Effect of capillary waves on the double layer capacitance of the interface between two immiscible electrolytes

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Abstract

The effect of capillary waves on the double layer capacitance of the interface between two immiscible electrolytes has been studied. We have found that a corrugation of the interface due to capillary waves leads to an increase in the capacitance, as compared with the Gouy–Chapman result for a flat interface. The theory offers a concept of a roughness function, \( \tilde{R} \), which determines the deviation of capacitance from the Gouy–Chapman result. \( \tilde{R} \) is a function of Debye lengths of the two immiscible electrolytes. Analytical expression for the roughness function has been derived which shows a strong dependence of \( \tilde{R} \) on the interfacial tension and the dielectric constants of contacting solutions. Predictions amenable to experimental tests have been discussed. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Studies of the electrical double layer at the interface between two immiscible electrolyte solutions have recently drawn considerable attention [1–3]. Indeed, liquid–liquid interfaces are interesting model systems for reaction kinetics and biological physics and are promising media for phase transfer catalysis [1–3]. These interfaces are polarizable, and their response to charging influence a variety of phenomena. However, in spite of the importance of the electrical properties of these interfaces, the experimental data are still limited [1,2,4–7], and there is no unambiguous picture for their interpretation. For instance, the treatment of interfacial capacitance in terms of the capacitance of two ‘back-to-back’ Gouy–Chapman double layers works fairly well for some liquid/liquid combinations, while it fails for the majority of others [8]. This discrepancy has stimulated theoretical works, which go beyond the classical Gouy–Chapman scheme including the ion pairing at the interface and the ‘mixed boundary layer’ [8,9].

The Gouy–Chapman theory itself corresponds to a flat interface. It is, however, clear that liquid/liquid interfaces are never ideally flat. The reason being the thermal excitation of capillary waves on them [10–16]. It is therefore natural to study the consequences of the simple modification of the classical Gouy–Chapman theory taking account of capillary waves which give rise to dynamic corrugation of the interface. This is to be the subject of the present report. Our analysis will be based on the extension of the theory of the double layer on rough surfaces [17–19], which establishes the relationship between the capacitance of the interface and the height–height correlation function of roughness. Here, we explore the correlation function corresponding to capillary waves. This is possible because the
frequencies of the capillary waves are orders of magnitude smaller than the relaxation of ionic Debye atmospheres.

2. Basic equation

Consider a contact between two immiscible electrolyte solutions characterized by dielectric constants, \( \varepsilon_1 \) and \( \varepsilon_2 \), and Debye lengths, \( \kappa_1 \) and \( \kappa_2 \), respectively (Fig. 1). For 1–1 binary electrolyte solutions \( \kappa_1 = (\varepsilon_1 k_B T/8\pi n_e e^2)^{1/2} \), where \( n_e \) is the electrolyte concentration in the corresponding phase (i), \( e \), the charge of electron, \( T \), the temperature, and \( k_B \), the Boltzmann constant. The interface is given by the equation \( z = \xi(x, y) \), which determines the local height of fluctuations with respect to a reference plane, \( z = 0 \). The average value of the profile function \( \langle \xi(x, y) \rangle = 0 \).

In the Gouy–Chapman theory, the distribution of the electrostatic potential \( \phi(r) \) at the interface is described by the Poisson–Boltzmann equation. In this paper we restrict our consideration to its linearized version, valid for low overall electrode potential drop, \( V < \kappa_0 T/e \):

\[
(\nabla^2 - \kappa_1^2)\phi_1(r) = 0 \quad \text{for} \ z < \xi(x, y)
\]

(1)

\[
(\nabla^2 - \kappa_2^2)(\phi_2(r) - V) = 0 \quad \text{for} \ z > \xi(x, y)
\]

(2)

The boundary conditions for the potential include:

(a) the continuity of the potential at the interface:

\[
\phi_1(x, y, z = \xi(x, y)) = \phi_2(x, y, z = \xi(x, y))
\]

(3)

(b) the continuity of the normal component of the displacement at the interface:

\[
\frac{\partial \phi_1(x, y, z = \xi(x, y))}{\partial n} = \frac{\partial \phi_2(x, y, z = \xi(x, y))}{\partial n}
\]

