




Electrostatic potential between charged particles at an oil-water interfaceAlexander Morozov , Iain Muntz , Job H. J. Thijssen, and Davide Marenduzzo 

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(Received 18 December 2019; revised 1 July 2020; accepted 18 August 2020; published 31 August 2020)

Electrostatic interactions between point charges embedded into interfaces separating dielectric media are omnipresent in soft matter systems and often control their stability. Such interactions are typically complicated and do not resemble their bulk counterparts. For instance, the electrostatic potential of a point charge at an air-water interface falls off as r^{-3} , where r is the distance from the charge, exhibiting a dipolar behavior. This behavior is often assumed to be generic, and is widely referred to when interpreting experimental results. Here we explicitly calculate the in-plane potential of a point charge at an interface between two electrolyte solutions with different, finite dielectric permittivities and Debye screening lengths, such as oil and water. We show that the asymptotic behavior of this potential is neither a dipole, which characterizes the potential at air-water interfaces, nor a screened monopole, which describes the bulk behavior in a single electrolyte solution. By considering the same problem in arbitrary dimensions, we find that the physics behind this difference can be traced to the asymmetric propagation of the interaction in the two media. Our results should be relevant to understand the effective potential acting between interfacial proteins in biofilms, and the self-assembly of charged colloids at droplet surfaces in oil-water emulsions.

DOI: [10.1103/PhysRevE.102.020801](https://doi.org/10.1103/PhysRevE.102.020801)

The physics of charged objects at, or near, liquid interfaces is full of subtle and nontrivial effects [1–12]. For instance, charged particles trapped at the air-water interface interact electrostatically via a long-range dipole-dipole repulsion, even if mobile ions screen any Coulombic interaction in the water phase [2,13]; this interaction can be harnessed to create tunable plasmonic materials [14]. An oil-water interface can itself acquire a negative charge due to the adsorption of hydroxyl ions [15], leading to a generic repulsion between uncharged hard spheres trapped at the interface [16]. Interfacial electrostatics is also important in biological physics, as it underlies the self-assembly of charged proteins within biofilms [17], or at the droplet surfaces in water-oil emulsions studied in food science [18].

A popular approximate treatment for electrostatic effects in a bulk electrolyte is the Debye-Hückel theory [19], which is valid when the electrostatic potential is small everywhere in the system so that nonlinear effects can be disregarded. While simplified, this theory includes the effects of ionic fluctuations at a Gaussian level [3]. The main successful prediction of the Debye-Hückel theory is that mobile ions in an electrolyte generically screen charges, so that the potential of a point charge is proportional to $e^{-\kappa r}/r$, instead of being $\sim 1/r$. The quantity κ is the inverse of the Debye screening length: it depends on ionic charge and concentration, and quantifies the efficiency of screening.

The Debye-Hückel theory has been generalized for systems with an interface [1–3,13], with most results focusing on the case where one of the electrolytes has no mobile ions, so that its Debye length is infinite. In this case, which is directly relevant to air-water interfaces, the interaction potential of a

point charge along the interface was shown to decay as r^{-3} [13], as for bulk dipolar interactions. While this result is not directly applicable to interfaces separating media with *finite*, yet different screening lengths, like oil-water interfaces, it is often assumed that there should at least be a large range of distances over which the r^{-3} decay is observed in such situations as well (as reviewed, for instance, in [20]). Here we demonstrate that this is in general not the case. We study the simple but fundamental problem of a point charge at an interface between two electrolytes with different (but finite) Debye screening lengths (Fig. 1). We show that the in-plane potential at the interface decays with an anomalous scaling, which differs from both the screened Coulomb potential characterizing charge interactions in bulk electrolytes and the dipolar decay, relevant for water-air interfaces. We argue that the potential we derive should regulate the self-assembly of colloidal monolayers at oil-water interfaces, such as those formed in “bijels” [21,22] or Pickering emulsions [23,24].

