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The effect of electric field on capillary waves at the interface of two immiscible electrolytes

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Abstract

The effect of electric field on the corrugation of the interface between two immiscible electrolytes is theoretically studied within the linearized Poisson–Boltzmann approximation. It is shown that charging of the interface leads to an enhancement of the surface corrugation, which may cause a destruction of the interface by a sufficiently strong field. Dependencies of the mean-square height of corrugation on the overall potential drop across the interface V and on the ionic concentrations in the two electrolytes are analyzed. Predictions amenable to experimental tests are discussed.

1. Introduction

Liquid/liquid interfaces are interesting model systems for reaction kinetics, biological physics and the phase transfer catalysis [1,2]. One of the phases is usually water, and the other one is a less or low polar phase. The interface separates hydrophilic and hydrophobic ions. When the two salts are dissolved in this system, one of them composed of hydrophobic and the other one of hydrophilic ions, they form two back-to-back ionic double layers [1,2]. This allows to charge the interface. The net charge influences the variety of phenomena which occur at the interface.

Liquid/liquid interfaces are never ideally flat because of the thermal excitation of capillary waves [3–9]. The interface is therefore spontaneously corrugated, and the amplitudes of corrugation the stronger the smaller the interfacial tension. The effect of corrugation on the electrical properties of the interface and charge transfer phenomena has drawn considerable attention [8,9]. The electric field, which is in many cases a driving force of a number of phenomena at the interface, also affects this corrugation. Although it has never been explicitly demonstrated for the interface of two immiscible electrolytes, the studies of liquid helium films [10] and of the surface of liquid metals [11–13] have unambiguously shown a dramatic enhancement of interfacial

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corrugation by an external electric field. Moreover, it was found that above a certain critical field the interface becomes unstable with respect to fluctuations [14–16].

Here, we perform a theoretical analysis of the effect of electric field on the capillary waves at the interface of two immiscible electrolytes. In contrast to the previous studies of interfaces between dielectric media [10–17], here electric field is not homogeneous. The presence of ions introduces Debye screening length which localizes the field near the interface. The Debye length competes with the scales of corrugation. This affects the coupling of the electric field with the capillary waves. The maximum effect is on the wavelengths comparable with the Debye length. Varying, e.g., ionic concentration one can vary the Debye length and, thereby, probe the coupling to the waves with different wave vectors. We derive an analytical expression for the experimentally measurable quantity, the mean-square height of corrugation as a function of the overall potential drop across the interface and the ionic concentrations in the two phases.

2. Basic equations

Consider a contact between two immiscible electrolyte solutions characterized by dielectric constants, ε_1 and ε_2, and Debye lengths, κ_1^{-1} and κ_2^{-1}, respectively. For 1–1 binary electrolyte solutions $\kappa_i^{-1} = (\varepsilon_i k_B T / 8\pi n_i^0 e^2)^{1/2}$, where n_i^0 is the bulk 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 relative to a reference plane, $z = 0$. The mean value of the profile function $\langle \xi(x,y) \rangle = 0$.

2.1. Free energy functional

We start with the functional of a free energy of the interface, which contains of the *surface tension* term, the *electrostatic energy* term, and the entropy of dilute electrolytes:

$$
\begin{aligned}
F = F_0 &+ \frac{1}{2}\int \mathrm{d}\boldsymbol{R}\,\gamma\left[\left(\nabla\xi(\boldsymbol{R})\right)^2 + k_{\mathrm{gr}}^2\xi^2(\boldsymbol{R})\right] \\
&+ \frac{\varepsilon_1}{8\pi}\int \mathrm{d}\boldsymbol{R}\int_{-\infty}^{\xi(\boldsymbol{R})}\mathrm{d}z\left[\nabla\varphi_1(z,\boldsymbol{R})\right]^2 \\
&+ \frac{\varepsilon_2}{8\pi}\int \mathrm{d}\boldsymbol{R}\int_{\xi(\boldsymbol{R})}^{\infty}\mathrm{d}z\left[\nabla\varphi_2(z,\boldsymbol{R})\right]^2 \\
&+ k_B T\int \mathrm{d}\boldsymbol{R}\int_{-\infty}^{\xi(\boldsymbol{R})}\mathrm{d}z \\
&\times\left[n_1^+(z,\boldsymbol{R})\log\left(\frac{n_1^+(z,\boldsymbol{R})}{n_1^0}\right)\right. \\
&+ n_1^-(z,\boldsymbol{R})\log\left(\frac{n_1^-(z,\boldsymbol{R})}{n_1^0}\right) \\
&\left.-\left(n_1^+ + n_1^- - 2n_1^0\right)\right] + k_B T\int \mathrm{d}\boldsymbol{R} \\
&\times\int_{\xi(\boldsymbol{R})}^{\infty}\mathrm{d}z\left[n_2^+(z,\boldsymbol{R})\log\left(\frac{n_2^+(z,\boldsymbol{R})}{n_2^0}\right)\right. \\
&+ n_2^-(z,\boldsymbol{R})\log\left(\frac{n_2^-(z,\boldsymbol{R})}{n_2^0}\right) \\
&\left.-\left(n_2^+ + n_2^- - 2n_2^0\right)\right] + VQ_2 .
\end{aligned}
\qquad (1)
$$

