

Validity of the Derjaguin Approximation on Electrostatic Effect in the Frumkin–Derjaguin Approach

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The Frumkin–Derjaguin theory relates the macroscopic contact angle of a droplet with the disjoining pressure of the thin film in equilibrium with the droplet. To obtain the analytic expressions of the disjoining pressure, the Derjaguin approximation has been used, combined with the Debye–Hückel theory on the electrical double layer. As a result, the disjoining pressure can be determined without consideration of the overall geometry of the liquid surface. The validity of the Derjaguin approximation has been regarded to be limited to small contact angles, and its validity for large contact angles has rarely been assessed analytically. In this paper, the electrostatic force acting on the meniscus of a droplet (which enforces the droplet to spread) is obtained by integrating the Maxwell stress and the osmotic pressure acting on the liquid surface. The Debye–Hückel theory is employed for direct comparison with the results of the Derjaguin approximation in the two cases of the constant surface potential and the constant surface charge boundary conditions. The present electromechanical approach provides an exact result for the electrostatic contribution to the contact angle for a given model of the electrical double layer. It is shown (for the constant potential case) that if the modification of the interfacial energy at the liquid–surrounding fluid interface by the electrocapillary effect is separately considered, the Derjaguin approximation gives an exact interaction free energy, regardless of the magnitude of the contact angle. For the constant charge case, on the contrary, the interaction free energy derived based on the Derjaguin approximation for prediction of the contact angle is shown to have evident deficiency except for the case of vanishing surface charge density at the liquid surface. Such deficiency originates from the neglect of the contribution of the tangential-stress component.

Introduction

Young's equation relates the (macroscopic) contact angle (θ_∞) at a three-phase contact line with the (solid) substrate–liquid (γ_{sl}), the substrate–surrounding fluid (γ_{sv}), and the surrounding fluid–liquid interfacial energy (γ); that is,¹

$$\cos \theta_\infty = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma} \quad (1)$$

The three phases are mutually in equilibrium, and thus, there usually exists an adsorbed or wetting film on the solid substrate, which usually lowers γ_{sv} .^{1,2} The degree of adsorption of vapor and the subsequent modification of γ_{sv} is dependent mainly on the surface energy of the substrate.^{2,3}

When there exists a thick wetting film on the solid surface, the Frumkin–Derjaguin theory relates the value of γ_{sv} with the known disjoining pressure (π_t) and the so-called interaction free energy ($V_t = \int_{h_0}^{\infty} \pi_t dh$) of the thin wetting film as $\gamma_{sv} = \gamma + \gamma_{sl} + V_t(h_0)$. Then, the contact angle can be predicted by using the following equation (see Figure 1):^{1,3–8}

$$\cos \theta_\infty = 1 + \frac{1}{\gamma} \int_{h_0}^{\infty} \pi_t(h) dh = 1 + \frac{V_t(h_0)}{\gamma} \quad (2)$$

where h_0 represents the thickness of the flat film in

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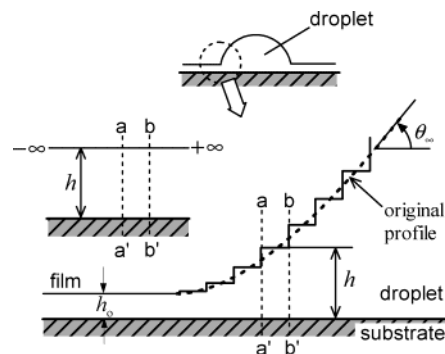


Figure 1. A droplet in stable equilibrium with a thin film and the main concept of the Derjaguin approximation.

equilibrium with the meniscus of the droplet. Various physical factors can be taken into account in V_t (or in π_t), such as the molecular V_m (π_m), the electrostatic V_{el} (π_{el}), and the structural V_s (π_s) components.^{3–8}

To obtain the analytic expression for the electrostatic interaction free energy (V_{el}), the electrostatic field around the liquid layer (droplet and film) should be analyzed (usually) by using the Poisson–Boltzmann equation. Actually, however, it is almost impossible to obtain a closed

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form solution of the electrostatic field for this kind of geometry. As an approximation method, therefore, the celebrated Derjaguin approximation has been invoked. The Derjaguin approximation assumes that the slope of the liquid profile is very small and considers the liquid profile as a sum of infinitesimal segments of infinite surfaces parallel to the substrate, as shown schematically in Figure 1 (see, for details, ref 9). The gradient of the electrostatic potential in the horizontal direction is neglected in the analysis of the Poisson–Boltzmann equation. Then, the electrostatic field can be localized; that is, the electrostatic field at a certain cross section of the meniscus region can be determined only with the local surface potential or the surface charge values, without need to consider the global shape of the liquid surface.

