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Screened Electrostatics of Charged Particles on a Water Droplet

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We study the electrostatic properties of charged particles trapped at an interface in a water-in-oil microemulsion. The electrostatic potential and the counterion distribution in the water droplet are given in terms of the ratio of the Debye screening length κ^{-1} and the droplet radius R . In the limit $R \rightarrow \infty$ we recover the well-known results for a flat interface. Finite-size corrections are obtained in terms of the small parameter $1/\kappa R$. Part of the counterions spread along the interface and form a charged layer of one Debye length thickness. In particular, there is a uniform surface charge contribution. We derive explicit expressions for the electric field, the mobile charge density, and the charge-induced pressure on the interface.

I. INTRODUCTION

Since Pieranski's observation of crystallization of highly charged particles dispersed at a liquid interface [1], the properties of such two-dimensional colloids have been found to depend crucially on electrostatic interactions. Uncharged or strongly screened particles coagulate due to dispersion forces and may form solid capsules [2]. Highly charged micron-sized particles of valency $Z \sim 10^6$ at an air-water interface, are stabilized by their electrostatic repulsion and form 2D hexagonal crystals [1, 3, 4]; a variety of structures have been reported for particles of different shape and size [5–8]. The most recent experiments involve colloidal particles trapped on the interfaces of a water-in-oil or oil-in-water microemulsion [9, 10]; the observation of clusters indicates a subtle interplay of electrostatic and capillary forces. A detailed study of PMMA particles on water-in-oil droplets of 50 μm diameter [9] gives clear evidence for the existence of a long-range attraction, which has been discussed in terms of a charge-induced capillary interaction [11–16].

The counterions of an interfacial particle of charge Q are confined to the electrolyte halfspace, where they are concentrated in a layer that is about one Debye length κ^{-1} thick. As first realized by Pieranski, this charge distribution carries a dipole moment Q/κ and leads to an effective interaction of two particles, $V \sim (Q/\kappa)^2 \rho^{-3}$, that is repulsive and varies with the inverse cube of their distance ρ [1]. In subsequent work, this picture was given a sound theoretical basis, and it was shown that the interaction potential depends on the ratio of the dielectric constants of the two liquid phases [17, 18]. The power law for the resulting force $F \sim \rho^{-4}$ was verified experimentally for polystyrene particles of 3 micron diameter at an air-water interface [4].

The effective electrostatic potential of interfacial particles is closely related to the distribution of the mobile charges in the electrolyte. Most of the counterions are confined to a screening cloud within one Debye length from the charged particle; yet a small fraction spread along the interface and form a charged layer that decays as r^{-3} with the lateral distance r [17, 18]. Significant modifications occur if the insulating halfspace is reduced

to a thin slab, or the electrolyte phase to an aqueous film of finite thickness [19, 20]. The algebraic tail of the counterion distribution gives rise to an electric stress on the interface, which, in turn, leads to a deformation field that follows a power law [12, 13]. All theoretical studies carried out so far dealt with an infinite flat interface separating an electrolyte from an insulating phase. Yet this geometry does not apply to the most recent measurements that involve charged particles trapped on the surface of a water droplet in an oil phase [9], or the inverse system [10].

In the present paper, we study the screened electrostatics of a charge trapped on a water droplet. From the finite area of the interface it is clear that the electric field and charge distribution then differ significantly from those of an infinite flat interface, and that the mentioned power laws are modified by the spherical geometry. Moreover, because of the finite droplet volume, the total number of salt ions and counterions released by the particle has to be treated carefully; the normalization of the ion densities is achieved by introducing chemical potentials.

Since one expects to recover, in the limit $R \rightarrow \infty$, the properties of an infinite flat interface, we are mainly concerned with the effects arising from the finite droplet size. The ratio of the Debye screening length κ^{-1} and the droplet radius R satisfies

$$\frac{1}{\kappa R} \ll 1.$$

In the framework of the Debye-Hückel approximation, we perform a systematic expansion of the electrostatic properties of a droplet in terms of this small parameter.

In Sect. II we obtain the screened electrostatic potential of a charge on a sphere. The electric field at both sides of the interface, the mobile charge density in the droplet, the pair potential, and the interface pressure are derived in Sects. III–VI. In the final Sect. VI we discuss and summarize our findings. Technical details of the asymptotic expansion for the screened potential are given in an Appendix.

II. THE SCREENED POTENTIAL

Consider a colloidal particle of charge $Q = Ze$ trapped at an electrolyte-insulator interface, typically an oil-water phase boundary. The Z counterions are soluted in the electrolyte; we suppose that all mobile ions are monovalent. The electrostatic potential $\phi(\mathbf{r})$ has to be evaluated separately in the two phases. The dielectric constant is denoted ε_I in the insulator and ε_{II} in the electrolyte. The boundary conditions of electrostatics require that the potential is continuous at the interface,

$$\phi_I = \phi_{II} \quad (1)$$

and the normal components of the displacement vector $\mathbf{D} = -\varepsilon\nabla\phi$ on both sides differ by the surface charge density,

$$\mathbf{n} \cdot \mathbf{D}_I - \mathbf{n} \cdot \mathbf{D}_{II} = Q\delta^2(\mathbf{r} - \mathbf{r}_Q), \quad (2)$$

where \mathbf{r}_Q are the particle's coordinates. In addition, we require that the potential vanishes at infinity,

$$\phi_I(\mathbf{r}) \rightarrow 0 \quad \text{for } r \rightarrow \infty.$$

Because of the absence of charges, the potential in the insulator satisfies Laplace's equation

$$\Delta\phi_I = 0. \quad (3)$$

In the electrolyte one has to take to account both salt and soluted counterions, resulting in the Poisson equation

$$\Delta\phi_{II} = \frac{e}{\varepsilon_{II}}(n_+ - n_-), \quad (4)$$

with the positive and negative ion densities $n_{\pm}(\mathbf{r})$. Resorting to a mean-field approximation, we replace these quantities with their average

$$n_{\pm} = n_0 \exp\left(\frac{\mp e\phi_{II} + \mu_{\pm}}{k_B T}\right), \quad (5)$$

where μ_{\pm} are pseudo-chemical potentials and n_0 is the salinity of the electrolyte. Eqs. (1-5) constitute a closed set of equations for the electrostatic potential and the mobile charge densities.

Because of the large dielectric constant of water, $\varepsilon_{II}/\varepsilon_0 \approx 80$, electrostatic energies at micron distances are small as compared to the thermal energy. Thus we may simplify the Poisson-Boltzmann equation (4,5) by using the Debye-Hückel approximation, and linearize the densities n_{\pm} . We rewrite the chemical potentials of positive and negative ions as

$$\mu_{\pm} = \mu_0 \mp \mu_1,$$

absorb the first term in the effective salinity parameter

$$\tilde{n}_0 = n_0 e^{\mu_0/k_B T}, \quad (6)$$

and expand n_{\pm} with respect to the quantity

$$X = \frac{e\phi_{II} + \mu_1}{k_B T}.$$

The mobile ion densities then read

$$n_{\pm} = \tilde{n}_0 \left(1 \mp X + \frac{1}{2}X^2 + \mathcal{O}(X^3)\right). \quad (7)$$

In the remainder of this paper, these series are truncated at second order in X , i.e., we neglect terms of cubic and higher order.

