

## Multipole expansion of the electrostatic interaction between charged colloids at interfaces

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The general form of the electrostatic potential around an arbitrarily charged colloid at a flat interface between a dielectric and a screening phase (such as air and water, respectively) is analyzed in terms of a multipole expansion. The leading term is isotropic in the interfacial plane and varies with  $d^{-3}$  where  $d$  is the in-plane distance from the colloid. The effective interaction potential between two arbitrarily charged colloids is likewise isotropic and proportional to  $d^{-3}$ , thus generalizing the dipole-dipole repulsion first found for point charges at water interfaces. Anisotropic attractive interaction terms can arise only for higher powers  $d^{-n}$  with  $n \geq 4$ . The relevance of these findings for recent experiments is discussed.

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The self-assembly of stably trapped, submicrometer colloidal particles at water-air or water-oil interfaces has gained much interest in recent years. For the specific case of charge-stabilized colloids at interfaces, the *repulsive* part of their mutual interaction resembles a dipole-dipole interaction at large separations. This may be understood theoretically by approximating the colloid as a point charge located either right at the interface [1,2] (i.e., assuming charges on the colloid-water interface) and/or above the interface [3] (i.e., assuming charges on the colloid-air or colloid-oil interface). Additionally, the formation of metastable mesostructures with such colloids points to the possible existence of inter-colloidal *attractions* far beyond the range of van der Waals forces [4–6]; however, care must be taken to avoid contaminations of the interface which lead to colloid mesostructures with similar appearance [7]. Previous work [8–12] aimed at relating this attractive minimum to capillary interactions due to interfacial deformations caused by a homogeneous surface charge on the colloids but with no conclusive answer. In recent work [5,6], it was experimentally shown that the charge-carrying surface groups used for charge-stabilizing polystyrene colloids are actually distributed quite inhomogeneously and patchily over the colloid surface. Thus it was speculated in Refs. [5,6] that through this inhomogeneous charge distribution like-charged colloids could acquire effective dipole moments in the interface plane and attractive electrostatic interactions of dipole-dipole type could arise, which might overcome the repulsion at shorter distances. Motivated by the finding of inhomogeneous surface charge on colloids, we extend the asymptotic results for the electrostatic potential and interaction of point charges at water interfaces [2] to the general case of an arbitrary, localized colloidal charge distribution using a multipole expansion. The presence of the interface leads to restrictions in the multipole coefficients of the potential around a single colloid and of the interaction energy between two colloids. In particular, we find that the leading term in the effective interaction energy between two colloids at lateral distance  $d$  is isotropic in the interfacial plane, repulsive and proportional to  $d^{-3}$  regardless of the inhomogeneities of the charge distributions on the col-

loids. Angular dependencies enter the effective interaction potential only in higher orders.

For a quick insight into the effect of an interface on the multipole expansion of the electrostatic potential, we consider a toy model with the water phase as a perfect conductor. The flat interface is located at  $z=0$  and the colloid is modeled by a fixed charge distribution  $\rho_C(\mathbf{r})$  above the water phase. The boundary condition at  $z=0$  simply implies that there is no tangential (or in-plane) electric field and the potential for  $z > 0$  can be obtained with the method of image charges. Therefore, the effective (real+image) charge distribution is spatially localized and can be enclosed in a ball of finite radius  $R$  (see Fig. 1 with  $\kappa^{-1} \rightarrow 0$ ). In standard spherical coordinates  $(s, \theta, \varphi)$  measured from the center of this ball, the potential in the upper phase for  $s > R$  can be written as a multipole expansion  $\Phi_+(s, \theta, \varphi) = \sum_{\ell m} a_{\ell m} s^{-\ell-1} Y_{\ell m}(\theta, \varphi)$ , in terms of normalized spherical harmonics  $Y_{\ell m}$  [in the remainder of the paper, the + (–) index will refer to evaluation in the upper (lower) phase]. The boundary condition of vanishing in-plane electric field at the interface ( $\theta = \pi/2$ ) implies  $a_{\ell m} = 0$  for  $\ell + m$  even. Thus, the monopole vanishes ( $a_{00} = 0$ ) as well as the in-plane dipole ( $a_{1\pm 1} = 0$ ), and the leading decay is described generically by a dipole perpendicular to the interface ( $a_{10} \neq 0$ ). Consider a second, identical colloid located at an in-plane position  $\mathbf{d} = (d_x, d_y)$ . The total potential