Furthermore, by introducing the Debye–Hückel theory for the electrical double layer, we avoid the complications associated with solving the nonlinear Poisson–Boltzmann equation for the parallel plate geometry. Then, the electrostatic component of the interaction free energy is obtained for both the constant potential (V_{el}^{φ}) and the constant charge (V_{el}^{σ}) cases as follows:^{2–4,10}

$$V_{el}^{\varphi}(h_0) = \frac{\epsilon\kappa}{2} [2\varphi_1\varphi_2 \operatorname{csch} \kappa h_0 - (\varphi_1^2 + \varphi_2^2)(\coth \kappa h_0 - 1)] \quad (3a)$$

$$V_{el}^{\sigma}(h_0) = \frac{\epsilon\kappa}{2} [2\varphi_{1\infty}\varphi_{2\infty} \operatorname{csch} \kappa h_0 + (\varphi_{1\infty}^2 + \varphi_{2\infty}^2)(\coth \kappa h_0 - 1)] \quad (3b)$$

where κ is the inverse Debye length, and φ_1 ($\varphi_{1\infty}$) and φ_2 ($\varphi_{2\infty}$) denote the surface potential at the substrate and the liquid surfaces. Here, $\varphi_{1\infty}$ and $\varphi_{2\infty}$ denote the surface potentials without double-layer interaction.

The Derjaguin approximation has been regarded, in wetting problems, as being reliable only for small contact angle systems (see, e.g., ref 9). At least for the electrostatic contribution, there seems to rarely exist any theory which systematically assesses the validity of the approach at large contact angles, although there have been some efforts to improve the validity of the approach, for instance, by considering the surface-curvature effect.¹¹ In this paper, we derive an analytic expression for the electrostatic wetting tension (which will be shown to be equivalent to V_{el} in meaning) by using the electromechanical approach. The electromechanical approach was recently introduced to the electrowetting problem by Jones.¹² Later, the approach was extended to consider the effect of the electrical double layer, and then the usefulness of the approach in charge-related wetting problems was manifested by Kang et al.¹³

For the two limiting cases of the constant potential (CP) and the constant charge (CC) boundary conditions, the contact angle equations are derived in eqs 19 and 28 based on the Frumkin–Derjaguin approach. Any geometrical simplification, such as done by the Derjaguin approximation, is not necessary. Thus, the results are exact within the framework of the given model for the electrical double

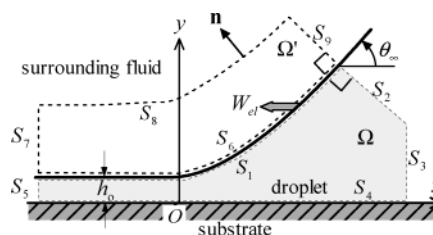


Figure 2. Coordinate system and definition of variables.

layer. For the CP case, the electrostatic interaction free energy (V_{el}^{φ}) derived under the Derjaguin approximation is valid irrespective of the value of the contact angle, if the electrocapillary effect on the liquid surface is considered separately. On the contrary, for the CC case, there exists an evident deficiency in using the interaction free energy of the Derjaguin approximation (V_{el}^{σ}) to predict the contact angle. The deficiency arises mainly due to neglect of the tangential-stress component in the conventional thermodynamic method combined with the Derjaguin approximation.

Electromechanical Determination of Wetting Tension

We consider a droplet in stable equilibrium with a film (of the same fluid) on a solid substrate, submerged in another liquid or air. The equilibrium film thickness is denoted as h_0 , and the droplet has a tangent angle of θ_{∞} at a (microscopically) infinite distance from the origin, which in fact represents the macroscopic contact angle of the droplet (see Figure 2). A Cartesian (x, y) coordinate system is introduced in which the origin is placed close to the intersection point of the thin film and the droplet. The x - and y -axes are parallel and normal to the substrate surface, respectively.

Here we call the combination of the droplet and the film regions the *liquid region* or the liquid layer. The surrounding fluid will be called the *fluid* for brevity. The liquid and the fluid regions are denoted by Ω and Ω' . The primed variables in this paper are associated with the fluid region. We introduce two control surfaces $\Sigma = S_1 \cup S_2 \cup S_3 \cup S_4 \cup S_5$ and $\Sigma' = S_6 \cup S_7 \cup S_8 \cup S_9$ which enclose the liquid and the fluid regions, respectively (see Figure 2). The surfaces $S_2, S_3, S_5, S_7, S_8,$ and S_9 are located far from the origin. All the surfaces through S_1 and S_6 have unit depth normal to the page. Note that the two surfaces S_1 and S_6 indicate the liquid–fluid interfaces in Σ and Σ' , respectively. The surfaces $S_3, S_5,$ and S_7 indicate the surfaces vertical to the substrate surface located at a sufficiently large distance from the origin. The two surfaces S_2 and S_9 are set to be normal to the droplet surface.