(4)

where \( \partial / \partial n \) denotes the normal derivative; and (c) the fixed value of the overall potential drop, \( V \):

\[
\phi_1 \rightarrow 0 \quad \text{as} \ z \rightarrow -\infty, \quad \text{and} \quad \phi_2 \rightarrow V \quad \text{as} \ z \rightarrow \infty
\]

(5)

The perturbation technique developed for the calculation of a capacitance at rough electrode surfaces [17], can be easily extended to the contact between two electrolyte solutions. A method for calculating the potential distribution at the rough interface and correspondingly the capacitance is outlined in Appendix A. The result reads:

\[
C = \tilde{R}(\kappa_1, \kappa_2) C_{GC}
\]

(6)

where \( C_{GC} \) is the Gouy–Chapman capacitance of the flat interface between two electrolyte solutions:

\[
C_{GC} = \frac{\varepsilon_1 \varepsilon_2 \kappa_1 \kappa_2}{4\pi (\varepsilon_1 \kappa_1 + \varepsilon_2 \kappa_2)}
\]

(7)

and the roughness function, which describes the deviation from the Gouy–Chapman theory, has the form:

\[
\tilde{R}(\kappa_1, \kappa_2) = 1 + 2 C_{GC} \\
\int_{0}^{\infty} dk g(k) \left( \frac{k}{\varepsilon_1 q_1 + \varepsilon_2 q_2} \right)
\]

(8)

Here we introduce the Fourier transform of the height–height correlation function:

\[
g(k) = \int d^2\mathbf{R} \langle \xi(\mathbf{R}) \xi(0) \rangle \exp(-i\mathbf{kR})
\]

(9)

and:

\[
q_1 = \sqrt{\kappa_1^2 + k^2} \quad \text{and} \quad q_2 = \sqrt{\kappa_2^2 + k^2}
\]

(10)

The mean square height of roughness, \( \langle \xi^2 \rangle \), is expressed through the correlation function as:

\[
\langle \xi^2 \rangle = \int \frac{d^2k}{(2\pi)^2} g(k)
\]

(11)

Both \( \langle \xi^2 \rangle \) and \( g(k) \) can be measured in optical, neutron and X-ray scattering experiments [10–13]. For \( \langle \xi^2 \rangle = 0 \), Eq. (8) gives \( \tilde{R}(\kappa_1, \kappa_2) = 1 \) reproducing the Gouy–Chapman result for the capacitance of a flat interface. On metal electrodes the effect of roughness on the double-layer capacitance is determined by an interplay between the electrolyte Debye length and the scales of roughness [17–19]. For liquid–liquid interfaces \( \tilde{R} \) is a function of the Debye lengths of the two immiscible electrolytes. As expected, Eq. (8) shows that for the small Debye lengths, \( \kappa_1 \rightarrow 0 \) and \( \kappa_2 \rightarrow 0 \), the roughness function, \( \tilde{R}(\kappa_1, \kappa_2) \), approaches the geometrical roughness factor \( R = S_{\text{real}}/S_i \), i.e. the ratio of the true surface to the apparent surface. At very large Debye lengths, \( \kappa_1 \rightarrow \infty \) or \( \kappa_2 \rightarrow \infty \), the roughness of the interface is not ‘seen’ in the capacitance and \( \tilde{R} = 1 \). The equation which is similar to Eq. (8) has been recently
derived in Ref. [20]. The use of the non-local boundary condition suggested in Ref. [20] is equivalent to the procedure described in the present work. Actually, the additional non-local boundary condition [20] is not a boundary condition, it just defines the form of the approximation used for the potential distribution at the interface. This condition includes unknown functions which are determined by substituting it into the usual boundary conditions (Eqs. (3) and (4)).