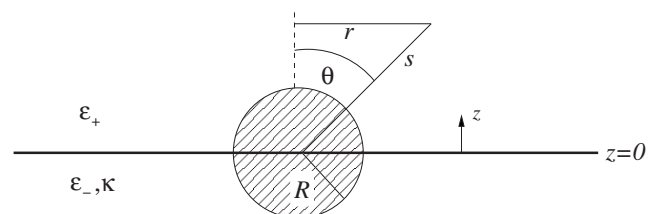


FIG. 1. Geometrical configuration of the electrostatic problem: the potential is calculated in the domain outside the sphere of radius  $R$ , which encloses the colloidal particle. The flat interface at  $z=0$  separates an upper dielectric phase (dielectric constant  $\epsilon_+$ ) from a lower electrolytic phase (dielectric constant  $\epsilon_-$ , Debye screening length  $\kappa^{-1}$ ).

$\Phi_+$  is now the linear superposition of the single-particle potentials  $\Phi_+^0$  for each colloid, and the electrostatic energy of the two-particle configuration is  $U=U^0+\int d^3r \rho_C(\mathbf{r})\Phi_+^0(\mathbf{r}+\mathbf{d})$ , where  $U^0$  is the energy in the limit  $d\rightarrow\infty$ . Taylor expanding  $\Phi_+^0$  about  $\mathbf{r}=\mathbf{0}$ , one obtains to leading order in  $1/d$

$$U-U^0\sim\frac{p_z^2}{2d^3}\quad(d\rightarrow\infty),\quad(1)$$

where  $p_z=2\int d^3r z\rho_C(\mathbf{r})=a_{10}\sqrt{3/(4\pi)}$  is the dipolar moment of  $\rho_C$  and its image charge in the direction normal to the interface. This dipole-dipole interaction energy differs by a factor of one-half from the textbook result because the electrostatic energy of only the colloid charges is half of that of the system with image charges.

The image charge construction in the case of perfectly conducting water provides an intuitive explanation of the origin of the normal dipole and the absence of the in-plane dipole. In the following we demonstrate that this finding still holds in the more realistic case of water being an electrolyte and the colloidal particle having an arbitrary shape, possibly protruding into the region  $z<0$ . Assuming linear screening, the electrostatic potential satisfies  $(\Delta-\kappa_\pm^2)\Phi_\pm(\mathbf{r})=0$  with  $\kappa_+=0$  and  $\kappa_-=\kappa$  being the inverse screening length in water. We search for a solution outside a ball of radius  $R$  whose center is the coordinate origin and which encloses the colloid (see Fig. 1) with the boundary conditions that the potential (i) vanishes at infinity, (ii) reduces to a given potential  $\Phi_R(\theta,\varphi)$  at the surface of the ball  $s=R$ , and (iii) is continuous at the interface  $z=0$ , and that (iv) the associated electric displacement perpendicular to the interface is continuous, i.e.,

$$\epsilon_+\left.\frac{\partial\Phi_+}{\partial z}\right|_{z=0}=\epsilon_-\left.\frac{\partial\Phi_-}{\partial z}\right|_{z=0}\quad(r>R).\quad(2)$$

The function  $\Phi_R(\theta,\varphi)$  is determined by the solution of the electrostatic problem inside the ball and contains the relevant information on the precise geometrical and electric properties of the particle. The properties of the electrostatic potential *outside* the ball (derived below) will be independent of the specific form of  $\Phi_R$  and thus of the charge distribution *inside* the ball. By decomposing the problem in the full domain into the solution of problems in simpler domains (the exterior of the sphere  $s=R$  and each of the half spaces defined by  $z=0$ —details can be found in Ref. [13]), one can finally write the solution as the superposition  $\Phi_\pm(\mathbf{r})=\Phi_\pm^{\text{cyl}}(r,z,\varphi)+\Phi_\pm^{\text{sph}}(s,\theta,\varphi)$ , where the contribution  $\Phi_\pm^{\text{cyl}}(r,z,\varphi)$  [using standard cylindrical coordinates  $(r,z,\varphi)$ ] is given by