The electrostatic force \mathbf{F} acting on the liquid–fluid interface per unit depth, which forces the meniscus to move, is obtained by integrating the electrically induced stress acting on the surface enclosing the liquid–fluid interface:¹³

$$\mathbf{F} = - \int_{S_1} \mathbf{T} \cdot \mathbf{n} \, dS - \int_{S_6} \mathbf{T} \cdot \mathbf{n} \, dS \quad (4)$$

Here, $\mathbf{T} = -(\Pi + \epsilon E^2/2)\mathbf{I} + \epsilon \mathbf{E}\mathbf{E}$ is the sum of the Maxwell stress tensor and the osmotic pressure (Π) tensor, \mathbf{n} is the outward unit normal vector at the surfaces, $\mathbf{E} = -\nabla\varphi$ is the electric field, $E = |\mathbf{E}|$, φ is the electrostatic potential, ϵ is the electric permittivity, and \mathbf{I} is the second-order isotropic tensor.

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The electrostatic contribution to the wetting tension (W_{el}) is the horizontal component of \mathbf{F} , here in the negative x -direction, that is,¹³

$$W_{el} = -\mathbf{F} \cdot \mathbf{e}_x \quad (5)$$

where \mathbf{e}_x represents the unit vector in the positive x -direction. Since $V_{el} = \int_{h_0}^{\infty} \tau_{el} dh$ is equivalent to the net electrostatic force acting on the liquid surface in the horizontal direction, W_{el} can be regarded as the electromechanical version of V_{el} in eq 2. (We will discuss this matter later in the discussion section.) Note that the units of W_{el} , V_{el} , and γ are identically newtons per meter.

We assume that the electrical double layer in the liquid and in the fluid regions satisfies the Poisson–Boltzmann equation of $\nabla^2 \varphi = (\kappa^2/\beta) \sinh \beta \varphi$. Here, $\kappa^{-1} = (2n_b z^2 e^2 / \epsilon k T)^{-1/2}$ represents the Debye length, n_b is the number density of ionic species far from the interfaces, k is the Boltzmann constant, T is the absolute temperature, $\beta = ze/kT$ for $z:z$ electrolytes, z is the valency of ionic species, and e is the electronic charge. The osmotic pressure is given by $\Pi = 2n_b k T [\cosh \beta \varphi - 1]$.¹⁴

The evaluation of the force acting on the liquid surface in eq 4 can be simplified by using the following mechanical equilibrium condition of the system in consideration.¹³

$$\int_{\Sigma} \mathbf{T} \cdot \mathbf{n} dS = \int_{\Sigma} \mathbf{T} \cdot \mathbf{n} dS = 0 \quad (6)$$

Then, the integration domains in eq 4 can be converted to more convenient surfaces to integrate by using eq 6, so that

$$\mathbf{F} = \int_{\Sigma + \Sigma' - S_1 - S_6} \mathbf{T} \cdot \mathbf{n} dS \quad (7)$$

Constant Potential Case

First, we consider the case in which the surface potentials at the liquid–substrate and the liquid–fluid interfaces are fixed at φ_1 and φ_2 , respectively. We derive each contribution from the m th surface (\mathbf{F}_m) to \mathbf{F} and eventually obtain the wetting tension by $W_{el} = -\mathbf{e}_x \cdot \sum_m \mathbf{F}_m$.

At S_2 , S_3 , S_5 , S_7 , and S_9 , there is no electrostatic field normal to the control surface, that is, $\mathbf{E} \cdot \mathbf{n} = 0$. Since $\mathbf{n} = \mathbf{e}_x$ at S_3 , the contribution from S_3 to \mathbf{F} becomes

$$\begin{aligned} \mathbf{F}_3 &= \int_{S_3} \left[-\left(\Pi + \frac{1}{2} \epsilon E^2 \right) \mathbf{n} + \epsilon (\mathbf{E} \cdot \mathbf{n}) \mathbf{E} \right] dS \\ &= -\mathbf{e}_x \int_{S_3} \left[\Pi + \frac{1}{2} \epsilon E^2 \right] dS \end{aligned} \quad (8)$$

On the other hand, the free energy (per unit surface area) of the plane electrical double layer, in which the surface potential (φ_s) is constant, becomes¹⁵

$$G(\varphi_s, \kappa) = - \int_S \left[\Pi + \frac{1}{2} \epsilon E^2 \right] dS = \frac{8n_b k T}{\kappa} \left[1 - \cosh \frac{\beta \varphi_s}{2} \right] \quad (9)$$

Therefore, $\mathbf{F}_3 = G_3(\varphi_1, \kappa) \mathbf{e}_x$ in which $G_3 = - \int_{S_3} (\Pi + \epsilon E^2/2) dS$. Hereafter, all the functions G_m have the same form as G in eq 9. The index m of G_m is given to specify the associated surface.

At the leftmost surface in the surrounding fluid region (S_7), $\mathbf{n} = -\mathbf{e}_x$. Therefore, $\mathbf{F}_7 = \int_{S_7} \mathbf{T} \cdot \mathbf{n} dS = -G_7(\varphi_2, \kappa) \mathbf{e}_x$.