Here γ is the interfacial surface tension, k_{gr}^2 is the small wave-vector gravitational cutoff given by $\Delta\rho g/\gamma$, where g is the gravitational acceleration and $\Delta\rho > 0$ is the difference of densities of two liquids, $\varphi_i(z,\boldsymbol{R})$ and $n_i^{\mp}(z,\boldsymbol{R})$ are the electrostatic potential and the concentrations of positive and negative ions in the phase (i), $\boldsymbol{R} = (x,y)$ and V is the overall potential drop across the interface and Q_2 is the overall charge in the second phase. The first term in Eq. (1), F_0, is the free energy of the contacting solutions for a flat interface at the zero potential. The last term, VQ_2, originates from the consideration of the free energy for a fixed overall potential V and presents the extra work which is needed to maintain the potential difference V imposed on the interface [18].

The free energy functional depends on three types of fields: surface fluctuations $\xi(\boldsymbol{R})$, electrostatic potential $\varphi_i(\boldsymbol{R},z)$, and the ionic concentrations $n_i^{\pm}(\boldsymbol{R},z)$. By minimizing the functional with respect to ϑ_i and $n_i^{\pm}$ at a given $\xi(\boldsymbol{R})$, we obtain two coupled Poisson–Boltzmann equations, that describe the distribution of the electrostatic potential and ionic concentrations in contacting media. In this Letter, we restrict our consideration by the linearized variant of the Poisson–Boltzmann approximation, which is valid for low potential drops across the interface $V < k_B T/e$. In this case we, arrive at

$$\left(\nabla^2 - \kappa_1^2\right)\varphi_1(r) = 0 \quad \text{for } z < \xi(x,y), \tag{2}$$

$$\left(\nabla^2 - \kappa_2^2\right)\varphi_2(r) = 0 \quad \text{for } z > \xi(x,y), \tag{3}$$

where the ionic concentrations are given by

$$n_1^{\pm}(z,\boldsymbol{R}) = n_1^0 \exp\left[\mp \frac{e\varphi_1(z,\boldsymbol{R})}{k_B T}\right],$$

$$n_2^{\pm}(z,\boldsymbol{R}) = n_2^0 \exp\left[\mp \frac{e(\varphi_2(z,\boldsymbol{R}) - V)}{k_B T}\right].$$

The boundary conditions, imposed on the potential, are:

(a) the continuity of the potential at the interface

$$\varphi_1(x,y,z=\xi(x,y)) = \varphi_2(x,y,z=\xi(x,y)), \tag{5}$$

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

$$\varepsilon_1 \frac{\partial\varphi_1(x,y,z=\xi(x,y))}{\partial n} = \varepsilon_2 \frac{\partial\varphi_2(x,y,z=\xi(x,y))}{\partial n}, \tag{6}$$

where $\partial/\partial n$ denotes the normal derivative and

(c) the fixed value of the overall potential drop V

$$\varphi_1 \to 0 \text{ as } z \to -\infty, \quad \varphi_2 \to V \quad \text{as } z \to \infty. \tag{7}$$

These equations have been solved by an extension of a perturbation technique, developed in Ref. [19] in the context of a calculation of a capacitance at rough electrode surfaces, on the case of the contact between two electrolytes [1]. Substituting the solutions of Eqs. (2)–(4) into the expression (1) we obtain the free energy functional of one field, $\xi(\boldsymbol{R})$

$$F = F_0 - \frac{S}{2} V^2 C_{GC} + \Delta F[\xi(\boldsymbol{k}),V], \tag{8}$$

where S is the apparent interfacial area, and C_{GC} is the Gouy–Chapman capacitance of the flat interface between two electrolyte solutions [1]

$$C_{GC} = \frac{\varepsilon_1 \varepsilon_2 \kappa_1 \kappa_2}{4\pi(\varepsilon_1\kappa_1 + \varepsilon_2\kappa_2)}. \tag{9}$$

