

Geometry Dependence of Wetting Tension on Charge-Modified Surfaces

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The electrostatic field around a wedge-shaped region of three-phase contact of a (electrolyte) liquid layer on a charged (or ionizable) substrate is analyzed to determine the Coulombic contribution to wetting tension. The linearized Poisson–Boltzmann equation is analyzed by introducing the Kantorovich–Lebedev transformation. The Maxwell stress acting on the droplet surface is integrated to obtain the wetting tension due to the Coulombic interaction. In addition, a numerical method based on the variational calculus is used to analyze the electrostatic field by solving the nonlinear Poisson–Boltzmann equation. The present theory clearly exhibits, although only the case of a straight profile is considered, that the Coulombic contribution to the wetting tension is dependent on the shape of the region of three-phase contact. It is also shown that the Coulombic wetting tension can be significantly greater than that predicted by the conventional theory of electrocapillarity.

Introduction

In the interfacial processes of practical importance, the electrical charge plays an important role. They include the adhesion of particles^{1,2} and vesicles on surfaces,^{3,4} the adsorption of ionic species,⁵ and the formation of Langmuir–Blodgett films.^{6,7} The (macroscopic) contact angle of a liquid layer (droplet or film) is significantly influenced by the degree of surface charge on the substrate⁸ and the pH value of the solution,^{9,10} or externally applied potential.^{11–13} After the pioneering work of Lippmann on electrocapillarity,¹⁴ numerous investigations have been performed to explore the electrical effect on wetting and subsequent contact-angle change. Despite the significant progress made in the past, a clear understanding of the governing mechanism of the phenomenon is still lacking, and there are arguments among the existing theories on charge-related wetting phenomena.^{15–18}

There have been several approaches that take account of the electrical effects for prediction of the contact angle of a liquid layer on a charged (or ionizable) substrate.^{9,15–18} Among them is an approach based on the notion of Lippmann in which the interfacial tension is modified as $\gamma_{sl}' = \gamma_{sl} + g_{el}$ (see, e.g., refs 10 and 17).¹⁹ Here, γ_{sl}' and γ_{sl} are the interfacial tensions at the liquid–substrate interface with and without the electrical effect, and g_{el} represents the portion of the interfacial tension contributed by the free energy (per unit surface area) of the electrical double layer at the interface (i.e., the electrocapillary effect).

In the notion of Lippmann, the change of the interfacial energy is correlated with the bulk properties of the liquid, such as the electrolyte concentration, and the surface charge density. Thus, the approach is a very reasonable one if there arises no significant edge effect on wetting from the three-phase contact line (TCL). As noted by Digilov,¹⁸ however, that is not the case. This approach has an evident deficiency in interpreting the empirical results on the change of contact angle. For instance, past experience manifests that the Lippmann effect alone cannot satisfy the force balance at the three-phase contact line.¹¹ This suggests that there exists a certain degree of edge effect from the TCL region.

From the mechanical viewpoint, the electrical modification of wettability can be viewed as a consequence of adjustment of the location of TCL to maintain the mechanical equilibrium. Since the Coulombic interaction is a long-range interaction, it extends over a macroscopic distance. On the other hand, the Coulombic interaction is weakened by the screening effect of the electrical double layer. Since the electrical double layer of the liquid–substrate surface is blocked by the liquid–surrounding fluid interface, it is anticipated that the electrostatic field near TCL is significantly different from that in the distant neighborhood. In addition, the Coulombic interaction will

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(19) The interrelationship between this approach and the alternative approach based on Frumkin–Derjaguin theory (refs 6 and 16) will be briefly discussed at the end of this paper.

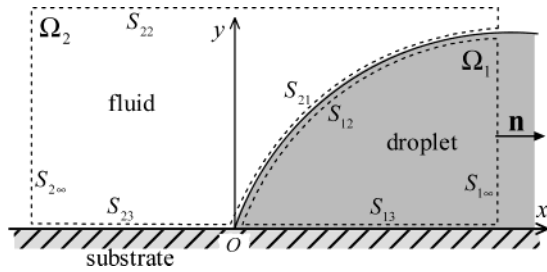


Figure 1. Coordinate system and definition of variables.

also be influenced by the geometry of the liquid layer in the TCL corner.