$$\Phi_\pm^{\text{cyl}}(r,z,\varphi)=\sum_{m=-\infty}^{+\infty}e^{im\varphi}\int_0^\infty dq A_m(q)J_{|m|}(qr)e^{-K_\pm z}\quad(3)$$

with  $K_\pm=\pm\sqrt{q^2+\kappa_\pm^2}$ , and the contribution  $\Phi_\pm^{\text{sph}}$  (using spherical coordinates) reads

$$\Phi_\pm^{\text{sph}}(s,\theta,\varphi)=\sum_{\ell=0}^\infty\sum_{m=-\ell}^{+\ell}C_{\ell m}^\pm\mathcal{R}_\ell^\pm(s)Y_{\ell m}(\theta,\varphi)\left[\mathcal{R}_\ell^\pm(s):=s^\ell\frac{d^\ell}{(s ds)^\ell}\left(\frac{e^{-\kappa_\pm s}}{s}\right)\right].\quad(4)$$

The coefficients  $C_{\ell m}^\pm$  are given by

$$C_{\ell m}^\pm=[1-(-1)^{\ell-m}]\int_0^{2\pi}d\varphi\int_0^{\pm 1}d(\cos\theta)Y_{\ell m}^*(\theta,\varphi)\times[\Phi_R(\theta,\varphi)-\Phi_\pm^{\text{cyl}}(r=R\sin\theta,z=R\cos\theta,\varphi)],\quad(5)$$

such that  $\Phi_\pm^{\text{sph}}=0$  at  $z=0$ ,  $\Phi_\pm(s=R)=\Phi_R(\theta,\varphi)$ , and the boundary conditions (i)–(iii) are satisfied automatically. The coefficients  $A_m(q)$  in the expression for  $\Phi_\pm^{\text{cyl}}$  [Eq. (3)] must be chosen to enforce the boundary condition (2). This condition can be extended to the region  $0<r<R$  by continuing the fields  $\Phi_\pm(\mathbf{r})$  with any virtual solution into the interior of the ball,  $s<R$ . The precise form of the continuation is irrelevant, since the solution outside the ball depends only on the potential at the surface of the ball,  $\Phi_R(\theta,\varphi)$  (Faraday's cage effect). Thus, by using orthonormality and closure of the set of Bessel functions  $\{J_{|m|}(qr)\}_{q\in[0,\infty)}$  in the domain  $0<r<\infty$ , Eq. (2) can be solved for the coefficients  $A_m(q)$ :

$$A_m(q)=\frac{q\sum_{\ell=0}^\infty[\epsilon_+\hat{C}_{\ell m}^+\gamma_{\ell m}^+(q)-\epsilon_-\hat{C}_{\ell m}^-\gamma_{\ell m}^-(q)]}{\epsilon_+q+\epsilon_-\sqrt{q^2+\kappa^2}},\quad(6)$$

with  $\hat{C}_{\ell m}^\pm:=e^{-im\varphi}\partial_\theta Y_{\ell m}(\theta=\pi/2,\varphi)C_{\ell m}^\pm$  and  $\gamma_{\ell m}^\pm(q):=\int_R^{+\infty}dr\mathcal{R}_\ell^\pm(r)J_{|m|}(qr)$ , which are the Hankel transforms of the radial dependence of the spherical part  $\Phi_\pm^{\text{sph}}$  [see Eq. (4)] continued into the region  $s<R$  by zero.<sup>1</sup> Equation (6) is not the explicit expression for the coefficients  $A_m(q)$  because they appear implicitly also in the coefficients  $C_{\ell m}^\pm$  [see Eq. (5)], but it does provide their dependence on  $q$ . In particular, for  $\ell-m$  odd (i.e., when  $C_{\ell m}^\pm\neq 0$ ), the functions  $\gamma_{\ell m}^\pm(q)$  possess a Taylor expansion around  $q=0$  with the lowest term being of order  $q^{|m|}$ , so that

$$A_m(q)=\sum_{j=0}^\infty a_{jm}q^j\quad\text{with }a_{jm}=0\text{ if }j\leq|m|.\quad(7)$$