At S_2 and S_9 , $\mathbf{n} = \mathbf{e}_x \cos \theta_{\infty} + \mathbf{e}_y \sin \theta_{\infty}$. In a similar way to obtaining the foregoing \mathbf{F}_3 and \mathbf{F}_7 , we get

$$\mathbf{F}_2 = G_2(\varphi_1, \kappa) (\mathbf{e}_x \cos \theta_{\infty} + \mathbf{e}_y \sin \theta_{\infty}) \quad (10a)$$

$$\mathbf{F}_9 = G_9(\varphi_2, \kappa') (\mathbf{e}_x \cos \theta_{\infty} + \mathbf{e}_y \sin \theta_{\infty}) \quad (10b)$$

At the film region far from the origin (S_5), $\mathbf{n} = -\mathbf{e}_x$. Hence

$$\mathbf{F}_5 = - \int_{S_5} \mathbf{n} \left[\Pi + \frac{1}{2} \epsilon E^2 \right] dS = -\Gamma_5^{\varphi} \mathbf{e}_x \quad (11)$$

where $\Gamma_5^{\varphi} = - \int_{S_5} [\Pi + \epsilon E^2/2] dS$. There is no contribution from S_8 , that is, $\mathbf{F}_8 = \mathbf{0}$. Then, the net force acting on the liquid–fluid interface becomes

$$\mathbf{F} = (G_3 - \Gamma_5^{\varphi} - G_7) \mathbf{e}_x + (G_2 + G_9) (\mathbf{e}_x \cos \theta_{\infty} + \mathbf{e}_y \sin \theta_{\infty}) + \mathbf{F}_4 \quad (12)$$

At the horizontal substrate surface (S_4), $\mathbf{n} \cdot \mathbf{e}_x = 0$, and the electrostatic potential is constant so that $\mathbf{E} \cdot \mathbf{e}_x = 0$. Therefore, the contribution from S_4 to W_{el} is null, that is, $\mathbf{e}_x \cdot \mathbf{F}_4 = \mathbf{0}$. Then, the net horizontal component of the force acting on the liquid–fluid interface toward the *negative* x -direction, which is the wetting tension $W_{el}^f = -\mathbf{F} \cdot \mathbf{e}_x$, becomes

$$W_{el}^f = \Gamma_5^{\varphi} + G_7 - G_3 - (G_2 + G_9) \cos \theta_{\infty} \quad (13)$$

In the electrostatic disjoining pressure, the contributions from the fluid region usually have not been considered. Note that this assumption is valid when the free energy contribution from the fluid region is negligible. This condition is satisfied when the fluid phase is filled with a perfect dielectric fluid, so that there is no electric flux into the fluid region. It will be a good approximation in the case of air as the surrounding fluid. Hereinafter, we omit these two terms of G_7 and G_9 for the direct comparison with the existing results of the Derjaguin approximation.

To obtain Γ_5^{φ} , the electrostatic field in the film region should be analyzed. In general, it is complicated to obtain a closed form solution of the nonlinear Poisson–Boltzmann equation. For a qualitative observation, therefore, it is customary to use the linear solution of the Poisson–Boltzmann equation (Debye–Hückel theory). The resulting electrostatic potential between the two surfaces having different surface potentials of φ_1 and φ_2 is given by^{10,14}

$$\varphi^{\varphi}(y) = \varphi_1 \cosh \kappa y + \left(\frac{\varphi_2 - \varphi_1 \cosh \kappa h_0}{\sinh \kappa h_0} \right) \sinh \kappa y \quad (14)$$

Then, the charge density at the substrate and the liquid surfaces becomes

$$\sigma_1 = -\epsilon \frac{d\varphi^{\varphi}}{dy} \Big|_{y=0} = \frac{\epsilon \kappa (\varphi_1 \cosh \kappa h_0 - \varphi_2)}{\sinh \kappa h_0} \quad (15a)$$

$$\sigma_2 = \epsilon \frac{d\varphi^{\varphi}}{dy} \Big|_{y=h_0} = \frac{\epsilon \kappa (\varphi_2 \cosh \kappa h_0 - \varphi_1)}{\sinh \kappa h_0} \quad (15b)$$

The osmotic pressure term in eq 11 is linearized as $\Pi \approx (1/2) \epsilon \kappa^2 \varphi^2$. Then, by using the linearized Poisson–

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Boltzmann equation of $\nabla^2\varphi = \kappa^2\varphi$, we obtain

$$\Gamma_5^\varphi \cong -\frac{\epsilon_1}{2} \int_0^{h_0} \left[\kappa_1^2 \varphi^2 + \left(\frac{\partial\varphi}{\partial y} \right)^2 \right] dy = \frac{\epsilon_1}{2} \left[\varphi \frac{\partial\varphi}{\partial y} \Big|_{y=0} - \varphi \frac{\partial\varphi}{\partial y} \Big|_{y=h_0} \right] = -\frac{1}{2} (\sigma_1 \varphi_1 + \sigma_2 \varphi_2) \quad (16)$$

Substituting σ_1 and σ_2 in eq 15 into the above equation, it follows that

$$\Gamma_5^\varphi = \frac{\epsilon\kappa}{2} [2\varphi_1\varphi_2 \operatorname{csch} \kappa h_0 - (\varphi_1^2 + \varphi_2^2) \coth \kappa h_0]$$