In most of the past investigations, however, such an aspect has not been properly accounted for. Only recently, Chou²⁰ showed with the local thermodynamic approach^{21,22} that the local interaction near TCL generates extra *edge effect*, aside from the electrocapillary effect. The same conclusion was obtained also by Kang et al.²³ using the electromechanical analysis. Chou has explicitly derived an expression for the electrical potential at TCL. However, as will be pointed out later in this paper, his analysis seems to include an unrealistic result. That is, when the inverse Debye length is zero and the surface charge density at the interface of the substrate–surrounding fluid is also zero (as in the case of air), his analysis results in the vanishing electrostatic potential at TCL.

At all events, for correct assessment of the edge effect on wetting by either Chou²⁰ or Kang et al.,²³ information on the electrostatic field near TCL should be obtained. In the present paper, we consider a wedgelike configuration in order to obtain the electrostatic potential at TCL which is essential for demonstration of the contact-angle dependence (in a broader sense, the geometry dependence) of the Coulombic wetting tension. First, an exact analytical solution is obtained for the linearized Poisson–Boltzmann equation of the electrical double layer (Debye–Hückel theory). Then, a numerical method based on the variational calculus is also implemented for the solution of the nonlinear Poisson–Boltzmann equation. As will be shown later, the results from the linear and nonlinear analyses clearly demonstrate that the wetting tension is significantly influenced by the shape of the interface.

Electrostatic Wetting Tension

We consider a droplet of electrolyte in stable equilibrium on a horizontal solid substrate. The droplet is assumed to be large so that the contact line can be regarded as straight over a small macroscopic distance. A cross section of the droplet in the vicinity of TCL shown in Figure 1 can be imagined to continue normal to the page. We introduce two control surfaces of $\Sigma_1 = S_{12} \cup S_{13} \cup S_{1\infty}$ and $\Sigma_2 = S_{21} \cup S_{22} \cup S_{2\infty} \cup S_{23}$ which enclose the droplet (Ω_1) and the surrounding fluid region (Ω_2), respectively. Hereafter, the indices 1, 2, and 3 indicate the variables associated with the droplet, the surrounding fluid, and the substrate. All the surfaces such as S_{12} , S_{13} , and S_{23} have unit depth normal to the page. $S_{1\infty}$ and $S_{2\infty}$ indicate the normal surfaces to the substrate surface located at a sufficiently large distance from TCL. The surrounding fluid will be called the *fluid* for brevity.

We assume that the electrical double layer inside the droplet satisfies the following Poisson–Boltzmann equation:

$$\nabla^2 \varphi = \frac{\kappa^2}{\beta} \sinh \beta \varphi \quad (1)$$

Here, φ is the electrostatic potential, $\kappa^{-1} = (2n_b z^2 e^2 / \epsilon kT)^{-1/2}$ represents the Debye length in each region, n_b is the number density of ionic species far from the interfaces, ϵ is the electric permittivity, k is the Boltzmann constant, T is the absolute temperature, $\beta = ze/kT$ for z electrolytes, z is the valence of ionic species, and e is the electronic charge.

The electrical charge at the droplet–substrate interface can be induced due to adsorption (or dissociation) of ionic species depending on their pK_a values, or it can be supplied by an external battery. As shown by Kang et al.,²³ the wetting tension is independent of the interface profile in the case of a constant potential boundary condition. So, the present analysis is focused on the case of a constant charge condition.

On the droplet–substrate having constant charge density σ , the following Neumann boundary conditions should be satisfied:

$$\mathbf{n} \cdot \nabla \varphi = \sigma / \epsilon \quad \text{at } S_{13} \quad (2)$$

where \mathbf{n} is the outward unit normal vector at surfaces. In the foregoing condition, it is implicitly assumed that there is no electric flux toward the substrate layer. This condition is satisfied when the dielectric constant of the substrate is much smaller than that of the electrolyte. The polymeric substrate typically has a dielectric constant of about 2, while that of water is about 80. The condition is also satisfied when the substrate is a perfectly conducting material such as metal. There is no electrostatic field inside a perfect conductor.