The existence of a Taylor expansion in  $q$  of the coefficients  $A_m(q)$  allows us to extract the large- $r$  behavior of the potential and the  $z$  component of the electric field at the interface. Introducing the factors

<sup>1</sup>This specific choice of the continuation can be achieved by choosing appropriate charge and dipole densities inside the ball ( $s\leq R$ ) which, however, have no effect on the solution outside the ball since  $\Phi_R$  is fixed.

$$\mathcal{J}_{jm} := \lim_{z \rightarrow 0} \int_0^\infty dp p^j J_{|m|}(p) e^{-zp} = \frac{2^j \Gamma\left(\frac{|m|+j+1}{2}\right)}{\Gamma\left(\frac{|m|-j+1}{2}\right)}$$

and inserting the expansion (7) into the corresponding definitions of the fields, one obtains<sup>2</sup>

$$\begin{aligned} \Phi_\pm(r, \varphi, z=0) &\sim \sum_{j=0}^{\infty} \sum_{m=-j+1}^{j-1} \frac{e^{im\varphi}}{r^{j+1}} a_{jm} \mathcal{J}_{jm} \\ &\sim -\frac{a_{20}}{r^3} - \frac{3}{r^4} \sum_{\pm} a_{3\pm 1} e^{\pm i\varphi} \dots, \end{aligned} \quad (8)$$

$$\begin{aligned} \left. \frac{\partial \Phi_\pm}{\partial z} \right|_{z=0} &\sim \sum_{j,m} \frac{e^{im\varphi}}{r^{j+2}} [r^{j+1} \mathcal{R}_j^+(r) \hat{C}_{jm}^+ - a_{jm} \mathcal{J}_{j+1,m}] \\ &\sim \frac{a_{10} + \hat{C}_{10}^+}{r^3} + \frac{3}{r^4} \sum_{\pm} (a_{2\pm 1} \\ &\quad + \hat{C}_{2\pm 1}^+) e^{\pm i\varphi} \dots, \end{aligned}$$

where we have used that  $C_{jm}^+ = 0$  if  $|m| = j$  and  $\hat{C}_{jm}^+ = 0$  whenever  $\mathcal{J}_{j+1,m} = 0$ . Therefore, both the potential and the normal component of the electric field at the interface are asymptotically dominated by an *angular-independent* decay proportional to  $1/r^3$ ; anisotropic behavior arises only in subleading terms. By continuity, this conclusion also holds asymptotically for the fields at a fixed height  $h$  above or below the interface ( $r \gg |h|$ ).

This result is not exclusive of the single-particle configuration: if there are several particles at the interface, one can surround each of them by a ball of radius  $R$  and the solution  $\Phi(\mathbf{r})$  of the electrostatic problem will be written as a superposition of single-particle potentials determined by the total potential at the surface of each ball [in general different from the potential  $\Phi_R(\theta, \varphi)$  in the single-particle configuration]. For each of these single-particle potentials the expansion (7) still holds, since it does not depend on the precise value of the potential at the balls (which affects only the numerical value of the coefficients of the expansion).

We calculated as an illustrative two-dimensional example the electrostatic potential for an inhomogeneously charged cylinder at an air-water interface (see the inset of Fig. 2 for some definitions). Because of its two-dimensional nature, this problem is amenable to a numerical treatment. Here, the multipole expansion at the interface gives  $\Phi_\pm(z=0) \sim a_0 \ln|x| + p_x/x + q_{xx}/x^2 + \dots$  and  $\partial\Phi_\pm/\partial z|_{z=0} \sim p_z/x^2 + \dots$ . The numerical solution for  $\Phi_\pm$  shows that the in-plane dipole term proportional to  $x^{-1}$  is absent and the asymptotic expansion starts with the quadrupolar term (see Fig. 2). The asymptotics for  $\partial\Phi_\pm/\partial z|_{z=0}$  (not shown) also contains a term

<sup>2</sup>These are asymptotic expansions. There are also exponentially decaying terms which cannot be recovered from an expansion like Eq. (7).