The problem we are interested in is sketched in Fig. 1. Two point particles, each with charge Q , lie at the interface between two dielectric media, with dielectric permittivities ϵ_1 and ϵ_2 , respectively. The interface is normal to the z axis and located at $z = 0$, whereas \mathbf{r} denotes positions on the plane parallel to it (Fig. 1). While there are mobile ions in each of the two media, there are no ions at the interface (the case of a salty interface with mobile ions is qualitatively similar, and can be dealt with via a modified boundary condition [3,25]). We want to find the interparticle potential $U(r) = Q\phi(r)$, where r is the interparticle distance and $\phi(r)$ is the value of the electrostatic potential generated by the first particle at the position of the second particle. The equation for ϕ is given by the Maxwell equation $\nabla \cdot \mathbf{D} = \rho$, where \mathbf{D} is the electric displacement field and $\rho = Q\delta(\mathbf{r})\delta(z) + \rho_{\text{ion}}(\mathbf{r}, z)$ is the total charge density, which includes the interfacial point charge and

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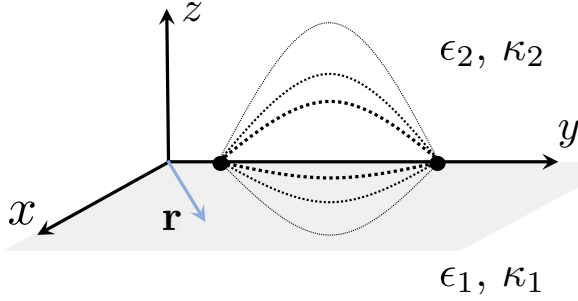


FIG. 1. Schematics of the problem we consider. A pair of charged point particles lies at the interface between two electrolytes with different screening length and dielectric permittivities. The lines connecting the two particles are examples of Debye strings contributing to the calculation of the interparticle potential (see text).

the ionic charges in the two media, $\rho_{\text{ion}}(\mathbf{r}, z)$ [note $\delta(\mathbf{r})$ refers to a two-dimensional Dirac delta function].

Following [1], we can find ϕ by using the Poisson-Boltzmann theory in each of the two media to approximate $\rho_{\text{ion}} = n_0 e^{-Ze_0\phi/k_B T}$, with n_0 the ionic concentration in the bulk of that medium, Z the valence of the ions, e_0 the elementary charge, k_B the Boltzmann constant, and T the temperature. The linearized version of this equation, valid for $\frac{Ze_0\phi}{k_B T} \ll 1$, is given by

$$\nabla \cdot [\epsilon(z)\nabla\phi] - \epsilon(z)\kappa^2(z)\phi = -Q\delta(\mathbf{r})\delta(z), \quad (1)$$

where $\kappa(z)$ is the inverse Debye length and $\epsilon(z)$ the dielectric permittivity of the medium. For our geometry, the parameters $(\epsilon(z), \kappa(z))$ equal (ϵ_1, κ_1) for the first medium ($z < 0$), and (ϵ_2, κ_2) for the second medium ($z > 0$). For an oil-water interface, such as dodecane-water, typical values are $\kappa_1 \sim 10\kappa_2 \sim 1 \mu\text{m}^{-1}$, and $\epsilon_1 \sim 40\epsilon_2 \sim 80\epsilon_0$ (with ϵ_0 the dielectric permittivity of free space).

Introducing the in-plane Fourier transform, so that $\phi(\mathbf{r}, z) = (2\pi)^{-2} \int d\mathbf{q} e^{i\mathbf{q}\cdot\mathbf{r}} \hat{\phi}(\mathbf{q}, z)$, in Eq. (1), we obtain the electrostatic potential in the two half-spaces,

$$\begin{aligned} \hat{\phi}(\mathbf{q}, z) &= A e^{\sqrt{q^2 + \kappa_1^2} z}, & z < 0, \\ \hat{\phi}(\mathbf{q}, z) &= B e^{-\sqrt{q^2 + \kappa_2^2} z}, & z > 0. \end{aligned} \quad (2)$$

From Eq. (1), it can be seen that the potential needs to be continuous at $z = 0$, so that $A = B$, and that there needs to be a discontinuity in its derivative, such that

$$\epsilon_2 \left[\frac{\partial \phi}{\partial z} \right]_{z=0^+} - \epsilon_1 \left[\frac{\partial \phi}{\partial z} \right]_{z=0^-} = -Q. \quad (3)$$