If the surrounding fluid is another immiscible electrolyte, the two fluids ionize the substrate differently depending on their pK_a values. However, most of the practically important situations involve air as a surrounding fluid. Thus, for simplicity of analysis, it is assumed that the surrounding fluid is air, and there exists no charge at the substrate–air interface, that is,

$$\mathbf{n} \cdot \nabla \varphi = 0 \quad \text{at } S_{23} \quad (3)$$

The electrostatic force \mathbf{F} acting on the droplet–air interface (per unit depth), which will force the meniscus to move, is obtained by integrating the electrically induced stress acting on the surface enclosing the droplet–air interface, that is,

$$\mathbf{F} = - \int_{S_{12} + S_{21}} \mathbf{T} \cdot \mathbf{n} \, dS \quad (4)$$

Here, $\mathbf{T} = -(\Pi + (1/2)\epsilon E^2)\mathbf{I} + \epsilon \mathbf{E}\mathbf{E}$ is the sum of the Maxwell stress tensor and the osmotic pressure ($\Pi = 2n_b kT [\cosh \beta \varphi - 1]$) tensor, $\mathbf{E} = -\nabla \varphi$ is the electric field, $E = |\mathbf{E}|$, and \mathbf{I} is the second-order isotropic tensor. The osmotic pressure term in eq 4 vanishes for the air phase.

It is shown by Kang et al.²³ that the Coulombic contribution to the wetting tension (W_e), which is the component of the force in the *negative x*-direction ($W_{e1} = -\mathbf{F} \cdot \mathbf{e}_x$, \mathbf{e}_x is the unit vector in the *x*-direction), for a droplet

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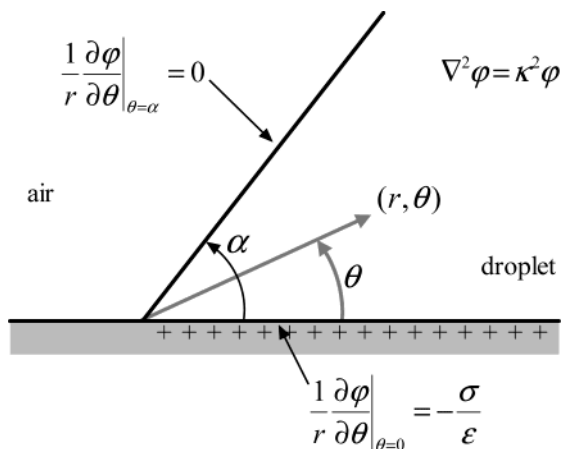


Figure 2. The domain of analysis of the electrostatic field.

surrounded by another fluid, becomes (see eq 11 in Kang et al.²³)

$$W_{el} = \left\{ \frac{8n_{1b}kT}{\kappa_1} \left[\cosh \frac{\beta\varphi_{1\infty}}{2} - 1 \right] - \sigma_1\varphi_{1\infty} \right\} - \left\{ \frac{8n_{2b}kT}{\kappa_2} \left[\cosh \frac{\beta\varphi_{2\infty}}{2} - 1 \right] - \sigma_2\varphi_{2\infty} \right\} + (\sigma_1 - \sigma_2)\varphi_0 \quad (5)$$

In the above, σ_2 is the surface charge density at S_{23} which is null in the present investigation by eq 3. $\varphi_{1\infty}$ and $\varphi_{2\infty}$ are the electrostatic potential at far distance away from TCL in each region, respectively, and φ_0 is the electrostatic potential at TCL. Moreover, it is assumed that there is no free charge in air, so that $n_{2b} = 0$. Then, the foregoing wetting tension becomes (dropping the subscripts for brevity)

$$W_{el} = \left\{ \frac{8n_bkT}{\kappa} \left[\cosh \frac{\beta\varphi_{1\infty}}{2} - 1 \right] - \sigma\varphi_{\infty} \right\} + \sigma\varphi_0 \quad (6)$$

The first term in W_{el} originates from the free energy of the electrical double layer far from TCL. The second term of $\sigma\varphi_0$ in W_{el} results from the electrostatic interaction at TCL. The electrostatic potential at TCL (φ_0) is anticipated to be dependent on the geometry of the interface. Thus, to determine φ_0 , the electrostatic field in the neighborhood of TCL should be analyzed.