When inserting the approximate ion densities (7) in (4), the quadratic terms cancel each other, and we obtain the linear Debye-Hückel equation

$$\Delta\phi_{II} - \kappa^2\phi_{II} = \kappa^2\mu_1/e. \quad (8)$$

Note that the screening parameter

$$\kappa = \sqrt{8\pi\ell_B\tilde{n}_0}$$

depends on the effective salinity and thus differs from the usual definition $\sqrt{8\pi\ell_B n_0}$. In water, the Bjerrum length

$$\ell_B = \frac{e^2}{4\pi\varepsilon_{II}k_B T}.$$

takes a value of about 7 Å.

A. Flat interface

We briefly recall well-known results for the potential of a charge trapped at a flat interface [17–20]. The infinite electrolyte halfspace of salinity n_0 provides a mobile charge reservoir of zero chemical potential, $\mu_{\pm} = 0$. The resulting Debye-Hückel equation

$$\Delta\phi_{II} - \kappa^2\phi_{II} = 0$$

is solved in Fourier space with respect to the in-plane coordinates; we rewrite the potential $\phi_{II}(\rho, z)$ in the electrolyte halfspace ($z \geq 0$) in the form

$$\frac{Q}{2\pi\varepsilon_{II}} \int_0^{\infty} dq J_0(q\rho) \left(\frac{q}{\hat{q}} - \frac{\eta q^2}{\hat{q}(\hat{q} + \eta q)}\right) e^{-\hat{q}z}, \quad (9)$$

with $q = |\mathbf{q}|$, $\hat{q} = \sqrt{q^2 + \kappa^2}$.

For water as electrolyte, the ratio of the dielectric constants

$$\eta = \varepsilon_I/\varepsilon_{II}$$

is small, and the first term in brackets gives the screened potential, $\phi_{II} = (Q/2\pi\varepsilon_{II}r)e^{-\kappa r}$, that is relevant at distances $r = \sqrt{\rho^2 + z^2}$ within a few Debye lengths.

At large lateral distances $\rho \gg \kappa^{-1}$, the potential is dominated by the second term that is linear in the ratio η of dielectric constants. For $\rho\kappa \gg 1$ the inverse Fourier

transform is determined by small wave vectors ; expanding $\phi_{II}(\mathbf{q}, z)$ in powers of q and taking the inverse Fourier transform, one obtains a series in powers of $1/(\kappa\rho)$,

$$\phi_{II}(\rho, z) = \frac{Q\varepsilon_I}{2\pi\varepsilon_{II}\kappa^2} \frac{e^{-\kappa z}}{\rho^3} \left(1 + \mathcal{O}\left(\frac{1}{\kappa^2\rho^2}\right) \right) \quad (10)$$

Note that the leading term is proportional to η and varies with the lateral distance as ρ^{-3} . In both halfspaces the potential vanishes at infinity, $\phi \rightarrow 0$ for $\rho, z \rightarrow \infty$, and one easily verifies that the mobile charge density satisfies overall neutrality, $\int dV e(n_+ - n_-) = -Q$.

B. Debye-Hückel theory on a droplet

Now we turn to the case of a charge on a water droplet of radius R . Contrary to the Debye-Hückel equation on an infinite flat interface, the relation for a droplet (8) comprises a inhomogeneous term that is given by the chemical potential μ_1 .

Because of the axial symmetry, the problem involves only two coordinates, the distance from the center of the sphere r and the polar angle θ ; the particle's position is $r = R$ and $\theta = 0$. In the insulating phase outside the droplet, there are no charges; the most general solution of the Laplace equation (3) is given as a series in inverse powers of r ,

$$\phi_I = \frac{Q}{4\pi\varepsilon_{II}R} \sum_{\ell=0}^{\infty} a_\ell \hat{r}^{-(\ell+1)} P_\ell(x), \quad (11)$$

where we have defined reduced variables

$$\hat{r} = r/R, \quad x = \cos\theta, \quad (12)$$

and where $P_\ell(x)$ are Legendre polynomials. Since the total charge of the droplet is zero, the monopole term in ϕ_I vanishes, $a_0 = 0$. Because of the presence of mobile charges, the expansion inside the droplet

$$\phi_{II} = \frac{Q}{4\pi\varepsilon_{II}R} \left(C + \sum_{\ell=0}^{\infty} b_\ell \psi_\ell(\hat{r}) P_\ell(x) \right) \quad (13)$$

involves radial functions $\psi_\ell(\hat{r})$ that are solutions of the homogeneous equation $\Delta\phi_{II} - \kappa^2\phi_{II} = 0$, and a constant C that is related to the inhomogeneity of Eq. (8).

In a first step we solve the homogeneous equation and determine the expansion coefficients a_ℓ , b_ℓ , and C from the boundary conditions at the interface (1,2). Separating the radial and angular parts of the Laplace operator and defining the reduced Debye parameter

$$\hat{\kappa} = \kappa R,$$

the relation $\Delta\phi_{II} - \kappa^2\phi_{II} = 0$ takes the form

$$\left[\hat{r}^2 \partial_{\hat{r}}^2 + 2\hat{r} \partial_{\hat{r}} - \ell(\ell+1) - \hat{r}^2 \hat{\kappa}^2 \right] \psi_\ell(\hat{r}) = 0.$$

Its solutions are given in terms of modified spherical Bessel function of the first kind i_ℓ ,

$$\psi_\ell(\hat{r}) = i_\ell(\hat{\kappa}\hat{r})/i_\ell(\hat{\kappa}).$$

Here we used a normalization such that $\psi_\ell(1) = 1$, e.g.,

$$\psi_0(\hat{r}) = \frac{\sinh(\hat{\kappa}\hat{r})}{\hat{r} \sinh(\hat{\kappa})}.$$

The expansion coefficients a_ℓ , b_ℓ , and C are determined by the boundary conditions (1,2). For a particle at $\theta = 0$, we may discard the azimuthal angle and write

$$\delta^2(\mathbf{r} - \mathbf{r}_Q) = \frac{1}{2\pi R^2} \delta(\cos\theta - 1). \quad (14)$$

Expanding the delta function in terms of Legendre polynomials we have

$$\delta(\cos\theta - 1) = \sum_{\ell=0}^{\infty} (\ell + 1/2) P_\ell(\cos\theta), \quad (15)$$

with the convention $\int_{-1}^1 dx \delta(x-1) = 1$.