As a result, the potential as a function of position on the interface is given by the following (two-dimensional) inverse Fourier transform [1,3,13],

$$\phi(r) = \frac{Q}{4\pi^2} \int d^2\mathbf{q} \frac{e^{i\mathbf{q}\cdot\mathbf{r}}}{\epsilon_1 \sqrt{\kappa_1^2 + q^2} + \epsilon_2 \sqrt{\kappa_2^2 + q^2}}. \quad (4)$$

We can also write $\phi(r) = \frac{Q}{2\pi r} I(r)$, in terms of the following integral,

$$I(r) = \int_0^\infty dx \frac{x J_0(x)}{\epsilon_1 \sqrt{\kappa_1^2 r^2 + x^2} + \epsilon_2 \sqrt{\kappa_2^2 r^2 + x^2}}, \quad (5)$$

where we have defined $r = |\mathbf{r}|$, and we have introduced the zeroth-order Bessel function of the first kind, J_0 . The asymptotic behavior of the interaction potential between two interfacial point charges, $U(r) = Q\phi(r) = Q^2 I(r)/(2\pi r)$, is determined by the integral $I(r)$, which we study below.

Tailoring the procedure in [13] to our system, we express the integral $I(r)$ as

$$I(r) = \frac{1}{\epsilon_1^2 - \epsilon_2^2} [\epsilon_1 I_1(r) - \epsilon_2 I_2(r)], \quad (6)$$

where

$$I_i(r) = \int_0^\infty dx \frac{x J_0(x) \sqrt{\kappa_i^2 r^2 + x^2}}{\alpha r^2 + x^2}, \quad i = 1, 2, \quad (7)$$

with $\alpha = (\epsilon_1^2 \kappa_1^2 - \epsilon_2^2 \kappa_2^2)/(\epsilon_1^2 - \epsilon_2^2)$.

As detailed in the Supplemental Material [25], these integrals can be computed exactly to give, as a final result,

$$\begin{aligned} I_i &= e^{-\kappa_i r} - e^{-\kappa_i r} \frac{r \delta_i}{\kappa_i} \sum_{p=0}^{\infty} \frac{(-1)^p}{2p+1} \left(\frac{\delta_i}{\kappa_i} \right)^p \\ &\quad \times {}_1F_1 \left(2p+1; \frac{3}{2} + p; -\frac{r \delta_i}{2\kappa_i} \right), \end{aligned} \quad (8)$$

where we have introduced $\delta_i \equiv \alpha - \kappa_i^2$, and ${}_1F_1$ is the confluent hypergeometric function of the first kind [26]. The asymptotic behavior for large values of $r \delta_i/(2\kappa_i)$ is given by

$$I_i \sim -e^{-\kappa_i r} \left[\frac{\kappa_i}{r \delta_i} + \frac{3\kappa_i^2}{r^2 \delta_i^2} + \frac{1}{r^2 \delta_i} + O\left(\frac{1}{r^3}\right) \right]. \quad (9)$$

For an oil-water interface, the integral I is dominated by I_2 for $r \rightarrow \infty$ (as $\kappa_2 < \kappa_1$). The corresponding leading asymptotic behavior for the interaction potential U between two interfacial point charges is

$$U(r) \sim \frac{Q^2}{2\pi} \frac{\epsilon_2 \kappa_2}{\epsilon_1^2 (\kappa_1^2 - \kappa_2^2)} \frac{e^{-\kappa_2 r}}{r^2}. \quad (10)$$

As $\kappa_2 \rightarrow 0$, which is relevant for an air-water interface, Eq. (10) vanishes, so that we need to take the next term in the expansion, and we recover the dipole contribution, $U(r) \sim 1/r^3$, previously found and discussed in [2,13]. Notably, however, if $\kappa_2 \neq 0$, Eq. (10) differs from, and decays faster than, a screened monopole with decay constant κ_2 : we obtain $U(r) \sim e^{-\kappa_2 r}/r^2$, rather than $\sim e^{-\kappa_2 r}/r$. As expected, a simple screened monopole behavior is found, from Eq. (4), in the limiting case in which $\kappa_1 = \kappa_2$, where there is no interface.