For a limiting situation of $|\beta\varphi| < 1$, we expand the cosine hyperbolic terms in the foregoing equation as $\cosh(\beta\varphi_{\infty}/2) \cong 1 + (1/8)(\beta\varphi_{\infty})^2$. Far from TCL, the surface charge density is related with the surface potential as $\sigma = \epsilon\kappa\varphi_{\infty}$. Then eq 6 for this case becomes

$$W_{el,lin} \cong -\frac{1}{2}\sigma\varphi_{\infty} + \sigma\varphi_0 \quad (7)$$

Linear Analysis

The wetting tensions of eqs 6 and 7 are valid irrespective of the shape of the liquid surface. The length scale of the electrical double layer is assumed to be much smaller than the dimension of the droplet. Consequently, the electrical double layer is assumed to be localized within a small region near the contact line. Then, the interface is *microscopically* straight near TCL, and the shape of the edge of the liquid layer can be modeled as a wedgelike geometry (see Figure 2).

The Poisson–Boltzmann equation (eq 1) can be rewritten in the linearized form in the (r,θ) cylindrical coordinate system as

$$\nabla^2\varphi = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \varphi}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 \varphi}{\partial \theta^2} = \kappa^2\varphi \quad (8)$$

On the substrate surface, the constant charge boundary condition shown in eq 2 is rewritten in the cylindrical coordinate system as

$$\frac{1}{r} \frac{\partial \varphi(r,0)}{\partial \theta} = -\frac{\sigma}{\epsilon} \quad (9)$$

Here, $\theta = 0$ corresponds to the positive x -axis. The electric permittivity of the aqueous electrolyte solution is significantly greater than that of air. Therefore, at the droplet–air interface, the following insulating wall condition can be assumed:

$$\frac{\partial \varphi(r,\alpha)}{\partial \theta} = 0 \quad (10)$$

where α represents the wedge angle.

This problem is analogous to finding out the surface tension effects in a wedge. The problem was solved by Fowkes and Hood²⁴ by introducing the Kantorovich–Lebedev transform. The transform and its inverse transform are defined respectively as

$$\tilde{\varphi}(\theta;\lambda) = \int_0^{\infty} \varphi(r,\theta) K_{\lambda}(\kappa r) \frac{dr}{r}$$

$$\varphi(r,\theta) = \frac{2}{\pi^2} \int_0^{\infty} \tilde{\varphi}(\theta;\lambda) K_{\lambda}(\kappa r) \lambda \sinh(\pi\lambda) d\lambda$$

where $K_{\lambda}(\kappa r)$ is the modified Bessel function.^{25,26}

Applying the Kantorovich–Lebedev transform to the linearized Poisson–Boltzmann equation (eq 8), we obtain

$$\frac{\partial^2 \tilde{\varphi}}{\partial \theta^2} - \lambda^2 \tilde{\varphi} = 0 \quad (11)$$

The modified Bessel function $K_{\lambda}(\kappa r)$ can be rewritten as $K_{\lambda}(\kappa r) = \int_0^{\infty} e^{-\kappa r \cosh t} \cos \lambda t dt$.^{25,26} Then, it becomes²⁷

$$\int_0^{\infty} K_{\lambda}(\kappa r) dr = \frac{1}{\kappa} \int_0^{\infty} \frac{\cos \lambda t}{\cosh t} dt = \frac{\pi}{2\kappa} \frac{1}{\cosh(\lambda\pi/2)}$$

By using the foregoing formula, the Neumann boundary condition (eq 9) and the insulating boundary condition (eq 10) are transformed respectively as

$$\frac{\partial \tilde{\varphi}(\theta = 0;\lambda)}{\partial \theta} = -\frac{\pi(\sigma)}{2(\epsilon\kappa) \cosh(\lambda\pi/2)} \quad (12a)$$

$$\frac{\partial \tilde{\varphi}(\theta = \alpha;\lambda)}{\partial \theta} = 0 \quad (12b)$$

