipolar interaction V and the surface energy γa^2,

$$\Delta f(\rho) = \frac{V^2}{2^7 \pi \gamma a^2}. \qquad (14)$$

The total force $-\partial_\rho(V + \Delta f)$ is always repulsive. A change in the exponent occurs where $\partial_\rho V = \partial_\rho \Delta f$, defining the cross-over distance

$$\rho^* = \frac{1}{4} \left(\frac{\varepsilon_{\text{ins}}}{\pi^2 \varepsilon_{\text{el}}^2} \frac{p^2}{\gamma a^2} \right)^{1/3},$$

for $\rho < \rho^*$, the capillary repulsion $-\partial_\rho \Delta f \sim \rho^{-7}$ dominates, whereas at larger distances the dipolar force $-\partial_\rho V \sim \rho^{-4}$ takes over. For micron size particles at an oil-water interface with typical parameters, one finds that the cross-over distance hardly attains the micrometer range and thus is of little relevance. Quite a different situation arises if a significant fraction of the charge is located at the side of the particle immersed in the insulator. For micron size particles, the electrostatic potential φ is enhanced by a factor of the order $(\kappa a)^2$ [6], and the capillary interaction increases by a factor $(\kappa a)^4$. The modified dipole moment reads $p \sim Qa$ instead of Q/κ, resulting in a larger cross-over distance ρ^*. Note, however, that at distances much shorter than ρ^*, the gradient of the deformation $|\nabla \hat{u}|$ is no longer small, requiring to go beyond the quadratic approximation for the surface energy in (3).

In summary, we have studied the capillary interaction induced by the electric field of charged particles at an electrolyte-insulator interface. The electrostatic pressure of a single charge consists of a force acting on the particle and the opposite electrostrictive force on the interface that varies as ρ^{-6} with the lateral distance. The resulting deformation, $u \sim \rho^{-4}$, induces a capillary interaction that is repulsive and obeys a power law $\Delta f \sim \rho^{-6}$. As a consequence, this capillary force cannot be at the origin of the secondary minimum observed recently for charged PMMA particles at an oil-water interface [7].

Note added. After submission of this Letter, a comment by Megens and Aizenberg on the paper by Nikolaides et al. [7] appeared in Nature [22]. In agreement with our discussion and our Eq. (8), Megens and Aizenberg point out that there is no net force on the interface and thus invalidate the attractive logarithmic potential proposed in Ref. [7].

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