The exact functional form of $U(r)$, obtained by numerically evaluating the integral in Eq. (4), is compared to the asymptotic behavior coming from Eq. (9) in Fig. 2, for an oil-water interface. A good fit to the numerical solution for all r is provided by

$$U(r) \simeq \frac{Q^2}{2\pi \epsilon_1} \left[\frac{e^{-\kappa_1 r}}{r} + \frac{\epsilon_2}{\epsilon_1 \kappa_1^2} \frac{e^{-\kappa_2 r}}{r^3} + \frac{\epsilon_2 \kappa_2}{\epsilon_1 \kappa_1^2} \frac{e^{-\kappa_2 r}}{r^2} \right], \quad (11)$$

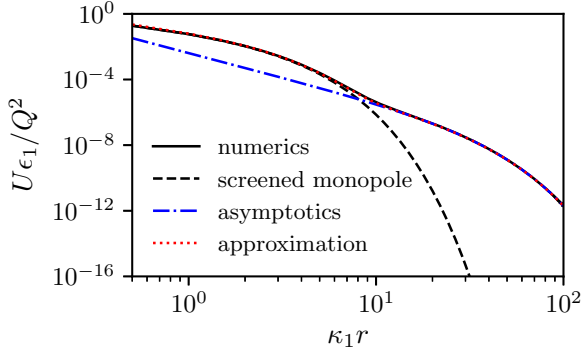


FIG. 2. Log-log plot of the numerical solution of U_{ϵ_1}/Q^2 versus $\kappa_1 r$, showing the crossover between small r behavior, corresponding to a screened monopole with decay constant κ_1 , and asymptotic behavior, computed via Eq. (9). The approximation in Eq. (11) is also shown. Parameters are $\kappa_1 = 10\kappa_2$, $\epsilon_1 = 40\epsilon_2$, relevant for a water-oil interface.

where we have accounted for the fact that $\kappa_2 \ll \kappa_1$ for an oil-water interface. Equation (11) describes a crossover between a screened monopole behavior at small r —with the decay length equal to that of the first medium, κ_1 —and the $\sim e^{-\kappa_2 r}/r^2$ behavior at large r . At intermediate r the second term, which is a dipole contribution (with screening, as $\kappa_2 \neq 0$), can in principle play a role. For an oil-water interface the crossover between screened monopole and dipole is at $r_{c,1} = -\frac{2}{\kappa_1 - \kappa_2} W_{-1}\left(-\frac{1}{2} \sqrt{\frac{\epsilon_2}{\epsilon_1} \frac{\kappa_1 - \kappa_2}{\kappa_1}}\right)$ where W_{-1} denotes the negative branch of the Lambert function [26]; the crossover between dipole and asymptotic behavior instead occurs at $r_{c,2} = \kappa_2^{-1}$ [27]. For parameters relevant to a dodecane-oil interface (Fig. 1), $r_{c,1} \simeq 9 \mu\text{m}$ and $r_{c,2} \sim 10 \mu\text{m}$, so that the dipole regime is essentially absent. For water-oil interfaces with $\epsilon_1/\epsilon_2 \sim 40$ –100, the screened dipole regime is of practical relevance only if $\kappa_1/\kappa_2 \gg 10$ (see Fig. 3 and [25]).

Equation (11) holds for pointlike particles and under the assumption of weak electrostatic potential, or $\frac{e_0 \phi}{k_B T} \ll 1$. To see whether relaxing these two simplifications changes the results significantly, we also numerically solved the nonlinear Poisson-Boltzmann equation for a charged colloidal particle of finite radius R at an oil-water interface (see [25] for details). Figure 4 shows the solution in 3D space and at the interface, for three different colloidal charge distributions: uniform [Fig. 4(a)], localized at the colloidal surface in the water phase [Fig. 4(b)], or dissociated in water around the surface [Fig. 4(c); this case is inspired by the physics discussed in [7]]. Notably, Eq. (11), with a renormalized, or effective, charge, provides the far-field (large r) behavior in all cases, and yields

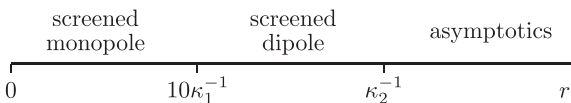


FIG. 3. Diagram showing the ranges in r where each of the regimes in Eq. (11) dominates for the potential between two point charges at an oil-water interface with $\epsilon_1 = 80\epsilon_2$.