The solution of eq 11 satisfying the boundary condition

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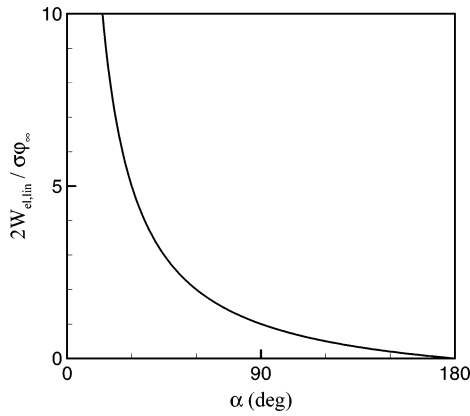


Figure 3. Dependence of wetting tension on contact angle.

of eq 12b becomes

$$\tilde{\varphi}(\theta; \lambda) = a(\lambda) \cosh \lambda(\theta - \alpha)$$

The coefficients $a(\lambda)$ can be obtained from eq 12a, and the resulting solution in λ space becomes

$$\tilde{\varphi}(\theta; \lambda) = \frac{\pi(\sigma)}{2\lambda(\epsilon\kappa)} \frac{\cosh \lambda(\theta - \alpha)}{\sinh(\lambda\alpha) \cosh(\lambda\pi/2)} \quad (13)$$

Applying the inverse transform to eq 13, then we obtain the following solution

$$\varphi(r, \theta) = \frac{2(\sigma)}{\pi(\epsilon\kappa)} \int_0^{\infty} \frac{\sinh \frac{\lambda\pi}{2}}{\sinh \lambda\alpha} K_{\lambda}(\kappa r) \cosh \lambda(\theta - \alpha) d\lambda \quad (14)$$

The electrostatic potential at TCL (φ_0) can be obtained by using the integral representation of the modified Bessel function and its asymptotic property,²⁰ such that

$$\varphi_0 = \lim_{\kappa r \rightarrow 0} \varphi = \lim_{\lambda \rightarrow 0} \lambda^2 \tilde{\varphi} = \frac{\pi\varphi_{\infty}}{2\alpha} \quad (15)$$

where $\varphi_{\infty} = \sigma/(\epsilon\kappa)$. Substituting eq 15 into eq 7, the linearized version of the wetting tension can be obtained as follows:

$$W_{el,lin} = \frac{\sigma\varphi_{\infty}}{2} \left(\frac{\pi}{\alpha} - 1 \right) \quad (16)$$

Note that according to the linear analysis, the wetting tension becomes $W_{el,lin} = \sigma\varphi_{\infty}/2$ when $\alpha = \pi/2$. The wetting tension $W_{el,lin}$ is inversely proportional to the contact angle. As shown in Figure 3, therefore, the dependence of $W_{el,lin}$ on the contact angle is significant, particularly for small values of α .

A physical explanation for such an increase of wetting tension in proportion to α^{-1} is possible. The wetting tension originates from the sum of electrostatic pressure and osmotic pressure at the droplet surface (see eq 4). As demonstrated in Figure 4, there exist image planes of the original charged plane due to the insulating boundary condition of eq 10. Note that there arise additional charge distributions due to images of image planes themselves. The number of image planes is proportional to α^{-1} , and therefore, the net surface charge inside an imaginary circle centered at the origin will be also proportional to α^{-1} . The electrostatic potential and electric field at the center region will increase in proportion to the net surface charge. The number density of ionic species is proportional to the electrostatic potential as described by the Boltzmann

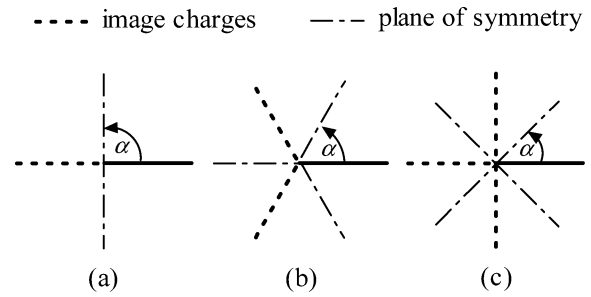


Figure 4. Interaction of charges on the droplet–substrate interface with its image charges: (a) $\alpha = \pi/2$, (b) $\alpha = \pi/3$, and (c) $\alpha = \pi/4$.

distribution. This results in the increase of the osmotic pressure near TCL.