If we linearize G in eq 9, it becomes $G \cong -\epsilon\kappa\varphi_s^2/2 = -\sigma\varphi_s/2$. Thus G_2 and G_3 in eq 13 can be written in the linearized form as $G_2 = -\sigma_{2\infty}\varphi_2/2 = -\epsilon\kappa\varphi_2^2/2$ and $G_3 = -\sigma_{1\infty}\varphi_1/2 = -\epsilon\kappa\varphi_1^2/2$, respectively. Here, $\sigma_{1\infty} = \epsilon\kappa\varphi_1$ and $\sigma_{2\infty} = \epsilon\kappa\varphi_2$ represent the surface charge density without double-layer interaction. The wetting tension therefore becomes

$$W_{\text{el}}^\varphi = \frac{1}{2} (\sigma_{1\infty}\varphi_1 + \sigma_{2\infty}\varphi_2 - \sigma_1\varphi_1 - \sigma_2\varphi_2) + \frac{\sigma_{2\infty}\varphi_2}{2} (\cos \theta_\infty - 1) \quad (17)$$

Then, substituting σ_1 and σ_2 in eq 15 into the above equation, we obtain

$$W_{\text{el}}^\varphi = \frac{\epsilon\kappa}{2} [2\varphi_1\varphi_2 \operatorname{csch} \kappa h_0 - (\varphi_1^2 + \varphi_2^2) (\coth \kappa h_0 - 1)] + \frac{\epsilon\kappa}{2} \varphi_2^2 (\cos \theta_\infty - 1) \quad (18)$$

Note that the interaction free energy becomes $V_{\text{el}}^\varphi = (1/2)(\sigma_{1\infty}\varphi_1 + \sigma_{2\infty}\varphi_2 - \sigma_1\varphi_1 - \sigma_2\varphi_2)$ under the Derjaguin approximation.^{2,10} Thus, the first term in eqs 17 and 18 is equal to the interaction free energy shown in eq 3a which is obtained under the Derjaguin approximation. The last term in eqs 17 and 18 is an additional term to the interaction free energy derived based on the Derjaguin approximation.

Now, we substitute W_{el}^φ into eq 2 instead of V_{el} , and then we obtain

$$\tilde{\gamma} \cos \theta_\infty = \tilde{\gamma} + \frac{\epsilon\kappa}{2} [2\varphi_1\varphi_2 \operatorname{csch} \kappa h_0 - (\varphi_1^2 + \varphi_2^2) (\coth \kappa h_0 - 1)] + \int_{h_0}^\infty \hat{\pi} dh \quad (19)$$

where $\gamma' = \gamma - \epsilon\kappa\varphi_s^2/2$, and $\hat{\pi} = \pi_t - \pi_{\text{el}}$ denotes the disjoining pressure without the electrostatic contribution. The difference between eq 2 and eq 19 is that only γ is changed to $\tilde{\gamma}$. The term $-\epsilon\kappa\varphi_s^2/2$ in $\tilde{\gamma}$ comes from \mathbf{F}_2 in eq 10a. For a one-dimensional plane electrical double layer, the change of the interfacial tension due to the electrocapillarity ($\Delta\gamma$) is written as¹⁶

$$\Delta\gamma = -\epsilon \int_0^\infty E^2 dy = \epsilon \int_0^{\varphi_s} E d\varphi \quad (20)$$

which becomes $-\epsilon\kappa\varphi_s^2/2$ under the Debye–Hückel theory. Therefore, it will be reasonable to interpret the term

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$-\epsilon\kappa\varphi_s^2/2$ as the change of the interfacial tension due to the electrocapillary effect.

Equation 18 is derived without any assumption concerning the geometry of the liquid surface, but the Debye–Hückel theory is invoked to obtain an analytic expression for φ . Only if we make an additional consideration for the change of the interfacial energy of the liquid surface due to the electrocapillary effect, the conventional interaction free energy derived under the Derjaguin approximation is exact, irrespective of the values of contact angle. It can be shown that if the nonlinear Poisson–Boltzmann equation is used to derive the electrostatic disjoining pressure, the Derjaguin approximation will again produce an exact result within the nonlinear Poisson–Boltzmann model.

Constant Charge Case

Next, we consider the CC case in which the surface charge densities at the liquid–substrate and the liquid–fluid interface are fixed at σ_1 and σ_2 , respectively. As before, we do not consider the contribution from the fluid region (i.e., those from S_6 , S_7 , S_8 , and S_9), without loss of generality of the present approach. As in the previous CP case, $\mathbf{E} \cdot \mathbf{n} = 0$ at S_2 , S_3 , and S_5 . Thus, the contributions from S_2 and S_3 are written as

$$\mathbf{F}_2 = G_2(\varphi_{2\infty}, \kappa) (\mathbf{e}_x \cos \theta_\infty + \mathbf{e}_y \sin \theta_\infty)$$

$$\mathbf{F}_3 = G_3(\varphi_{1\infty}, \kappa) \mathbf{e}_x$$

in which the functions G_2 and G_3 are identical to those of the CP case. Here, $\varphi_{1\infty} = \sigma_1/(\epsilon\kappa)$ and $\varphi_{2\infty} = \sigma_2/(\epsilon\kappa)$ denote the surface potentials at the substrate and the droplet surfaces which are at a remote distance from each other.