When inserting these series in the continuity relation for the potential and taking advantage of the linear independence of the Legendre polynomials, one finds for all ℓ

$$a_\ell = b_\ell + C\delta_{\ell 0}, \quad (16)$$

whereas the equation involving the displacement vector and the surface charge results in

$$\eta(\ell + 1) a_\ell + D_\ell b_\ell = (2\ell + 1), \quad (17)$$

with the shorthand notation

$$D_\ell = \partial_{\hat{r}} \psi_\ell(\hat{r})|_{\hat{r}=1}. \quad (18)$$

These equations are easily solved; for $\ell \geq 1$ we have

$$a_\ell = b_\ell = \frac{2\ell + 1}{D_\ell + \eta(\ell + 1)} \quad (\ell \geq 1). \quad (19)$$

The mode $\ell = 0$ involves the constants a_0 , b_0 , and C . The droplet being neutral implies $a_0 = 0$ and $b_0 = -C = 1/D_0$. Since $\hat{\kappa} \gg 1$ one has $D_0 = \psi_0'(1) = \hat{\kappa} \coth \hat{\kappa} - 1 \approx \hat{\kappa}$, and the coefficients

$$b_0 = -C = \frac{1}{\hat{\kappa}}. \quad (20)$$

One readily finds that both b_0 and C vanish as the system size diverges, i.e., as $\hat{\kappa} = \kappa R \rightarrow \infty$.

Note that the constant C has been determined through the continuity condition (1) and that we have not yet considered the inhomogeneity of Eq. (8).

C. The chemical potentials

In the absence of colloidal particles, the densities of positive and negative ions are given by the salinity $n_{\pm} = n_0$, and their total numbers are $N_{\pm} = n_0V$, where V is the droplet volume. A macroion of valency Z trapped at the interface, releases Z counterions and induces non-uniform mobile-ion densities n_{\pm} . Then the total ion numbers $N_+ \neq N_-$ are implemented most conveniently by introducing pseudo-chemical potentials $\mu_{\pm} = \mu_0 \mp \mu_1$ in the densities (5), i.e., we adopt a grandcanonical point of view where the fixed particle numbers are assured by choosing appropriate values for μ_0 and μ_1 .

Because of the linear relation between electrostatic potential and mobile ion densities in Debye-Hückel approximation, the relative chemical potential μ_1 may be taken directly from Eq. (8). When identifying the constant part of its left-hand side with the right-hand side, we find

$$\mu_1 = -\frac{eQ}{4\pi\epsilon_{II}R}C = \frac{eQ}{4\pi\epsilon_{II}\kappa R^2}, \quad (21)$$

which relates μ_1 to the valency of the macro-ion, the Debye length, and the droplet radius. Thus the relative chemical potential μ_1 exactly cancels the constant part of the potential energy $\mp e\phi$ in the expressions for the ion densities (5,7). As a consequence, the ion densities may be rewritten as

$$n_{\pm} = \tilde{n}_0 e^{\mp e\tilde{\phi}_{II}/k_B T}, \quad (22)$$

with the shifted potential

$$\tilde{\phi}_{II} = \phi_{II} + \mu_1/e.$$

We turn to the remaining term μ_0 that renormalizes the salinity. For the case of a negatively charged macroion, $Q = -Ze$, the number of negative ions is given by the salinity $N_- = n_0V$, whereas that of positive ions comprises both salt and soluted counterions, $N_+ = n_0V + Z$; in terms of the densities n_{\pm} we have

$$\int dV n_-(\mathbf{r}) = n_0V, \quad \int dV n_+(\mathbf{r}) = n_0V + Z. \quad (23)$$

When evaluating these integrals with the linearized expression (7), we obtain $e^{\mu_0/k_B T} - 1 = Z/2n_0V$, i.e.,

$$\mu_0 = k_B T \ln \left(1 + \frac{Z}{2n_0V} \right), \quad (24)$$

which holds for positive or negative charge, $Q = \pm Ze$. Both terms of the chemical potentials depend on number of the released counterions, i.e., on the valency Z , the bare salinity n_0 , and the droplet radius; the difference $\mu_1 = \frac{1}{2}(\mu_- - \mu_+)$ takes the sign of the charge Q and can be absorbed in the definition of the electrostatic potential. When rewriting the above expressions in

terms of the Bjerrum and Debye lengths and expanding the logarithm according to $\ln(1+x) \approx x$ for small x ,

$$\frac{\mu_0}{k_B T} = \frac{3Z\ell_B}{\kappa^2 R^3}, \quad \frac{\mu_1}{k_B T} = \frac{Z\ell_B}{\kappa R^2},$$

it is clear that both μ_0 and μ_1 vanish as the droplet radius tends towards infinity, albeit with different power laws. (In this paper, the limit $R \rightarrow \infty$ is always taken at constant salinity n_0 .)

In a finite droplet, the released counterions affect both the salinity and the screening length. Yet as long as the number of soluted counterions is much smaller than that of salt ions, the effective salinity \tilde{n}_0 hardly differs from its bare value n_0 . Similarly, the effective Debye parameter $\kappa = \sqrt{8\pi\ell_B\tilde{n}_0}$ is close to the value $\sqrt{8\pi\ell_B n_0}$ calculated with the bare salinity.

D. Asymptotic expansion

Although it entirely determines the screened potential, the series (13) with the coefficients (19,20) cannot be evaluated as it stands. In all relevant applications, the dielectric constant of the insulating side is much smaller than that of water, and the droplet radius significantly exceeds the Debye screening length, providing two small parameters $\eta = \epsilon_I/\epsilon_{II}$ and $1/\hat{\kappa} = 1/(\kappa R)$ that will be taken as the basis of a series expansion. (For example, the system studied in Ref. [9] satisfies $\eta \sim 1/30$ and $\hat{\kappa}^{-1} \sim 10^{-2}$.)

It turns out convenient to rewrite the potential as

$$\tilde{\phi}_{II} = \frac{Q}{4\pi\epsilon_{II}R}\Psi, \quad (25)$$

where the series

$$\Psi(\hat{r}, \cos\theta) = \sum_{\ell=0}^{\infty} b_{\ell}\psi_{\ell}(\hat{r})P_{\ell}(\cos\theta) \quad (26)$$

is evaluated in the Appendix and the term of leading order in η and $1/\hat{\kappa}$ is given in Eq. (51). When inserting this approximate expression in (25) and defining the angle-dependent function

$$\Gamma_R(\cos\theta) = 1 + \frac{1}{4} \frac{1}{\sin(\theta/2)^3}, \quad (27)$$

we obtain a main result of the present paper,

$$\tilde{\phi}_{II} = \frac{\epsilon_I Q}{4\pi\epsilon_{II}^2 \kappa^2 R^3} \Gamma_R(\cos\theta) e^{\kappa(r-R)}. \quad (28)$$

As in the case of an infinite flat interface, the potential decays in the normal direction exponentially within one Debye length κ^{-1} , whereas the lateral variation shows an intricate power law dependence. For a point charge, this expression is valid at lateral distances well beyond one Debye length, i.e., $\theta > 1/\hat{\kappa}$. In the following sections, we derive the resulting electric field, mobile ion density, and interface stress.