A similar problem has been analyzed before by Chou.²⁰ He analyzed the problem by using the Kantorovich–Lebedev transform for the two asymptotic cases of $\kappa_2 \cong \kappa$ and $\kappa_2 \ll \kappa$, in which κ_2^{-1} denotes the Debye length of the electrical double layer formed at the fluid–substrate interface. An apparent shortcoming of his analysis is that it gives an unrealistic result in the case of $\kappa_2 \ll \kappa$. As noted by Chou,²⁰ the case of $\kappa_2 = \sigma_2 = 0$ corresponds to the case of air as the surrounding fluid, in which σ_2 is the surface charge density at the fluid–substrate interface. In that case, the analysis gives $\varphi_0 = 0$, irrespective of the contact angle and the electric permittivity of each phase. Even if it is mathematically correct, it is physically unacceptable. Furthermore, it yields no information on the geometric dependence of the wetting tension in the present situation.

The present work provides an analysis which yields an exact solution for all contact angles. The validity of the linear analysis will be verified numerically in the following section.

Numerical Analysis

Various numerical methods can be invoked to analyze the nonlinear Poisson–Boltzmann equation. In the present problem, however, we have the following electrostatic free energy of the system (G_{el}) which can be written as shown below.²⁸

$$G_{el} = \int_{S_{12}} \sigma\varphi dS - \int_{\Omega_1} \left[\frac{1}{2} \epsilon |\nabla\varphi|^2 + \Pi(\varphi) \right] d\Omega \quad (17)$$

where Ω_1 is the volume of the droplet. The natural choice of the numerical method is the finite element method with G_{el} as a functional to be minimized.

For each discretized element, the potential function $\varphi^{(e)}$ can be represented approximately as a linear combination of the interpolation function $N(x, y)$, that is,

$$\varphi^{(e)}(x, y) = \sum_{i=1}^m \varphi_i N_i(x, y) \quad (18)$$

where m is the number of nodes in an element and φ_i are the discretized potentials at the i th node point. In the present investigation, the six-node triangular elements with the Lagrange polynomial are used (see Figure 5).^{29,30} (For details on the numerical method, see the Appendix).

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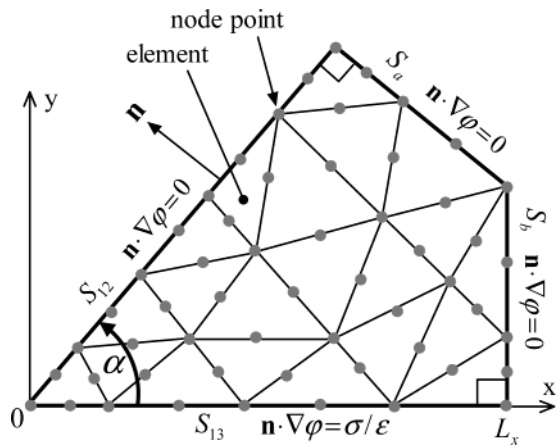


Figure 5. Computation domain.

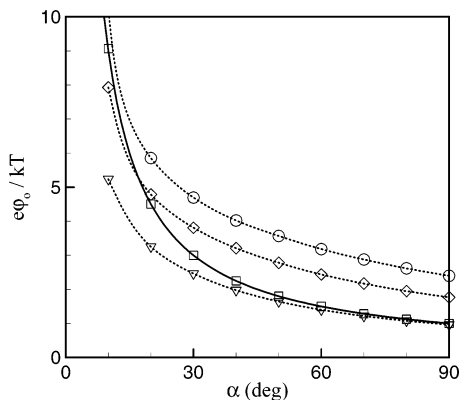


Figure 6. Electrostatic potential at the three-phase contact line for different contact angles. The solid line is for the analytical solution for the linear theory. Symbols indicate the numerical results. Squares are for the linearized equation with $\beta\sigma/(\epsilon\kappa) = 1$. Triangles, diamonds, and circles are for the nonlinear equation with $\beta\sigma/(\epsilon\kappa) = 1, 2, \text{ and } 3$, respectively.