The contribution from the film region (\mathbf{F}_5) also has the same form as the previous case, shown in eq 11; that is,

$$\mathbf{F}_5 = -\Gamma_5^\sigma(\varphi_{10}, \varphi_{20}, \kappa) \mathbf{e}_x$$

Here, φ_{10} and φ_{20} denote the surface potentials at the substrate and the film surface (far from the origin to the left), and they are determined by using the following electrostatic field corresponding to the present CC case.¹⁰

$$\varphi^\sigma(y) = \left(\frac{\varphi_{2\infty} + \varphi_{1\infty} \cosh \kappa h_0}{\sinh \kappa h_0} \right) \cosh \kappa y - \varphi_{1\infty} \sinh \kappa y \quad (21)$$

From this equation, φ_{10} and φ_{20} are related with $\varphi_{1\infty}$ and $\varphi_{2\infty}$ as shown below.

$$\varphi_{10} = \varphi^\sigma(0) = \varphi_{1\infty} \coth \kappa h_0 + \varphi_{2\infty} \operatorname{csch} \kappa h_0 \quad (22a)$$

$$\varphi_{20} = \varphi^\sigma(h_0) = \varphi_{2\infty} \coth \kappa h_0 + \varphi_{1\infty} \operatorname{csch} \kappa h_0 \quad (22b)$$

The function Γ_5^σ can be written, under the linear approximation, by way of φ_{10} and φ_{20} as

$$\begin{aligned} \Gamma_5^\sigma &= -\frac{1}{2} (\sigma_1 \varphi_{10} + \sigma_2 \varphi_{20}) \\ &= -\frac{\epsilon\kappa}{2} [2\varphi_{1\infty}\varphi_{2\infty} \operatorname{csch} \kappa h_0 + (\varphi_{1\infty}^2 + \varphi_{2\infty}^2) \coth \kappa h_0] \end{aligned} \quad (23)$$

Then, neglecting the contribution from S_7 , S_8 , and S_9 in eq 12, the net force is written as

$$\mathbf{F} = (G_3 - \Gamma_5^\sigma) \mathbf{e}_x + G_2 (\mathbf{e}_x \cos \theta_\infty + \mathbf{e}_y \sin \theta_\infty) + \mathbf{F}_4 \quad (24)$$

in which $G_2 = -\sigma_2\varphi_{2\infty}/2$ and $G_3 = -\sigma_1\varphi_{1\infty}/2$ in the linearized form. Unlike the CP case, the contribution from \mathbf{F}_4 to W_{el}^p does not vanish. At the liquid–substrate interface (S_4), $\mathbf{n}\cdot\mathbf{e}_x = 0$ and $\epsilon(\mathbf{n}\cdot\mathbf{E}) = -\sigma_1$. Thus, \mathbf{F}_4 in eq 24 becomes

$$\mathbf{F}_4 = \int_{S_4} \epsilon(\mathbf{n}\cdot\mathbf{E})\mathbf{E} dS = -\int_{-\infty}^{+\infty} \sigma_1\mathbf{E} dx$$

Since $\sigma_1\mathbf{E}\cdot\mathbf{e}_x = -\sigma_1(\partial\varphi/\partial x)$, the contribution from S_4 to W_{el}^p (denoted by $(W_{el}^p)_4$) becomes

$$(W_{el}^p)_4 = -\mathbf{e}_x\cdot\mathbf{F}_4 = \mathbf{e}_x\cdot\int_{-\infty}^{+\infty} \sigma_1\mathbf{E} dx = -\sigma_1\int_{-\infty}^{+\infty} \frac{\partial\varphi}{\partial x} dx = \sigma_1(\varphi_{10} - \varphi_{1\infty})$$

The wetting tension in this case, therefore, is reduced to

$$W_{el}^p = \Gamma_5^\sigma - G_3 - G_2 \cos \theta_\infty + \sigma_1(\varphi_{10} - \varphi_{1\infty}) = \frac{1}{2}(\sigma_1\varphi_{10} - \sigma_2\varphi_{20} + \sigma_2\varphi_{2\infty} - \sigma_1\varphi_{1\infty}) + \frac{\sigma_2\varphi_{2\infty}}{2}(\cos \theta_\infty - 1) \quad (25)$$

It can be written alternatively as

$$W_{el}^p = \frac{1}{2}(\sigma_1\varphi_{10} + \sigma_2\varphi_{20} - \sigma_1\varphi_{1\infty} - \sigma_2\varphi_{2\infty}) + \sigma_2(\varphi_{2\infty} - \varphi_{20}) + \frac{\sigma_2\varphi_{2\infty}}{2}(\cos \theta_\infty - 1) \quad (26)$$

It can be easily shown that the first term of the above equation corresponds to V_{el}^σ in eq 3b, while the second and the third terms are the new terms appearing in the present analysis. The Derjaguin approximation, therefore, gives exact interaction free energy when the surface charge density at the liquid surface vanishes (i.e., $\sigma_2 = 0$). The case of air as the surrounding fluid, without the surfactant layer at the liquid–fluid interface, will satisfy this condition.