3. Correlation function for capillary waves

Experiments on optical [12,13] and neutron reflectivity [11], X-ray scattering [14] and molecular dynamics simulations [15,16] show unambiguously that the liquid–liquid interface is highly corrugated. The corrugation originates from the thermal fluctuations of the interface which are known as capillary waves. Capillary wave theories [10] result in the following expression for the Fourier transform of the height–height correlation function:

\[ g(k) = \frac{k_B T}{\gamma (k^2 + k_{gr}^2)} \]  

(12)

where \( \gamma \) is the interfacial tension and \( k_{gr} \) is the 'small wave-vector gravitational cutoff' given by \( (\Delta \rho g / \gamma)^{1/2} \). \( \Delta \rho \) is the difference in mass density across the interface and \( g \) is the acceleration due to gravity. Both, experiments and molecular dynamics simulations [11,14–16] demonstrate that the macroscopic capillary wave theory works surprisingly well down to nanometer range.

Using Eq. (12) for the calculation of the mean square fluctuation \( \langle \zeta^2 \rangle \) one finds that the integral (Eq. (11)) diverges at high values of the wave-vector \( k \). This problem has been resolved by the introduction of the upper wave-vector cutoff \( k_{\text{max}} \) [21]. Clearly, \( \pi / k_{\text{max}} \) cannot be less than the molecular lengths in the problem. In the literature \( k_{\text{max}}^{-1} \) is proposed to be proportional to the molecular diameter [22], to the largest bulk correlation length of the contacting liquids [23], to the root mean square height [24], or to the intrinsic thickness (characteristic smearing) of the interface [12]. Here we do not specify this quantity and propose to use it as an adjustable parameter.

![Fig. 2. Parsons–Zobel plots calculated by varying the concentration of electrolyte in water for a given concentration of electrolyte in the non-aqueous phase, \( n_2 = 0.1 \text{ M} \). Dotted is shown the Gouy–Chapman reference line. (a) \( \gamma = 30 \text{ dyn cm}^{-1}, k_{\text{max}} = 2 \text{ Å}^{-1} \). The effect of dielectric constant of the non-aqueous solvent. \( \varepsilon _2 = (1) 4, (2) 10, (3) 30 \). (b) \( \varepsilon _2 = 10, k_{\text{max}} = 2 \text{ Å}^{-1} \). The effect of interfacial tension at room temperature \( \gamma _r \), dyn cm\(^{-1}\) = (1) 30, (2) 15, (3) 7.5. (c) \( \gamma = 30 \text{ dyn cm}^{-1}, \varepsilon _2 = 10 \). The effect of the upper wave-vector cutoff \( k_{\text{max}} \), Å\(^{-1}\) = (1) 2, (2) 1, (3) 0.5.](image-url)
Below we use the correlation function (Eq. (12)) to study the effect of capillary waves on the diffuse layer capacitance of an interface between two electrolyte solutions. We analyze the dependencies of the capacitance on concentrations of the contacting electrolytes, dielectric constants of the solvents and the interfacial surface tension.

4. Results and discussion

Plotting the roughness function is the most informative way of presenting the results. However, we first show the typical scale of the effect in terms of 'traditional' Parsons–Zobel plots.

In Fig. 2 we vary the concentration of electrolyte in water (one of the contacting phases) keeping the concentration constant in the non-aqueous phase. The deviation from the Gouy–Chapman result depends on the interfacial tension and the dielectric constant of the non-aqueous medium. When this medium is changed, both of the parameters change simultaneously. However, we show the effect of these two parameters separately. In accordance with experimental data [4–7] we see that the effect of capillary waves leads to an increase in the capacitance, as compared with \( C_{GC} \). The lower the dielectric constant of the non-aqueous medium, the stronger the deviation (Fig. 2(a)). The reason for this effect is clear. The smaller dielectric constants will decrease the effective Debye length, \((1/\kappa_1) + (1/\kappa_2)\). Electric field then probes the Fourier components of the height fluctuations with higher wave vectors that give the largest contribution to the roughness function. The increase of the interfacial tension depresses capillary waves (the mean square fluctuation scales as \( \gamma \)) and the deviation from the Gouy–Chapman result is smaller (Fig. 2(b)). The typical absolute values of the effect lie in the observed interval [8]. They depend strongly on the cutoff (Fig. 2(c)).