III. THE ELECTRIC FIELD AT THE INTERFACE

We write the electric field at the aqueous side of the interface in terms of its radial and tangential components,

$$E_R^{II} = -\frac{\partial\phi_{II}}{\partial r}\Big|_{r=R}, \quad E_T^{II} = -\frac{1}{R}\frac{\partial\phi_{II}}{\partial\theta}\Big|_{r=R}.$$

Taking the derivative $\partial_r = (1/R)\partial/\partial\hat{r}$ of the potential (28) and defining the prefactor

$$E_0 = \frac{Q}{4\pi\varepsilon_{II}\kappa R^3} \quad (29)$$

we have

$$E_R^{II} = -\eta E_0 \Gamma_R(\cos\theta). \quad (30)$$

The constant term present in Γ_R is particular to the spherical geometry considered here, whereas the angle-dependent part corresponds to the power law well known from a flat interface. Indeed, for not too large angles we have $\sin(\theta/2) \approx \theta/2$ and $\rho \approx \theta R$ and thus find

$$E_R^{II} = -\frac{\varepsilon_I Q}{2\pi\varepsilon_{II}^2\kappa\rho^3},$$

which is identical to the result obtained by Hurd [18].

We turn to the tangential component of the electric field. Applying the derivative $\partial/\partial\theta$ on (28) and rewriting the result in terms of $\sin(\theta/2)$ we find

$$E_T^{II} = E_0 \frac{\eta}{\kappa R} \Gamma_T(\cos\theta),$$

with

$$\Gamma_T(\cos\theta) = \frac{3\cos(\theta/2)}{8\sin(\theta/2)^4}.$$

At lateral distances beyond one Debye length, E_T^{II} is significantly smaller than the radial component. This is obvious for large angles $\theta > \frac{\pi}{2}$, when noting $\cot(\theta/2) < 1$ and $\kappa R \gg 1$. For smaller angles, we may put $\sin(\theta/2) \approx \theta/2$, $\cos(\theta/2) \approx 1$, $\rho \approx \theta R$, and thus find the power law

$$E_T^{II} = \frac{\varepsilon_I Q}{4\pi\varepsilon_{II}^2\kappa^2\rho^4},$$

which, again, is by a factor $(\kappa\rho)^{-1}$ smaller than the radial component; since in the range of validity of the asymptotic expansion one has $\kappa\rho \gg 1$, we may conclude that the tangential electric field is small, $E_T^{II} \ll E_R^{II}$.

The field at the insulating side is given by the continuity conditions of electrostatics,

$$\varepsilon_I E_R^I = \varepsilon_{II} E_R^{II} + Q\delta(\mathbf{r} - \mathbf{r}_Q), \quad E_T^I = E_T^{II}.$$

At finite distance from the colloidal particle, the source term is irrelevant and the radial field outside, is by a factor $\varepsilon_{II}/\varepsilon_I$ larger than that inside and reads

$$E_R^I = -E_0 \Gamma_R(\cos\theta). \quad (31)$$

The tangential component is continuous at the interface. A schematic view of the electric field lines in the vicinity of the droplet is given in Fig. 1.

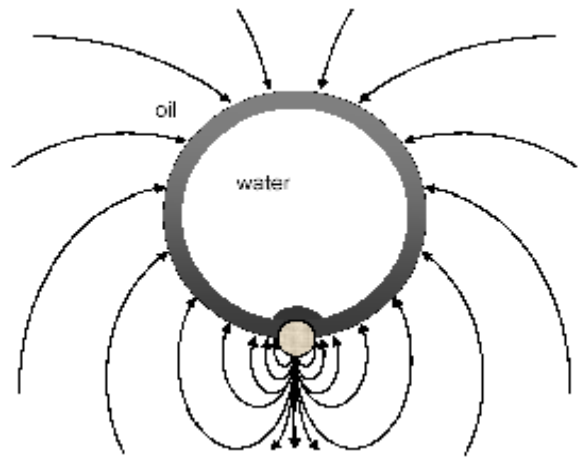


FIG. 1: Schematic view of the electric-field lines in the vicinity of the water droplet. The grey region indicates the net charge density due to the accumulation of counterions.

IV. MOBILE-ION DENSITY

The electric field lines penetrating the water droplet are screened within a distance of one Debye length from the phase boundary, i.e., they end at the charge that arises from the accumulation of counterions at the interface. The net charge density is readily evaluated,

$$\sigma(\mathbf{r}) = e(n_+ - n_-) = -\frac{2e^2\tilde{n}_0}{k_B T} \tilde{\phi}_{II}(\mathbf{r}),$$

its sign is opposite to that of the charge Q carried by the macroion. Using the definition of the Debye length in Eq. (7) and inserting (28) we find

$$\sigma(r, \theta) = \sigma_0 \left(1 + \frac{1}{4} \frac{1}{\sin(\theta/2)^3}\right) e^{\kappa(r-R)}, \quad (32)$$

with the prefactor

$$\sigma_0 = -\frac{\varepsilon_I}{\varepsilon_{II}} \frac{Q}{4\pi R^3}.$$

The “1” in brackets corresponds to an isotropic charge distribution; both the constant and the angular dependent terms are plotted in Fig. 2. We recall that the series expansion for the electrostatic potential, and thus the above expression for $\sigma(\mathbf{r})$, are valid at finite angles only.

When integrating over the radial coordinate, we obtain the charge density per unit area,

$$s(\theta) = -\frac{\varepsilon_I}{\varepsilon_{II}} \frac{Ze}{4\pi\kappa R^3} \left(1 + \frac{1}{4} \frac{1}{\sin(\theta/2)^3}\right).$$

We briefly discuss the total charge accumulated in the surface layer. Multiplying the constant term in $s(\theta)$ with

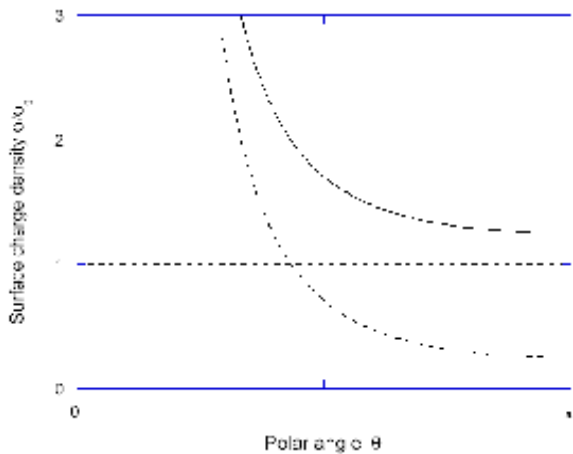


FIG. 2: Mobile charge density at the interface as a function of the polar angle θ . The dashed lines give the constant and the angle-dependent contributions of (32). The constant σ_0 is defined in the text.