After linearization of the other terms, the wetting tension becomes

$$W_{el}^p = \frac{\epsilon\kappa}{2}(\varphi_{1\infty}^2 - \varphi_{2\infty}^2)(\coth \kappa h_0 - 1) + \frac{\epsilon\kappa}{2}\varphi_{1\infty}^2(\cos \theta_\infty - 1) \quad (27)$$

As in the CP case, W_{el}^p is introduced to eq 2 instead of V_{el}^σ of eq 3b, and then we obtain

$$\tilde{\gamma} \cos \theta_\infty = \tilde{\gamma} + \frac{\epsilon\kappa}{2}(\varphi_{1\infty}^2 - \varphi_{2\infty}^2)(\coth \kappa h_0 - 1) + \int_{h_0}^{\infty} \hat{\pi} dh \quad (28)$$

where $\tilde{\gamma}$ is again the liquid–fluid interfacial energy modified due to the electrocapillary effect. The term $\epsilon\kappa\varphi_{1\infty}\varphi_{2\infty} \operatorname{csch} \kappa h_0$ in eq 3b does not appear in eq 28, and the sign of $(\epsilon\kappa/2)\varphi_{2\infty}^2(\coth \kappa h_0 - 1)$ is also changed. Thus, unlike the CP case, there is a significant difference, being concerned with V_{el}^σ , between the result of the present electromechanical approach and that of the conventional thermodynamic method which is combined with the Derjaguin approximation. We will discuss why such a difference takes place in the next section.

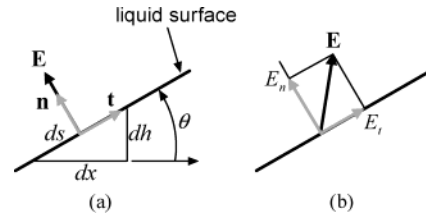


Figure 3. Electric field at the liquid surface: (a) constant potential case; (b) constant charge case.

Discussion

We will discuss here why such a significant deviation arises in the CC case in contrast to the CP case. First, we derive W_{el} and π_{el} by using the electromechanical method with the Derjaguin approximation and then compare the results with those derived by the conventional thermodynamic method (see, e.g., ref 10).

The wetting tension in eq 5 is rewritten, for the CP and the CC cases, as

$$W_{el} = \mathbf{e}_x\cdot\int_{S_1} \left[-\left(\Pi + \frac{1}{2}\epsilon E^2\right)\mathbf{n} + \epsilon(\mathbf{E}\cdot\mathbf{n})\mathbf{E} \right] ds \quad (29)$$

For the CP case, there exists no tangential electric field at the liquid surface (as in the case of a perfect conductor),¹⁷ and therefore $\mathbf{E} = E\mathbf{n}$ and $\mathbf{E}\cdot\mathbf{n} = E$ (see Figure 3a). Thus, the above equation is reduced to

$$W_{el} = -\int_{S_1} \left[\Pi(s) - \frac{1}{2}\epsilon E^2(s) \right] \mathbf{e}_x\cdot\mathbf{n} ds$$

The unit normal vector is related to the local tangent angle as $\mathbf{n} = -\mathbf{e}_x \sin \theta + \mathbf{e}_y \cos \theta$ at the liquid surface, and therefore $\mathbf{e}_x\cdot\mathbf{n} = -\sin \theta$. It becomes $\sin \theta ds = dh$ from the geometrical relationship (see Figure 3a). Accordingly, the above equation is changed to (with respect to the unit depth of the liquid layer)

$$W_{el} = \int_{h_0}^{\infty} \left[\Pi(h) - \frac{1}{2}\epsilon E^2(h) \right] dh \quad (30)$$

If we linearize the osmotic pressure term, it becomes

$$W_{el} = \int_{h_0}^{\infty} \frac{\epsilon}{2} [\kappa^2\varphi^2(h) - E^2(h)] dh \quad (31)$$

For the CP case, we can let $\varphi(h) = \varphi_2$ (=constant) and $E(h) = -\sigma_2/\epsilon$. Then, we use the Derjaguin approximation to determine σ_2 which is already given in eq 15b. By using eq 15b, the above equation becomes

$$W_{el}^p = \int_{h_0}^{\infty} \frac{\epsilon\kappa^2}{2} \left[\varphi_2^2 - \frac{(\varphi_2 \cosh \kappa h - \varphi_1)^2}{\sinh^2 \kappa h} \right] dh \quad (32)$$

in which the integrand becomes identical to the following disjoining pressure which has been derived by using the thermodynamic method:^{8,10}

$$\pi_{el}^p = \frac{\epsilon\kappa^2}{2} \frac{2\varphi_1\varphi_2 \cosh \kappa h - (\varphi_1^2 + \varphi_2^2)}{\sinh^2 \kappa h} \quad (33)$$