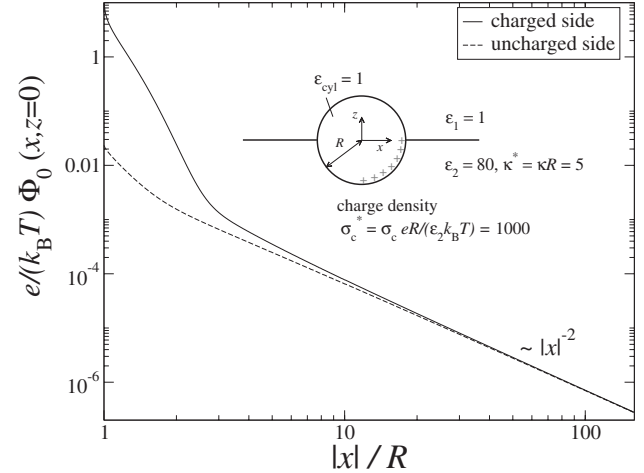


FIG. 2. Potential along the interface for an inhomogeneously charged cylinder half-immersed in water. Maxwell's equations hold in the upper phase and the cylinder and the Poisson-Boltzmann equation holds in the lower phase. The parameters are given in the inset, the numerical calculations have been done using FEMLAB.

proportional to  $x^{-2}$ , which is interpreted as the effect of a counterion-generated dipole component  $p_z$  perpendicular to the interface. These findings, most notably the absence of  $p_x$ , match the previous ones in three dimensions.

The free energy functional of a multiparticle configuration in the linear screening approximation reads [14]

$$F[\Phi] = \int d^3r \left( \rho_C(\mathbf{r}) \Phi - \frac{\epsilon(\mathbf{r})}{8\pi} [\kappa^2(\mathbf{r}) \Phi^2 + |\nabla\Phi|^2] \right), \quad (9)$$

where the charge density  $\rho_C(\mathbf{r})$  is localized on the colloidal particles. This includes the electrostatic energy as well as the entropy associated with the ion distribution. The extremum of  $F[\Phi]$  provides the field equation in thermal equilibrium,  $\nabla \cdot (\epsilon \nabla \Phi) = \epsilon \kappa^2 \Phi - 4\pi \rho_C$ . With the help of this equation, the free energy in equilibrium simplifies to

$$F_{\text{eq}}(\{\mathbf{x}_\alpha\}) = \frac{1}{2} \int d^3r \rho_C(\mathbf{r}) \Phi(\mathbf{r}), \quad (10)$$

which is known as the potential of mean force for the degrees of freedom  $\mathbf{x}_\alpha$  (position of the center of a ball of radius  $R$  enclosing the  $\alpha$ th particle). One may decompose  $F_{\text{eq}} = F^0 + \delta F$ , where  $F^0$  is the equilibrium free energy in the limit  $|\mathbf{x}_\alpha - \mathbf{x}_\beta| \rightarrow \infty$  (isolated particles). The total potential can be similarly written as  $\Phi = \sum_\alpha \Phi_\alpha^0 + \delta\Phi$ , where  $\Phi_\alpha^0(\mathbf{r})$  denotes the potential field generated by the  $\alpha$ th particle in isolation and  $\delta\Phi(\mathbf{r}; \{\mathbf{x}_\alpha\})$  is the total perturbation induced by the presence of other particles. Due to the linear nature of the problem, the perturbation  $\delta\Phi$ ,

$$\delta\Phi(\mathbf{r}) = \sum_{\alpha \neq \beta} \int_{|\mathbf{r}' - \mathbf{x}_\alpha| < R} d^3r' G_{\alpha\beta}(\mathbf{r}, \mathbf{r}') \Phi_\beta^0(\mathbf{r}'), \quad (11)$$

can be written in terms of a generalized susceptibility  $G_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$  depending on the precise shape and charge distribution of the particles.