the surface area of the droplet $4\pi R^2$, one finds that it comprises a fraction $\eta/\hat{\kappa} = (\varepsilon_I/\varepsilon_{II}\kappa R)$ of the Z soluted counterions. An estimate for the integral of the angle-dependent part is obtained by cutting at a polar angle corresponding to the particle radius a . One thus calculates that a fraction $(\varepsilon_I/\varepsilon_{II}\kappa a)$ of the counterions are spread along the interface; for typical parameter values $\varepsilon_I/\varepsilon_{II} \sim 1/30$ and $\kappa a \sim 3$, this corresponds to about one percent. The remaining 99 percent of the counterions are confined to the exponential screening cloud within one Debye length from the particle; for highly charged macroions, the majority of these screening ions are more strongly bound and condense in a “diffuse layer” of a few nanometer thickness [23–25].

V. ELECTROSTATIC REPULSION OF LIKE CHARGES

The Debye-Hückel approximation implies a linear relation between the charge density and the effective potential. As a consequence, the electrostatic potential of several macro-ions is given by the superposition of their one-particle potentials, and the pair interaction reduces to the potential of one particle evaluated at the position of the other, $V_{ij} = Q_j\phi_i(\mathbf{r}_j)$. This result is valid in general; an explicit calculation for particles on a flat interface is given in Ref. [20]. In the present case of two charges on a droplet at polar angles $\theta_1 = 0$ and $\theta_2 = \theta$, one finds, with the effective electrostatic potential (28), the repulsive interaction $V = Q\phi(\theta)$. Discarding the constant term that is irrelevant here, we have

$$V(\theta) = \frac{Q^2\varepsilon_I}{16\pi\varepsilon_{II}^2\kappa^2R^3\sin(\theta/2)^3}. \quad (33)$$

The inverse power law $\sim \sin(\theta/2)^{-3}$ is closely related to the algebraic screening due to the mobile-ion charge density (32) at the interface. This interaction is very different from the Yukawa type potential $Q^2/(4\pi\varepsilon_{II}r)e^{-\kappa r}$ in a bulk electrolyte, which decays exponentially with the distance r of the two charges.

Eq. (33) is based on the Debye-Hückel approximation which is valid as long as the electrostatic energy of a single charge is smaller than the thermal energy, $e\phi < kT$. In terms of the two-particle potential, this condition reads as $V < ZkT$. We conclude that for large valencies, $Z = 10^4 \dots 10^7$, the interaction potential may exceed the thermal energy by several orders of magnitude.

The angle dependence of $V(\theta)$ results in a lateral two-particle force, $F = -(1/R)dV/d\theta$, that reads as

$$F(\theta) = \frac{3Q^2\varepsilon_I}{32\pi\varepsilon_{II}^2\kappa^2R^4} \frac{\cos(\theta/2)}{\sin(\theta/2)^4}. \quad (34)$$

At small angles, $\theta \ll \pi$, the potential shows a power law dependence $V \propto \theta^{-3}$. Accordingly, the repulsive force varies as $-dV/d\theta \propto \theta^{-4}$, whereas close to the opposite pole $\theta \approx \pi$, it reads $-dV/d\theta \propto \cos \frac{\theta}{2}$ and thus disappears as $\theta \rightarrow \pi$.

In order to relate this result to the pair potential at an infinite flat interface, we consider the limit $R \rightarrow \infty$, $\theta \rightarrow 0$. Then the lateral distance ρ of the two charges is given by $\rho = \theta R$, and we have

$$V = \frac{Q^2\varepsilon_I}{2\pi\varepsilon_{II}^2\kappa^2\rho^3}, \quad \rho \ll R, \quad (35)$$

which corresponds to (10) and is identical to Hurd’s result [18].

VI. INTERFACE PRESSURE

Particles trapped at a liquid interface are subject to surface-mediated interactions. For millimeter sized objects, such capillary forces are mainly due to gravity [21, 22], whereas the weight is irrelevant in the micrometer and nanometer domain. The interface deformation induced by the electric stress of highly charged macroions on a flat interface has been discussed controversially in recent years [11–16]. In view of the recent experiments on water droplets [9], we derive the pressure exerted by a charged particle on a sphere, and we discuss in detail the momentum conservation of an isolated system.

A. Pressure on the liquid interface

The interfacial pressure exerted by the charged particle and the mobile ions comprises two different contributions,

$$P_I(\cos \theta) = k_B T \delta n + \mathcal{T}^I - \mathcal{T}^{II}. \quad (36)$$

The first term is the ideal-gas entropic pressure of the excess density

$$\delta n(\mathbf{r}) = n_+ + n_- - 2\tilde{n}_0$$

of the mobile ions, whereas the remaining terms involve the normal component of the Maxwell tensor,

$$\mathcal{T} = \varepsilon \left((\mathbf{n} \cdot \mathbf{E})^2 - \frac{1}{2} \mathbf{E}^2 \right), \quad (37)$$

where the unit vector \mathbf{n} is perpendicular on the interface. The energy density of the electric field is different on both sides of the interface and thus gives rise to a finite stress $\mathcal{T}^I - \mathcal{T}^{II}$.

Eq. (36) accounts only for the pressure induced by the presence of the macroion. We have subtracted the uniform osmotic pressure $2k_B T \tilde{n}_0$ of the mobile ions, which may be absorbed in the definition of the interface tension, and retain the spatially varying part δn only. In order to calculate the entropic term in (36), we expand the excess ion density to second order in X ; inserting Eq. (28) we have

$$\delta n(\mathbf{r}) = \frac{1}{2} \tilde{n}_0 \left(e \tilde{\phi}_{II}(\mathbf{r}) / k_B T \right)^2. \quad (38)$$

Note that the mobile charge density at the interface is linear in the angle-dependent function Γ_R , whereas the excess ion density varies as Γ_R^2 . Using the definitions of the electric field E_0 and the Debye parameter $\kappa^2 = (2e^2 \tilde{n}_0 / \varepsilon_{II} k_B T)$, one finds that the entropic pressure cancels the radial part of \mathcal{T}^{II} ,

$$k_B T \delta n = \frac{\varepsilon_I}{2} (E_R^{II})^2. \quad (39)$$

Inserting the above asymptotic expressions for the electric field on both sides of the interface, we find the pressure

$$P_I(\cos \theta) = \frac{\varepsilon_I}{2} E_0^2 \left(\Gamma_R^2 + \frac{\varepsilon_{II} - \varepsilon_I}{\varepsilon_{II}} \frac{\eta^3}{(\kappa R)^2} \Gamma_R^2 \right). \quad (40)$$

Note that the contribution arising from the radial field, i.e., the first term in brackets, is always positive, whereas the sign of the pressure due to the tangential field depends on the relative magnitude of the dielectric constants.