The calculation is performed for three dimensionless surface charge densities of $\beta\sigma/(\epsilon\kappa) = 1, 2, \text{ and } 3$. The inverse Debye length (κ) is related to the ionic strength (I) for a 1:1 electrolyte as

$$\kappa = 3.288 \times 10^9 \sqrt{I} \quad \text{in units of } \text{m}^{-1}$$

When the ionic strength is 10^{-3} M , $\kappa^{-1} = 9.6 \text{ nm}$. Since $\epsilon = 7.26 \times 10^{-10} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$ for aqueous electrolytes and $\beta = e/(kT) = 38.9 \text{ V}^{-1}$ for monovalent ionic species, the conditions of $\beta\sigma/(\epsilon\kappa) = 1, 2, \text{ and } 3$ correspond to the surface charge densities of $\sigma = 1.94 \times 10^{-3}, 3.87 \times 10^{-3}, \text{ and } 5.81 \times 10^{-3} \text{ C/m}^2$, respectively. For a two-dimensional plane electrical double layer, the surface potential (φ_∞) is related to the surface charge density as $\varphi_\infty = \sigma/(\epsilon\kappa)$ for the linear theory and as $\varphi_\infty = (2/\beta) \sinh^{-1}[(1/2)\beta\sigma/(\epsilon\kappa)]$ for the nonlinear theory. Therefore, these conditions correspond to the surface potential values of 25.7, 51.4, and 77.1 mV, respectively, for the linear theory. For the nonlinear theory, they become 24.7, 45.3, and 61.4 mV, respectively.

To confirm the validity of the numerical method, the numerical results on the electrostatic potential at TCL (φ_0) of the linearized Poisson–Boltzmann equation (squares in Figure 6) are compared with the linear theory of eq 15 (solid line) for various contact angles. As shown in the figure, the numerical results for the linearized Poisson–Boltzmann equation agree with the analytical result very well. For $\beta\sigma/(\epsilon\kappa) = 1$, the nonlinear results show a smaller φ_0 than the linear results for all contact angles; for smaller contact angles, the deviation between

the linear and nonlinear results becomes greater as the contact angle decreases. This may be because the effect of field charge is underestimated due to the linearization of the sine hyperbolic term in the Poisson–Boltzmann equation. It is also shown that φ_0 increases in proportion to the surface charge density.

Discussion

We briefly consider the effect of the Coulombic interaction on the macroscopic contact angles. It is noted by Israelachvili³¹ that the macroscopic contact angle is independent of the nature of the forces so long as its influence is limited to a shorter range than the dimensions of the droplet. If we follow this notion, the wetting tension can be simply superposed to the surface tension. Therefore, the wetting tension (W_{el}) obtained in the present analysis can be implemented in Young’s equation in the form of

$$\cos \alpha = \cos \alpha_0 + \frac{W_{el}}{\gamma_{lf}} \quad (19)$$

where $\alpha_0 = \cos^{-1}[(\gamma_{sf} - \gamma_{sl})/\gamma_{lf}]$ indicates the contact angle without electrical effect. γ_{lf} , γ_{sf} , and γ_{sl} denote the interfacial tension at the liquid–fluid, solid–fluid, and solid–liquid interfaces, respectively. The difference between eq 19 and that of Fokkink and Ralston^{10,17} is that W_{el} in eq 19 includes the edge-effect term.

On the basis of the present investigation, the wetting tension is correlated with the contact angle (α) by combining eqs 7 and 15 and the modified equation of Young (eq 19) as

$$\cos \alpha = \cos \alpha_0 + \frac{\sigma^2}{2\epsilon\kappa} \left(\frac{\pi}{\alpha} - 1 \right) \quad (20)$$

For $\alpha < \pi/2$, the second term on the right-hand side of eq 20 is always greater than the electrocapillary term of (for the linear case) $\sigma^2/(2\epsilon\kappa)$. The above equation, therefore, predicts that (for $\alpha < \pi/2$) the contact angle becomes smaller than that predicted by considering only the electrocapillary term. The additional term to the electrocapillary effect arises from the edge effect, that is, the local electrostatic interaction at TCL which is mainly governed by the geometry of the interface (although only the contact-angle effect is considered in this paper).