Since  $\Phi^0(\mathbf{r})$  near the interface exhibits asymptotically an isotropic decay proportional to  $1/r^3$ ,  $\delta\Phi(\mathbf{r};\{\mathbf{x}_\alpha\})$  depends only on  $d_{\alpha\beta}=|\mathbf{x}_\alpha-\mathbf{x}_\beta|$  (and not on the orientation of  $\mathbf{x}_\alpha-\mathbf{x}_\beta$ ) in the asymptotic limit  $d_{\alpha\beta}\rightarrow\infty$ . Furthermore,  $\delta\Phi$  is rescaled by a factor  $\lambda^{-3}$  if all distances  $d_{\alpha\beta}$  are rescaled simultaneously by a factor  $\lambda$ . From Eq. (10) the same property holds for  $\delta F(\{\mathbf{x}_\alpha\})$ . In particular, for a two-particle configuration this yields an asymptotic potential of mean force of the form

$$F_{\text{eq}}(d) - F^0 \sim \frac{B}{d^3} \quad (d \rightarrow \infty), \quad (12)$$

and the constant  $B$  is positive for like particles. In analogy with Eq. (1), it is natural to interpret this expression as the interaction energy between two effective dipoles perpendicular to the interface.

In conclusion, we have shown that the forms of the multipole expansion of the potential around a charged colloid and of the effective interaction energy between two colloids trapped at a water interface are qualitatively different from the situation in bulk. The dominating interaction terms can be qualitatively understood by assuming water to be a perfect conductor. The leading interaction term between the colloids a distance  $d$  apart is of dipole-dipole type (proportional to  $d^{-3}$ ) and isotropic in the interfacial plane. In other words, even if the charges on the colloid surface are distributed arbitrarily the counterions arrange themselves such that asymptotically the configuration corresponds to an effective dipole perpendicular to the interface. The precise evaluation of the dipole strength for a given, arbitrary configuration is a difficult problem; for some insight see Ref. [17]. Orientation-dependent interactions and thus possible attractions for like-charged colloids arise only in subleading order. This is in marked contrast to the analysis of the experiment reported in Refs. [5,6]. Motivated by the experimentally found inhomogeneous surface charge, it was pictorially suggested (see Fig. 1 in Ref. [5]) that spontaneous fluctuations in the colloid's orientation would generate (via an instantaneously equilibrating

counterion cloud) effective in-plane dipoles  $\mathbf{p}_i$  with corresponding interactions proportional to  $[d^2(\mathbf{p}_1\cdot\mathbf{p}_2)-3(\mathbf{d}\cdot\mathbf{p}_1)\times(\mathbf{d}\cdot\mathbf{p}_2)]/d^5$ . After averaging over the orientation fluctuations, such an interaction would lead to an effective, isotropic attraction competing with the isotropic dipole-dipole repulsion. According to Ref. [6], the total interaction potential would exhibit an attractive minimum due to the effect of the fluctuating in-plane dipoles at rather small distances ( $d \approx 2.2$  colloid radii  $R_C$ , so small that already the use of a pure dipole-dipole interaction casts serious doubts on the reliability of the model). The analysis in Ref. [15] purporting to support this picture is actually incomplete and just states that no monopolar term arises, without entering into a systematic analysis of constraints on higher-order multipoles. The results of our work imply that asymptotically an in-plane dipolar interaction cannot arise if the counterions are equilibrated [see Eq. (12)]. Consequently, one cannot expect asymptotically relevant attractions from the orientational fluctuations of the colloids. However, for smaller  $d$  the asymptotic  $1/d$  expansion is likely to break down. For small colloid radius  $R_C \ll \kappa^{-1}$ , this becomes relevant when  $d \sim \kappa^{-1}$ : in this case the screening clouds of the colloids overlap and the interaction falls off exponentially with  $d$  before crossing over to an algebraic decay [2,12]. For large colloid radius  $R_C \gg \kappa^{-1}$ , the precise shape and charge distribution of the colloids will determine the interaction whenever  $d \sim R_C$ . However, even in that case the existence of attractions is doubtful, considering the general results on the absence of like-charge attraction in confined geometries [16]. In any case, the results from the model studied in Refs. [5,6] are not reliable since the model presupposes an interaction energy that does not satisfy the correct asymptotic decay given by Eq. (12).

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