For water as electrolyte, one always has $\varepsilon_{II} \gg \varepsilon_I$, i.e., all pressure components are oriented towards the insulating phase. In this case the factors appearing in the second term are small, $\eta \ll 1$ and $(\kappa R)^{-2} \ll 1$, and the pressure arising from the tangential component of the electric field may be neglected. The interfacial pressure then reads $P(\cos \theta) = \frac{1}{2} \varepsilon_I E_0^2 \Gamma_R^2$. Spelling out the angle-dependent function we find

$$P_I(\cos \theta) = \frac{\varepsilon_I}{2} E_0^2 \left(1 + \frac{1}{4 \sin(\theta/2)^3} \right)^2. \quad (41)$$

Because of its unphysical divergency at $\theta = 0$, this expression holds at finite angles $\theta > \theta_0$ only and ceases to be valid as $\theta \rightarrow 0$. For a pointlike particle, the cut-off angle $\theta_0 = 1/(\kappa R)$ is readily obtained from the convergence of the series expansion and is equal to the ratio of the Debye length and the droplet radius. For micron size particles and weak electrolytes, the particle size a exceeds the Debye length, and the cut-off angle is, in good approximation, given by the ratio of particle and droplet radii $\theta_0 = a/R$; note that this is the polar angle of the contact line, i.e., of the intersection of the particle surface and the liquid interphase.

B. Momentum conservation

When evaluating the interfacial forces one must keep in mind that the total force on the droplet vanishes, i.e., the charged particle and its counterions do not change the state of motion of the droplet as a whole. This means that the integral of the oriented pressure vanishes,

$$\int dS \mathbf{n} P = 0.$$

On a flat interface the normal vector is constant; the resulting expression for the normal component $\int dS P = 0$ has been used in previous work [11, 12].

For the present spherical geometry, it is sufficient to consider the projection of the force on the symmetry axis. The corresponding component of the normal vector \mathbf{n} is $\cos \theta$; using $x = \cos \theta$ and $dS = R^2 d\Omega$ we obtain the constraint

$$\int_{-1}^1 dx x P(x) = 0. \quad (42)$$

C. Force acting on the particle

The pressure P_I derived above acts on the liquid interface only, i.e., at angles $\theta > \theta_0$; it does not apply within the contact line at $\theta_0 = a/R$. The electric stress acting on the particle can be obtained from momentum conservation as expressed by Eq. (42). Separating these two contributions, the total pressure reads

$$P(\cos \theta) = P_I(\cos \theta) - \frac{F_1}{2\pi R^2} \delta(1 - \cos \theta). \quad (43)$$

Inserting this relation in (42) one obtains the total electrostatic force acting on the particle as the weighted surface integral of the pressure on the liquid interface,

$$F_1 = 2\pi R^2 \int_{-1}^{\cos \theta_0} dx x P_I(x). \quad (44)$$

The cut-off angle $\theta_0 = a/R$ is, at most, of the order of a few percent.

The above expressions for the interface pressure and the counterforce reduce, in the limit $R \rightarrow \infty$, to those on an infinite flat interface [12, 13]. Indeed, performing the limit $R \rightarrow \infty$ at finite lateral distance $\rho = R\theta$, one finds

$$P_I = \frac{\varepsilon_I}{2} \left(\frac{Q}{2\pi\varepsilon_{II}\kappa} \right)^2 \frac{1}{\rho^6},$$

whereas the conservation law (42) is satisfied by a counterforce that is given by the integrated pressure, $F_0 = \int dSP_I(x)$.

On a flat interface, the counterforce is given by the integrated pressure. This is different on a droplet: The force on the particle F_1 involves the integral of the oriented pressure, whereas the quantity

$$F_0 = 2\pi R^2 \int_{-1}^{\cos\theta_0} dx P_I(x)$$

has no obvious physical meaning. Since the electric stress is positive and strongly peaked at the contact line $\theta = \theta_0$, one has the strict inequality $F_1 < F_0$ and finds, in a good approximation, the explicit relation $F_1 \approx \cos\theta_0 F_0$.

The pressure $P(\mathbf{r})$ leads to a deformation of the liquid interface, with a profile that is determined by the Young-Laplace equation. The counterforce on a flat interface is given by F_0 ; as a consequence the integrated pressure $2\pi \int_0^r dr r P(r)$ decays as r^{-4} with the radius of the integrated area. The deformation field obeys the same power law, and the resulting capillary force on nearby particles has been found to be repulsive and in any case rather weak [12, 13]. On a droplet, however, the integrated pressure does not decay algebraically; there remains an uncompensated net force $F_1 - F_0 = (\cos\theta_0 - 1)F_0$ that leads to capillary phenomena that are different from those on a flat interface [26]. In this sense, momentum conservation has different physical implications for flat and spherical geometries.

VII. DISCUSSION AND SUMMARY

We have studied the electrostatic properties of a charged colloidal particle on a water droplet, and found them to differ significantly from those of a particle at an infinite flat interface. We briefly summarize the main results.

As a most striking feature, both the electrostatic potential and the surface charge density comprise a constant and an angle-dependent term of the form $1/\sin(\theta/2)^3$. The latter corresponds to the power law variation ρ^{-3} on an infinite flat interface, whereas the constant in (27) vanishes for an infinite droplet radius. The presence of an angle independent term in Eq. (32) means that a finite fraction of the counterions spread along the interface and form a uniformly charged surface layer on the droplet. From the expressions for charge density and the chemical potentials, it is clear that the effects studied here rely

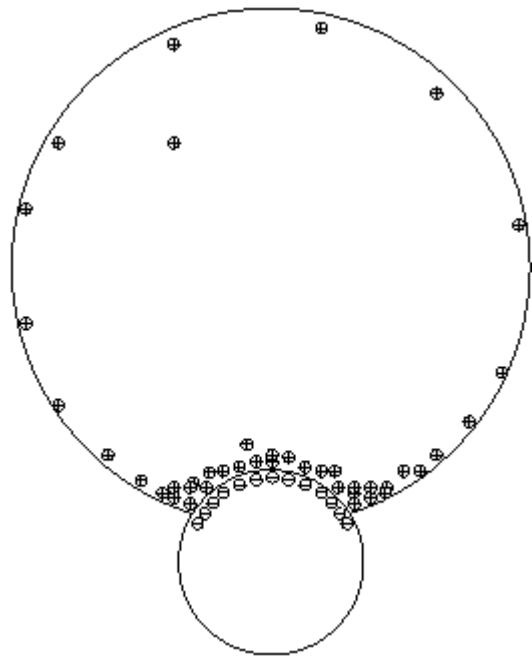


FIG. 3: Schematic view of a water droplet with a charged particle and the mobile counterions. Nonlinearities are important in the diffuse layer that covers the macro-ion and the interface very close to the particle. At distances beyond one screening length, the electrostatics are given by the expressions in Debye-Hückel approximation.

on the finite droplet size and disappear as its radius tends towards infinity. Thus all results of this paper arise from the finite curvature $1/R$ of the droplet.