In the context of this problem, the Parsons–Zobel plots are rather featureless. The effect of capillary waves is much better seen on the roughness function (Figs. 3 and 4). It is stronger, the larger the upper wave-vector cutoff (c.f. (a) and (b)). Fig. 3 shows the roughness function variation on the inverse Debye length in the aqueous electrolyte for several fixed values of the ionic concentration in the non-aqueous phase. The effect of the dielectric constant of the non-aqueous phase is shown in Fig. 4 for a fixed electrolyte concentration in the non-aqueous phase.

We thus suggest treating the experimental data in terms of the roughness function, varying the concentrations of electrolytes. Our theory gives a definite shape of this function, and if such a shape were observed experimentally, one could fit the data with one adjustable parameter of the theory: the upper wave-vector cutoff, \( k_{max} \). The latter lies in the range of 2–0.5 \( \text{Å}^{-1} \) [14,15,21] and is a constant for the given pair of liquids in contact. Indeed, the concentration dependence of \( k_{max} \) is negligible for low and moderate ionic strengths [10]. The same applies to \( \gamma \).

The capillary wave induced fluctuations are influenced by the external electric field [25,26]. Our recent results [26] show that at low potential drops, \( V \), the mean square height increases proportional to \( V^2 \):

\[
\langle \xi^2 \rangle \approx \langle \xi^2 \rangle_0 + \frac{V^2k_B T}{4\pi \gamma^2} C_{GC} \ln \left( \frac{\kappa_1 \kappa_2}{(\kappa_1 + \kappa_2)k_{gr}} \right) \quad (13)
\]

where \( \langle \xi^2 \rangle_0 \) is the mean square height at pzc. This effect should be taken into account in the theory of the double layer capacitance far from the pzc. A self-consistent nonlinear theory which includes this effect is in progress [27]. However, at the pzc the expressions (Eqs. (6) and (8)) used above, remain valid.
corresponding wave vectors transform the potential and the interfacial profile function from tangential coordinates.

Appendix A

The upper wave-vector cutoff $k_{\text{max}} = 1$. The effect of dielectric constant of the non-aqueous solvent: $\varepsilon_2 = (1)$ 4, (2) 10, (3) 30.

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Fig. 4. Roughness function versus the Debye length in the aqueous phase at a fixed interfacial tension, $\gamma = 15$ dyn cm$^{-1}$ and a given concentration of non-aqueous phase, $n_2 = 0.1$ M. The upper wave-vector cutoff $k_{\text{max}} = 1$. (a) 2, (b) 0.5. The effect of dielectric constant of the non-aqueous solvent: $\varepsilon_2 = (1)$ 4, (2) 10, (3) 30.

Solving Eqs. (1) and (2), it is convenient to Fourier transform the potential and the interfacial profile function from tangential coordinates $\mathbf{R} = (x, y)$ to the corresponding wave vectors $k = (k_x, k_y)$ as $f(\mathbf{k}) = \int \text{dR} f(\mathbf{R}) \exp(-i\mathbf{k}\mathbf{R})$. Eqs. (1) and (2) then transform to:

$$\frac{d^2}{dz^2} - k^2 - \kappa^2 z^2 \varphi_1(\mathbf{k}, z) = 0$$

(A1)

$$\frac{d^2}{dz^2} - k^2 - \kappa^2 z^2 \varphi_2(\mathbf{k}, z) = 0$$

(A2)

According to Rayleigh approximation [28] the solutions of Eqs. (A1) and (A2) in the half spaces $z < \zeta(x, y)$ and $z > \zeta(x, y)$, have the form:

$$\varphi_1(\mathbf{k}, z) = A_1(\mathbf{k}) \exp(q_1 z)$$

$$\varphi_2(\mathbf{k}, z) = A_2(\mathbf{k}) \exp(-q_2 z) + (2\pi)^2 V \delta(\mathbf{k})$$

(A3)

(A4)

where $\delta(\mathbf{k})$ is the two-dimensional Dirac $\delta$ function. The Rayleigh approximation neglects the terms proportional to $\exp(-q_1 z)$ in $\varphi_1(\mathbf{k}, z)$ and to $\exp(-q_2 z)$ in $\varphi_2(\mathbf{k}, z)$ respectively, which would be important inside deep protrusions at the interface, ignored in our consideration. This perturbation approach is applicable to weakly rough interfaces [17–19] for which the characteristic size of roughness in the $z$-direction is less than the tangential one and the Debye lengths, $k_1$ and $k_2$.