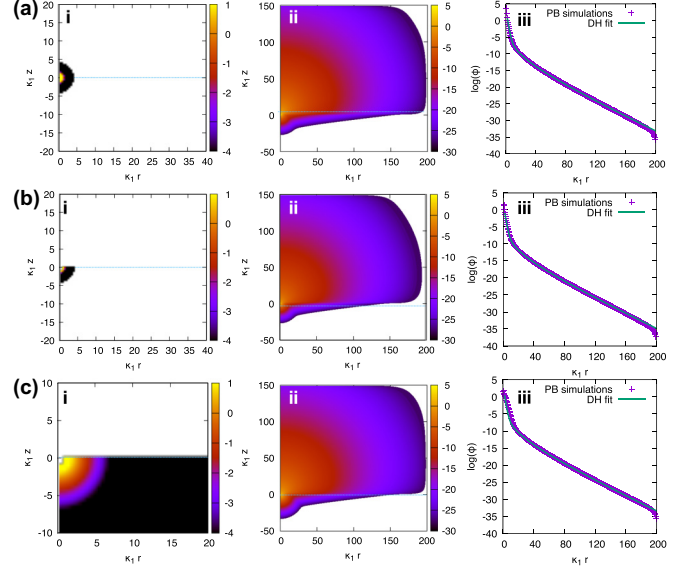


FIG. 4. Results of nonlinear Poisson-Boltzmann simulations for a charged colloid with $\kappa_1 R = 1.2$ at an oil-water interface ($\epsilon_1 = 40\epsilon_2$ and $\kappa_1 = 10\kappa_2$). In (a) the charge is uniformly distributed within the colloid; in (b) it is at the colloidal surface in the water phase; in (c) there is additionally a charge distribution in the water phase which decays exponentially from the colloidal surface (decay length equal to κ_1^{-1}). (i) Heat map of the logarithm of the input charge distribution. (ii) Heat map of the logarithm of the electrostatic potential solving the nonlinear Poisson-Boltzmann equation. (iii) Electrostatic potential on the interface ($z = 0$), as a function of r . The solid line is the fit to the Debye-Hueckel (DH) solution, Eq. (11), with an effective charge. For a full parameter list, see [25].

an excellent semiquantitative description for a large range of distances. Details of the charge distribution matter for small r , and determine the location of the crossover to far-field behavior [Figs. 4(a)(iii), 4(b)(iii), 4(c)(iii)] and [25].

Experimental studies of charged colloids at an oil-water interface typically report a good fit to a dipole potential, as for air-water interfaces [9,10]. However, analyzing the potential obtained by particle tracking in blinking optical traps for pairs of weakly charged particles shows that a screened $1/r^2$ potential provides a better fit than a dipole for the far-field behavior at a dodecane-water interface (Fig. S5 [25]). Interestingly, the near field in these experiments is poorly predicted by Eq. (11), whereas it is better described by Poisson-Boltzmann simulations accounting for charge dissociation near the colloidal surface, as in Fig. 4(c) (see Fig. S6 [25]).

To gain more physical insight into the physics behind Eq. (10), it is useful to consider the same interfacial Debye-Hückel problem defined by Eq. (1) in arbitrary dimension, d . This problem is equivalent to that of finding the d -dimensional Yukawa interaction at an interface. We find that, for generic $d \geq 3$, the interfacial potential $\phi(r)$ is given by [25]

$$\phi(r) = \frac{Q}{(2\pi)^{(d-1)/2} r^{d-2}} I_d, \quad (12)$$

$$I_d = \int_0^\infty dx \frac{x^{(d-1)/2} J_{(d-3)/2}(x)}{\epsilon_1 \sqrt{\kappa_1^2 r^2 + x^2} + \epsilon_2 \sqrt{\kappa_2^2 r^2 + x^2}},$$

where $J_\alpha(x)$, with α a real number, denotes the Bessel function of the first kind of order α .