The present work is based on linearized Poisson-Boltzmann theory. Formally, the Debye-Hückel approximation (7) is justified as long as the potential energy of an elementary charge is smaller than the thermal energy, $e\phi < kT$. For highly charged macro-ions it is well known that the Debye-Hückel expression is generally valid at distances beyond the screening length, albeit with effective values for the valency and the Debye parameter. In bulk solutions, colloidal particles carry an effective valency $Z^* = 4(a/\ell_B)(1 + \kappa a)$ that can be by orders of magnitude smaller than the bare value Z [24]; for micron sized particles in a weak electrolyte one has $Z^* \sim 10^4$ and $Z \sim 10^7$. Then the majority of counterions are condensed in a diffuse layer, the thickness of which is given by the Gouy-Chapman length and is of the order of nanometers.

A charged particle at a liquid interface constitutes a more complicated problem, which is not accounted for by available strong-coupling theories that deal with one-dimensional or isotropic geometries [23–25]. In this case, the diffuse layer of counterions spreads, in the immediate vicinity of the contact line, along the liquid interface, as shown in Fig. 3; the corresponding length scale is limited by the Debye and Gouy-Chapman lengths, i.e., it lies in the range 1...100 nanometers. At larger distances, beyond one Debye length, one recovers Debye-Hückel the-

ory with the effective valency Z^* .

Thus the Debye-Hückel potential (28) and the resulting expressions for the mobile ion density and the electric stress are valid at distances beyond the screening length. This implies, in particular, that the electrostatic repulsive force (34) applies quite generally to charge-stabilized interfacial colloids with micrometer spacings, even for high valencies $Z \gg Z^*$; one merely has to replace the charge Q with the effective value Z^*e . The force given in Eq. (34) is essential for the stabilization of the 2D colloidal aggregates observed in a water-in-oil emulsion [9].

A much more restricted criterion, however, arises for the interface pressure and thus for charge-induced capillary phenomena. From the functional form of the electric stress (41), it is clear that the dominant contribution to the counterforce acting on the particle, Eq. (44), stems from the domain very close to the particle. Yet in this range neither the Debye-Hückel approximation (7) nor the asymptotic expansion (51) are valid for high valencies. Only for moderately charged macro-ions with $Z \leq Z^*$, one can show that Eq. (28) provides a reasonable approximation even at short distances.

Recent work on charge-induced capillary forces emphasized the importance of momentum conservation, i.e., of taking into account the counterforce acting on the particle [11–14]. We find that the counterforce on a droplet, Eq. (44) differs from the corresponding expression on a flat interface. Because of the incomplete compensation of pressure on the liquid interface by the counterforce F_1 , there remains a net force $F_1 - F_0$ that is determined by electric stress close to the contact line. Yet in this range our Eqs. (41–44) do not apply to strongly charged particles, such as those investigated in [9], with a valency $Z \sim 10^7$ that by far exceeds the value Z^* .

We close with a brief discussion of additional structure that may occur in a surface layer of a few Ångströms and that we have not taken into account when calculating the charge density $\sigma(\mathbf{r})$ and the excess ion density $\delta n(\mathbf{r})$. For instance, the discontinuity of the dielectric constant at the phase boundary gives rise to an electrostatic repulsion of mobile charges, resulting in ion depletion very close to the interface [27]. Moreover, numerical simulations of the molecular dynamics indicate that specific interactions lead to significant structure of the ion densities at an air-water interface, and may even enhance them in the first molecular layers [28]. We have discarded these effects, since they are confined to a layer of less than one nanometer thickness, whereas the charge modulation (32) and the density inhomogeneity in (36) considered in this work, are spread over one Debye length, which is larger than 100 nanometers.

Helpful discussions with M. Deserno and R.R. Netz are gratefully acknowledged.

VIII. APPENDIX

A. Expansion scheme for Ψ

We evaluate the series (26) in terms of an asymptotic expansion that is valid at sufficiently large angles θ . Inserting the coefficients (19) we have

$$\Psi = \frac{\psi_0}{D_0} + \sum_{\ell=1}^{\infty} \frac{(2\ell+1)}{D_\ell + \eta(\ell+1)} \psi_\ell P_\ell \quad (45)$$

It turns out convenient to rewrite the coefficients for $\ell \geq 1$ as

$$\frac{(2\ell+1)}{D_\ell + \eta(\ell+1)} = \frac{2\ell+1}{D_\ell} - \eta \frac{(2\ell+1)(1+\ell)}{D_\ell(D_\ell + \eta(\ell+1))}. \quad (46)$$

Note that there is a close formal analogy to the 2D Fourier transform (9) of the potential at an infinite flat interface. The first term in (46) results in an exponentially screened potential at distances within one Debye length, whereas the second one dominates at larger distances and gives rise to a power law dependence.

There are two small parameters, the ratio of dielectric constants $\eta = \varepsilon_I/\varepsilon_{II}$, and the ratio of the Debye length and the droplet radius $\hat{\kappa}^{-1} = \kappa^{-1}/R$. We evaluate Ψ to lowest non-vanishing order in these parameters. Formally this is done by expanding D_ℓ and $\psi_\ell(\hat{r})$ in powers of $\ell + \frac{1}{2}$, the extrema of the underlying Bessel functions occurring at $\ell = -\frac{1}{2}$.

Thus we write D_ℓ as a series

$$D_\ell = d_0 + \left(\ell + \frac{1}{2}\right) d_1 + \left(\ell + \frac{1}{2}\right)^2 d_2 + \dots,$$

with

$$d_n = \frac{1}{n!} \partial^n D_\ell / \partial \ell^n |_{\ell=-1/2}.$$

From the definition in terms of Bessel functions one finds, to leading order in $\hat{\kappa}^{-1}$, the constant

$$d_0 = \hat{\kappa}.$$

The derivatives of odd order are exponentially small, $d_{2n+1} \sim e^{-\hat{\kappa}}$, whereas the even ones vary as powers of $\hat{\kappa}^{-1}$, e.g., $d_2 = \frac{1}{2}\hat{\kappa}^{-1}$.