The boundary conditions (Eqs. (3) and (4)) lead to the integral equations for the prefactors $A_1(\mathbf{k})$ and $A_2(\mathbf{k})$:

$$\int \frac{d\mathbf{k}}{2\pi^2} A_1(\mathbf{k}) \int \text{dR} \exp[q_2 \zeta(x, y)] \exp[-i(k' - k)\mathbf{R}]$$

$$= (2\pi)^2 V \delta(\mathbf{k})$$

$$+ \int \frac{d\mathbf{k}}{2\pi^2} A_2(\mathbf{k}) \int \text{dR} \exp[-q_2 \zeta(x, y)]$$

$$\times \exp[-i(k' - k)\mathbf{R}]$$

(A5)

and:

$$\varepsilon_1 \int \frac{d\mathbf{k}}{2\pi^2} A_1(\mathbf{k}) \int \text{dR} (q_1 - i\mathbf{kV}\zeta(x, y)) \exp[q_1 \zeta(x, y)]$$

$$\times \exp[-i(k' - k)\mathbf{R}]$$

$$- \varepsilon_2 \int \frac{d\mathbf{k}}{2\pi^2} A_2(\mathbf{k}) \int \text{dR} (q_2 + i\mathbf{kV}\zeta(x, y))$$

$$\times \exp[-q_2 \zeta(x, y)] \exp[-i(k' - k)\mathbf{R}]$$

(A6)

Eqs. (A5) and (A6) have been solved by iterations up to the second order with respect to the profile function $\zeta(x, y)$. We remark that in order to determine the first nonvanishing corrections to the capacitance caused by roughness it is enough to obtain the second order terms only for the zero value of the two dimensional wave vector $\mathbf{k}$.

To the lowest order we arrive at the results for the smooth interface between two electrolyte solutions:

$$A_1^{(0)}(\mathbf{k}) = 2(2\pi)^3 \delta(\mathbf{k}) \gamma V \varepsilon_2 \gamma V \varepsilon_1$$

$$A_2^{(0)}(\mathbf{k}) = -2(2\pi)^3 \delta(\mathbf{k}) \gamma V \varepsilon_2 \gamma V \varepsilon_1$$

(A7)

To the first and the second orders, we have:

$$A_1^{(1)}(\mathbf{k}) = -\frac{4\pi V \varepsilon_2 \gamma V \varepsilon_1}{\varepsilon_1 q_1 + \varepsilon_2 q_2} \{\kappa_2 + \kappa_1 - q_2(1 - \varepsilon_1 / \varepsilon_2)\},$$

$$A_2^{(1)}(\mathbf{k}) = -\frac{4\pi V \varepsilon_2 \gamma V \varepsilon_1}{\varepsilon_1 q_1 + \varepsilon_2 q_2} \{\kappa_2 + \kappa_1 - q_1(1 - \varepsilon_2 / \varepsilon_1)\},$$
In the linearized Poisson–Boltzmann approximation the charge density distribution is proportional to the potential and the integral charge on each side of the interface is given by:

\[
Q_1 = \frac{2\pi C_{GC}}{\varepsilon_1} \int \frac{dk}{(2\pi)^2} \zeta \frac{\varepsilon_2 k_2}{\varepsilon_2 K_2} \delta (k_1 - k_2)
\]

\[
Q_2 = \frac{2\pi C_{GC}}{\varepsilon_2} \int \frac{dk}{(2\pi)^2} \frac{\varepsilon_1 k_1}{\varepsilon_1 K_1} \frac{\varepsilon_2 k_2}{\varepsilon_1 K_1} \delta (k_1 - k_2)
\]

(A9)

Making the lateral Fourier transform of \(\varphi (r)\) and using Eqs. (A7) and (A8) we obtain the capacitance \(C = -Q_1/V\) in the form of Eq. (6) in the text.

References