The first two terms in Eq. (8) present the free energy of the contacting solutions with a flat interface for a given potential drop V, and $\Delta F[\xi(\boldsymbol{k}),V]$ is the correction due to the fluctuations of the interface

$$\Delta F[\xi(\boldsymbol{k}),V] = \frac{1}{2}\int \frac{d\boldsymbol{k}}{(2\pi)^2}\xi(\boldsymbol{k})\xi(-\boldsymbol{k}) \times \left\{\gamma\left(k^2 k_{gr}^2\right) - \Delta f_V(k)\right\}. \tag{10}$$

Here we introduced the following notations: $\xi(\boldsymbol{k})$ is the Fourier transform of the interface profile function

$$\xi(\boldsymbol{k}) = \int d\boldsymbol{R}\,\xi(\boldsymbol{R})\exp[-i\boldsymbol{k}\boldsymbol{R}] \tag{11}$$

and

$$\Delta f_V(k) = \frac{4\pi V^2 C_{GC}^2}{\varepsilon_1 q_1 + \varepsilon_2 q_2}\left[(q_2 - \kappa_2)(\varepsilon_1 q_1/\varepsilon_2 + \kappa_2) + (q_1 - \kappa_1)(\varepsilon_2 q_2/\varepsilon_1 + \kappa_1) - 2(q_1 - \kappa_1)(q_2 - \kappa_2)\right], \tag{12}$$

where

$$q_1 = \sqrt{\kappa_1^2 + k^2}, \quad q_2 = \sqrt{\kappa_2^2 + k^2}. \tag{13}$$

2.2. Height–height correlation function

Treating the functional $\Delta F[\xi(\boldsymbol{k}),V]$ as a Hamiltonian of the fluctuating variable $\xi(\boldsymbol{k})$ [20], we find the following expression for the Fourier transform of the height–height correlation function

$$g(k) = \int d^2\boldsymbol{R}\langle\xi(\boldsymbol{R})\xi(0)\rangle\exp(-i\boldsymbol{k}\boldsymbol{R}) = \frac{k_B T}{\gamma\left[k^2 + k_{gr}^2\right] - \Delta f_V(k)}. \tag{14}$$

[1] The perturbation theory is applicable to weakly rough interfaces for which the characteristic size of roughness in the z-direction is less than the tangential one and the Debye lengths, κ_1^{-1} and κ_2^{-1} (see Ref. [19]).

The function $\Delta f_V(k)$ bears the effect of charging on the interfacial corrugation. It has the following asymptotic behaviors in the regions of small and large wave vectors

$$\Delta f_V(k) \approx \frac{1}{2} k^2 V^2 C_{GC} \quad \text{for } k \ll \kappa_1, \kappa_2 , \tag{15}$$

$$\Delta f_V(k) \approx 4\pi V^2 C_{GC}^2 k \frac{(\varepsilon_1 - \varepsilon_2)^2}{(\varepsilon_1 + \varepsilon_2)\varepsilon_1 \varepsilon_2}$$

$$\text{for } k \gg \kappa_1, \kappa_2 . \tag{16}$$

The substitution of Eq. (15) into Eq. (14) shows that, for $k \ll \kappa_1, \kappa_2$, the electric field affects the corrugation merely via a decrease of the interfacial tension

$$\gamma_{\text{eff}} = \gamma - \frac{1}{2} V^2 G_{\text{GC}} \tag{17}$$

which is in line with a standard thermodynamic result given by the Lippmann equation [21].

However, for larger values of the wave vector, the effect of interfacial charging on the corrugation cannot be properly accounted by the effective reduction of γ.

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

$$\langle \xi^2 \rangle = \frac{1}{2\pi} \int_0^{k_{\max}} \mathrm{d}k\, k g(k) . \tag{18}$$

Here the upper wave-vector cutoff, $k_{\max}$, is introduced to eliminate the divergence of the integral, which takes place for $g(k)$ given by Eq. (14). Clearly, $\pi / k_{\max}$ cannot be less than the molecular lengths in the problem. Various estimated were proposed in the literature for $k_{\max}^{-1}$. It was assumed to be proportional to the root-mean-square height [22] or to the characteristic smearing of the interface [23], to the largest bulk correlation length of the contacting liquids [24], or the molecular diameter [25].

Both $\langle \xi^2 \rangle$ and $g(k)$ can be measured in optical, neutron and X-ray scattering experiments [5–7].