Regarding the radial function $\psi_\ell(\hat{r})$ we have

$$\psi_\ell(\hat{r}) = \xi_0 + \left(\ell + \frac{1}{2}\right) \xi_1 + \left(\ell + \frac{1}{2}\right)^2 \xi_2 + \dots$$

where the coefficients still depend on $\hat{r} = r/R$,

$$\xi_n(\hat{r}) = \frac{1}{n!} \left. \frac{d^n \psi_\ell(\hat{r})}{d\ell^n} \right|_{\ell=-\frac{1}{2}}.$$

It turns out that ψ_ℓ varies weakly with ℓ . The leading term of the series is well approximated by

$$\xi_0(\hat{r}) = e^{\hat{\kappa}(\hat{r}-1)}.$$

As above, the derivatives of odd order are exponentially small, $\xi_{2n+1} \sim e^{-\hat{\kappa}}$ whereas the even ones involve powers of $\hat{\kappa}^{-1}$, e.g., $\xi_2 \approx \frac{1}{2}(1-\hat{r})\hat{\kappa}^{-1}\xi_0$.

B. Case $\eta = 0$

First we consider the case where the dielectric constant of the insulating is much smaller than that of water, i.e., where their ratio approaches zero, $\eta = 0$. We show that the first term in (46) is irrelevant at distances beyond a few Debye lengths, i.e., that the series

$$\Psi_0(\hat{r}, x) = \sum_{\ell=0}^{\infty} \frac{2\ell+1}{D_\ell} \psi_\ell(\hat{r}) P_\ell(x)$$

does not contribute significantly to the potential.

The derivatives d_n and ξ_n of odd order are exponentially small and thus may be discarded. Expanding $1/D_\ell$ in terms of the derivatives of even order gives the series

$$\Psi_0(\hat{r}, x) = \frac{\xi_0}{d_0} M_1(x) + \left(\frac{\xi_2}{4d_0} - \frac{\xi_0 d_2}{4d_0^2} \right) M_3(x) + \dots$$

in terms of the moments

$$M_n(x) = \sum_{\ell=0}^{\infty} (2\ell+1)^n P_\ell(x).$$

Note that the series contains those of odd order only. Yet when evaluating the moments as derivatives $[(t\partial_t)^n f(t, x)]_{t=1}$ of the generating function

$$f(t, x) = \frac{1}{\sqrt{1-2xt+t^2}} = \sum_{\ell=0}^{\infty} t^\ell P_\ell(x), \quad (47)$$

one finds $M_{2m+1}(x) = 0$. In summary, the moments of odd order vanish, whereas the coefficients of those of even order are negligible because of the small coefficients $d_{2n+1} \sim e^{-\hat{\kappa}}$. We conclude that, beyond a few Debye lengths, Ψ_0 does not contribute to the potential.

C. Case of finite η

Now we turn to the remaining part of the coefficients (46) that is proportional to the ratio η of dielectric constants. When rearranging the term $\ell = 0$ in (26) we have

$$\Psi(\hat{r}, x) = \frac{\eta}{D_0(D_0 + \eta)} \psi_0(\hat{r}) - \eta \sum_{\ell=0}^{\infty} \frac{(2\ell+1)(1+\ell)}{D_\ell(D_\ell + \eta(\ell+1))} \psi_\ell(\hat{r}) P_\ell(x). \quad (48)$$

As above we linearize with respect to η and retain only the leading terms of the series for D_ℓ and ψ_ℓ , i.e., we put $D_\ell = d_0 = \hat{\kappa}$ and $\psi_\ell = \xi_0 = e^{\hat{\kappa}(\hat{r}-1)}$. We thus find

$$\Psi = \frac{\eta}{\hat{\kappa}^2} e^{\hat{\kappa}(\hat{r}-1)} \left(1 - \sum_{\ell=0}^{\infty} (1+3\ell+2\ell^2) P_\ell(x) \right). \quad (49)$$

The sum over ℓ is evaluated in terms of the generating function (47).

Taking on both sides the derivative with respect to t and then multiplying with t gives

$$\sum_{\ell=0}^{\infty} \ell P_\ell(x) t^n = t \partial_t f(t, x) = \frac{t(x-t)}{(1-2xt+t^2)^{3/2}}.$$

Evaluating f and $t\partial_t f$ at $t = 1$ one finds

$$\sum_{\ell=0}^{\infty} P_\ell(x) = \frac{1}{\sqrt{2-2x}}, \quad \sum_{\ell=0}^{\infty} \ell P_\ell(x) = -\frac{1}{2\sqrt{2-2x}}.$$

Repeating the derivative and evaluating $t\partial_t t\partial_t f$ at $t = 1$ gives the second moment

$$\sum_{\ell=0}^{\infty} \ell^2 P_\ell(x) = t \partial_t [t \partial_t f(t, x)]|_{t=1} = -2^{-5/2} \frac{1+x}{(1-x)^{3/2}}.$$

When inserting these three contributions in (49) we obtain

$$\sum_{\ell=0}^{\infty} (1+3\ell+2\ell^2) P_\ell(x) = -\frac{2^{-1/2}}{(1-x)^{3/2}}. \quad (50)$$

Noting $1-x = 2\sin(\theta/2)^2$ we finally have

$$\Psi(\hat{r}, \cos \theta) = \frac{\eta}{\hat{\kappa}^2} \left(1 + \frac{1}{4\sin(\theta/2)^3} \right) e^{\hat{\kappa}(\hat{r}-1)}. \quad (51)$$

This expression is the leading term of a systematic expansion in terms of $1/\hat{\kappa}$, and accounts for $d_0 = \hat{\kappa}$ and $\xi_0 = e^{\hat{\kappa}(\hat{r}-1)}$. Both the corrections to d_0 and ξ_0 , and the coefficients d_n and ξ_n of higher order $n \geq 1$, involve powers of the small parameter $1/\hat{\kappa}$ and thus have been neglected. Eq. (51) is valid at angles θ well beyond $1/\hat{\kappa}$, which, in physical terms, corresponds to distances well beyond one Debye length.

D. Comparison with the flat interface

There is a close analogy between the two contributions to the coefficients of the potential on a droplet, Eq. (46), and the two terms in brackets in the expression for the flat interface, Eq. (9). Formally one may identify $(\ell + \frac{1}{2})/R$ with the wave vector q . Moreover, for $\hat{\kappa} \gg 1$ the quantity D_ℓ is well approximated by $D_\ell = \sqrt{(\ell + 1/2)^2 + \hat{\kappa}^2}$ and thus satisfies the relation $D_\ell = \hat{q}/R$ where $\hat{q} = \sqrt{q^2 + \hat{\kappa}^2}$.

These relations become mathematically exact in the limit of an infinite droplet radius, $R \rightarrow \infty$. A finite lateral distance ρ then corresponds to an infinitely small angle $\theta = \rho/R$. For $\theta \rightarrow 0$ the Legendre polynomials and the Bessel function are related by $P_\ell(\cos \theta) \rightarrow J_0[(2\ell+1)\sin(\theta/2)]$, and the series (13) tends towards the inverse Fourier transformation of (9). In this limit we recover Hurd's result for a flat interface [18].

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