In the case when $\kappa_2 \neq 0$ (and $\kappa_2 \ll \kappa_1$), which gives the d -dimensional analog of an oil-water interface, we find [25] the following generic form for the potential in $d \geq 3$ and for large r ,

$$\phi(r) \sim \frac{e^{-\kappa_2 r}}{r^{(d+1)/2}}. \quad (13)$$

As in $d = 3$, while the dominant contribution is an exponential screening with a typical length scale κ_2^{-1} , there is a different power-law correction with respect to the Yukawa potential in the bulk, which is $\phi(r) \sim \frac{e^{-\kappa_2 r}}{r^{(d-1)/2}}$. In this d -dimensional case, a suitable approximation for the potential is therefore

$$\phi(r) \simeq A_d \frac{e^{-\kappa_1 r}}{r^{(d-1)/2}} + B_d \frac{e^{-\kappa_2 r}}{r^{(d+1)/2}}, \quad (14)$$

where A_d and B_d are d -dependent constants. (For simplicity we neglect here intermediate regimes, which leads to a slightly poorer approximation with respect to the $d = 3$ case [25].)

Mathematically, the difference in the power-law correction for a particle at the interface arises due to the different structure in the branch-cut singularities in Eqs. (5) and (12) with respect to the bulk case ($\kappa_1 = \kappa_2$). Specifically, as $q \rightarrow i\kappa_2$ there is a divergence in the bulk case, but not at the interface. This is similar to what happens in polymer physics for a random or self-avoiding walk close to a surface [28], where a similar change in the nature of the singularity leads to a change in the entropic exponent γ (the power-law correction), with no change in the connective constant (the leading exponential behavior). For instance, the probability that a random walk with N steps forms a loop in $d = 1$ decays with N as $N^{-1/2}$, but close to a hard surface the same probability is $\sim N^{-3/2}$ [29].

Physically, these considerations suggest a mechanism for the change in asymptotic behavior for the potential between two point charges at the interface, $U(r)$. The integral determining this potential may be viewed as an integral of a propagator of a field, with $\kappa_{1,2}$ playing the role of the inverse mass, or as a correlator in Landau-Ginzburg theory

[30]. Therefore the potential can be viewed as a sum of all contributions from interactions propagating from one particle to the other. The propagation occurs through lines which we call ‘‘Debye strings’’ (Fig. 1). Computing the potential then involves a summation over all fluctuating Debye strings. Because the two end points of a string are fixed at the interface (at the point-charge positions), and because the screening in the first phase (i.e., water) is stronger, the strings are more likely to propagate through the second phase (i.e., oil). The statistics of the Debye strings contributing to the interaction is therefore different than in the bulk, where the propagation is symmetric, and the problem becomes qualitatively similar to that of a polymer close to a surface, thereby providing a simple physical picture to explain the change in the power-law correction, or the anomalous asymptotic decay of the potential.

In summary, we have computed the potential of a point charge at an interface between two electrolytes with distinct Debye length and dielectric permittivity, such as oil and water. We found that the asymptotic behavior of the potential is anomalous, and, quite notably, it differs from a screened charge monopole, which characterizes the interactions in the bulk, and from a dipole, which describes interactions at an air-water interface. An analysis of experimental data for the interaction of charged colloidal particles at a dodecane-water interface confirms that this anomalous far field describes observations more accurately than a dipole potential.

It will be of interest to extend our study to particles with prescribed shapes, such as anisotropic colloids [31], spherocylinders [32], RNA or DNA viruses, or interfacial proteins encountered in biofilms or food [17,18]. It would also be desirable to study situations where the interface is curved, such as in a bijel or a water-oil Pickering emulsion. In the latter case, the Debye strings linking interfacial particles could either follow geodesics on the interface, or straight lines through the water phase, according to which liquid is inside the droplets. This can lead to further tunability and potential for self-assembly, which could be experimentally probed by the methods in [7]. In bijels, the asymmetry in Debye strings may create an effective coupling between interfacial curvature and particle concentration, potentially affecting the macroscopic properties of the emerging composite material [33].

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