For small potential drops, $V \ll (\gamma / C_{\text{GC}})^{1/2}$, one can derive from Eqs. (12), (14) and (18) an asymptotic expression

$$\langle \xi^2 \rangle \approx \langle \xi^2 \rangle_0 + \frac{V^2 k_B T}{4\pi\gamma^2} C_{\text{GC}} \ln \frac{\kappa_1 \kappa_2}{(\kappa_1 + \kappa_2) k_{\text{gr}}} , \tag{19}$$

where $\langle \xi^2 \rangle_0$ is the mean-square height of interfacial corrugation at the potential of zero net charge of the interface (pzc). Eq. (19) shows that charging of the interface leads to an enhancement of surface corrugation. Note, that the increase of the mean-square height of corrugation compared to the corresponding value at the pzc does not depend on the upper cutoff.

3. Results and discussion

Expression (14) describes the effect of the interface charging on the static fluctuation spectrum. The height–height correlation function can be measured, but it is more subtle experimentally than to measure the integral characteristics of interfacial fluctuations, $\langle \xi^2 \rangle$, [5–7]. The interface of two immiscible electrolytes gives rich possibilities for the study of these quantities, as one can vary electrolyte concentrations in both phases and the overall potential drop.

In Fig. 1 we show the dependence of the mean-square height on the potential drop at a given (typical) electrolyte concentration for several values of the interfacial tensions. For low, but quite realistic, surface tensions the effect is large enough even for moderate potential drops. The asymptotic V^2 dependence (19) works fairly well in this region. Note that computer simulations for two contacting solvents

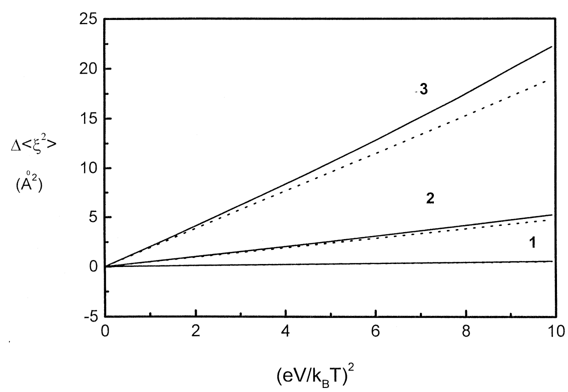

Fig. 1. The increase of the mean-square height of corrugation, $\Delta\langle \xi^2 \rangle = \langle \xi^2 \rangle - \langle \xi^2 \rangle_0$, versus the square of the potential drop. The effect of interfacial tension at room temperature γ, dyn/cm = (1) 30, (2) 10, (3) 5. Solid lines present the results of calculations according Eqs. (12), (14) and (18), dotted curve shows the asymptotic solution given by Eq. (19). $\varepsilon_1 = 80$, $\varepsilon_2 = 10$, $k_{\max} = 2$ Å^{-1}, $k_{\text{gr}} = 6\ 10^{-8}$ Å^{-1}, $n_1 = n_2 = 0.1$ M.

(with no solute ions) in external field show V^2 law in a much wider range of potentials [26].

Fig. 2 shows the dependence of $\langle \xi^2 \rangle$ on electrolyte concentration for a given, moderate potential drop. The effect is the larger the greater the electrolyte concentration. One should be careful, however, in extending this conclusion on very high concentration. The mean field Poisson–Boltzmann theory does not work at concentrations higher than the molar ones where the effects of ion packing and the formation of crystal-like structures are expected [27,28].

We remind that Eq. (14) was derived within the linearized variant of the Poisson–Boltzmann theory, which is justified, strictly speaking, when $eV/k_BT < 1$. It is known, however, that this expansion works not badly up to $eV/k_BT \approx 1$ [27,28]. We therefore show our results in the larger range of potentials than the rigorous limits of applicability of our theory. The corresponding extension of the theory on the case of high electrode potentials is possible along the lines of Ref. [29], but it leads to much more cumbersome expressions which will be considered elsewhere [30]. Our preliminary calculations [30] show that Eqs. (14) and (19) agree closely with the results of non-linear Poisson–Boltzmann theory up to $eV/k_BT \approx 3$–4.