Since V_{el}^p is defined as $V_{el}^p = \int_{h_0}^{\infty} \pi_{el}^p dh$, it is obvious that W_{el}^p in eq 32 becomes identical to V_{el}^p of eq 3a (under the Derjaguin approximation). The error in deriving W_{el}^p by using the Derjaguin approximation solely originated from

(17) Landau, L. D.; Lifshitz, E. M. *Electrodynamics of Continuous Media*; Pergamon Press: Sydney, 1960; Chapter 1.

the use of the Derjaguin approximation to determine the electrostatic field. The expression for W_{el}^{σ} of eq 31 itself is correct, but that is not the case for the CC case.

Although it is improper to use eq 31 for the CC case (which will be shown later), we proceed further with eq 31 to obtain W_{el}^{σ} and π_{el}^{σ} . For the CC case, $E(h) = -\sigma_2/\epsilon = -\kappa\varphi_{2\infty}$ is constant, and $\varphi(h) = \varphi_{20}$ which is given in eq 22b. Therefore,

$$W_{\text{el}}^{\sigma} = \int_{h_0}^{\infty} \frac{\epsilon\kappa^2}{2} \left[\frac{(\varphi_{2\infty} \cosh \kappa h + \varphi_{1\infty})^2}{\sinh^2 \kappa h} - \varphi_{2\infty}^2 \right] dh \quad (34)$$

The integrand of the above equation is also identical to the usual definition of the electrostatic disjoining pressure, that is,

$$\pi_{\text{el}}^{\sigma} = \frac{\epsilon\kappa^2}{2} \frac{2\varphi_{1\infty}\varphi_{2\infty} \cosh \kappa h + (\varphi_{1\infty}^2 + \varphi_{2\infty}^2)}{\sinh^2 \kappa h} \quad (35)$$

In this case too, W_{el}^{σ} in eq 34 naturally becomes identical to V_{el}^{σ} in eq 3b.

As shown above, the electromechanical method and the thermodynamic method give identical $\pi_{\text{el}}^{\varphi,\sigma}$ and $V_{\text{el}}^{\varphi,\sigma}$, as long as we use eq 31 which neglects the tangential component of the Maxwell stress. On the other hand, for the CC case, there exists the tangential component of the electric field $E_t = \mathbf{E} \cdot \mathbf{t}$ at the liquid surface, where \mathbf{t} denotes the unit tangential vector at the liquid surface (see Figure 3b). Therefore, the wetting tension of eqs 30 and 31 has an evident error when used for the CC case. The contribution of the tangential stress to W_{el}^{σ} becomes significant as the liquid layer becomes curved. This aspect is not considered in the conventional derivation of either π_{el}^{σ} or V_{el}^{σ} .

Additionally, the error arising due to the use of the Derjaguin approximation becomes (potentially) more significant for the CC case. In the Derjaguin approximation, the x -derivative of the electrostatic potential is neglected and only the y -directional dependence is considered to simplify the analysis of the electrostatic field. For the CP case, the potential is constant over the surfaces, and therefore, there is little freedom for the electrostatic potential to vary in the x -direction. For the CC case, however, there is no limit in the change of the potential. Considering the case in which the surface charge densities are the same, for instance, the surface potential can increase boundlessly as the two surfaces approach (see eq

22). Thus, the x -directional variation of the potential can become significant, which will certainly violate the condition of the validity of the Derjaguin approximation. The x -directional derivative of the potential in turn contributes to the tangential stress at the surface. In summary, the second and the third terms in eq 26 result from such deficiencies of the Derjaguin approximation. The second term in eq 26 itself manifests that the term arises due to the potential variation along the liquid surface.

Conclusion

The electrostatic contribution to the interaction free energy of the Frumkin–Derjaguin approach is derived by using the electromechanical approach. The present theory does not invoke the Derjaguin approximation, while the Debye–Hückel approximation is used to derive the analytic expressions. Thus, the results of the present theory (which are given in eqs 19 and 28 for the constant surface potential and the constant surface charge conditions, respectively) are exact within the framework of the Debye–Hückel theory.

The validity of the Derjaguin approximation for the wetting problem is assessed by comparison with the results of the present theory. For the constant potential case, it is shown that the electrostatic interaction free energy (V_{el}^{σ}) derived under the Derjaguin approximation is exact for all contact angles (within the framework of the Debye–Hückel theory). However, the change of the interfacial tension at the liquid surface due to the electrocapillary effect (which is derived by the present theory in eq 19) should be considered in using the Derjaguin approximation. For the constant charge case, there exists some mismatch between the results of the Derjaguin approximation and the present theory (except for the case of vanishing surface charge density at the liquid–fluid interface). This deviation arises due to the neglect of the tangential component of the Maxwell stress in the conventional thermodynamic method.

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