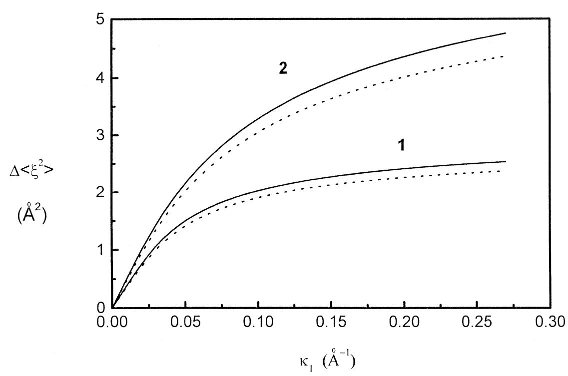

Fig. 2. The increase of the mean-square height of corrugation, $\Delta\langle \xi^2 \rangle = \langle \xi^2 \rangle - \langle \xi^2 \rangle_0$, versus the inverse Debye length in the aqueous phase, κ_1, at a fixed potential drop $eV = 2k_BT$. The effect of the inverse Debye length in the non-aqueous phase κ_2, Å^{-1} = (1) 0.1, (2) 0.2. Solid lines present the results of calculations according to Eqs. (12), (14) and (18), dotted line shows the asymptotic solution (19). $\varepsilon_1 = 80$, $\varepsilon_2 = 10$, $k_{max} = 2$ Å^{-1}, $k_{gr} = 6$ 10^{-8} Å^{-1}, $\gamma = 30$ dyn/cm.

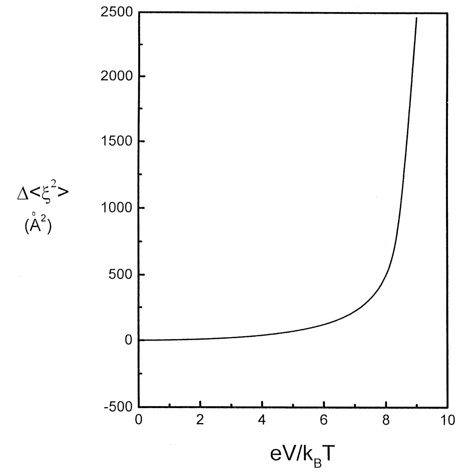

Fig. 3. The effect of strong electric field on the mean-square height of corrugation. $\varepsilon_1 = 80$, $\varepsilon_2 = 10$, $k_{max} = 2$ Å^{-1}, $k_{gr} = 6$ 10^{-8} Å^{-1} $n_1 = n_2 = 0.1$ M, $\gamma = 5$ dyn/cm. The picture shows the tendency of the interface destruction in the strong field.

In Fig. 3 we go definitely beyond the scopes of the linearized Poisson–Boltzmann theory in order to show a qualitative effect: a destruction of the interface by the strong electric field. Quantitatively, the non-linear response of the double layers may change the value of the critical potential where the instability of the interface takes place. There could be different trends here. Large potentials shorten the effective screening length [31] and that would lead to the decrease of the critical potential [30]. If the potentials are so large that they give rise to interfacial ion–molecular structure formation, which would increase surface tension, the tendency may be opposite. These complications require a special investigation [30].

The electric field induced corrugation should manifest itself in the measured capacitance of the interface between two immiscible electrolytes. We have recently shown that the double layer capacitance at the solid/liquid interface increases with the amplitude of surface corrugation, and it is always larger than the one prescribed by the flat interface Gouy–Chapman theory [19,29,32]. We introduced earlier a concept of *a roughness function* [19,29,32], which determined the deviation of capacitance from the Gouy–Chapman result. The findings of the present letter show that charging the liquid/liquid interface gives rise to an enhancement of the amplitude of capillary waves and thereby to larger 'dynamic corrugation'. This immediately leads to increased values of capacitance, as it is shown in the extension of our solid/liquid capacitance theory [33].

The enhancement of the roughness function induced by the potential drop across the interface was observed experimentally for various liquid/liquid interfaces [34,35]. The quantitative description of this phenomenon calls, however, for a self-consistent non-linear theory, as the effect is remarkable only in the range of potentials where the linearization of the Poisson–Boltzmann equation breaks down. The work towards such a non-linear theory is in progress [30].

It would be, nevertheless, timely to verify the quantitative predictions of the present results in neutron and X-ray scattering experiments [5–7], which both allow direct measurements of the mean-square height of the interfacial corrugation. In such experiments one may try to observe not only the increase of $\langle \xi^2 \rangle$ with potential but also the predicted dependencies of $\langle \xi^2 \rangle$ on ionic concentrations. Although our resulting formulae are not expected to work in the region of large fields and high electrolyte concentrations, where the non-linear theory is to be developed, but a certain extrapolation into the range of intermediate fields is worthwhile of trying. Such experiments will check the basic concept as well as reveal the actual limits of the linear theory.

We hope that the results reported above will stimulate scattering experiments at the interface of two immiscible electrolytes and corresponding computer simulations.

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