On the other hand, another widely used approach in contact-angle prediction with adsorbed film on the solid surface is based on the Frumkin–Derjaguin theory.^{15,16} In that approach, the interfacial tension at the solid–fluid interface is written as $\gamma_{sf} = \gamma_{lf} + \gamma_{sl} + \int_{h_0}^{\infty} \pi(h) dh$, where $\pi(h)$ represents the disjoining pressure and h_0 is the equilibrium thickness of the adsorbed film. The disjoining pressure is further decomposed as molecular ($\pi_m(h)$), electrostatic ($\pi_e(h)$), and structural ($\pi_s(h)$) components, so that $\pi(h) = \pi_m(h) + \pi_e(h) + \pi_s(h)$. Substituting γ_{sf} into Young’s equation, we obtain

$$\cos \alpha = 1 + \frac{1}{\gamma_{lf}} \int_{h_0}^{\infty} \pi(h) dh \quad (21)$$

In fact, $\int_{h_0}^{\infty} \pi_e(h) dh$ becomes the net horizontal component of the electrostatic force acting on the meniscus. Therefore, it is consistent with the definition of the wetting tension of the present investigation. The difference is that there exists an adsorbed film on the solid surface so that

(31) Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic Press: London, 1985; p 220, Chapter 12.

the integral domain is from h_0 to infinity. In reality, for the electrostatic disjoining pressure $\pi_e(h)$, the disjoining pressure of the flat film has been widely used (the Derjaguin approximation).³² The validity of the Derjaguin approximation for large contact angles is still questionable. Therefore, the validity of eq 21 for large contact angles has not been guaranteed yet, as long as the Derjaguin approximation is implemented to determine $\pi_e(h)$.

On the other hand, for a low-energy surface of rather large contact angle, there seldom exists an adsorbed film (ref 5, p 306). Moreover, as the present investigation indicates, the edge effect becomes negligible as the contact angle increases, and there is no edge effect for the constant potential boundary condition.²³ Note that when the surface charge is due to dissociation of ionizable species on the substrate surface, the application of the constant potential boundary condition is valid (see, e.g., p 107 of ref 16). Thus, the approach of Fokkink and Ralston^{10,17} is conjectured to be suitable either for the case of a constant boundary condition or for a contact angle of a large magnitude.

Another issue that must be noted is the charge-regulation phenomenon.^{7,31,33} As shown in the present paper, the electrical condition near TCL has a decisive influence on the electrostatic effect on wetting of a liquid layer. When the surface charge on a solid substrate originates from dissociation of the ionizable group on the solid surface, the degree of dissociation of ionizable species on the substrate surface is dependent on the local concentration of the ionic species. Consequently, it depends on the electrostatic potential itself. The surface charge density can also change due to the locally high electrostatic potential near TCL.

The current level of our understanding of the Coulombic interaction on wetting is far from being complete. Certainly more extensive theoretical and experimental investigations are necessary in the future to enhance our understanding. On the experimental side, the verification of the present theory is required, for instance, concerning the validity of eq 20. It is recommendable to measure the microscopic profile near TCL, as was done by Pompe and Herminghaus.³⁴ Among the several assumptions made here, we postulated that the interface profile is straight, which is a usual practice for the theoretical treatment of similar problems. However, the strong repulsion between the electrical double layers can lead to the deformation of the meniscus in the length scale of κ^{-1} ,^{20,35} which will limit the validity of the present theory.

Conclusion

We have presented a theoretical manifestation concerning the significant contribution of the local Coulombic interaction near TCL (which is mainly governed by the geometry of the interface) to the wettability change of electrolyte liquids on a charged (or ionizable) substrate. The relation between the Coulombic wetting tension (which forces a droplet to spread) and the electrostatic potential at TCL is derived with respect to the constant surface charge condition (in eqs 6 and 7), relying on the electromechanical approach. The electrostatic potential at TCL is obtained by the linear analysis of the Poisson–Boltzmann equation (in eq 15). The result of the linear

analysis of the electrostatic field is confirmed by a numerical method which is based on the variational calculus. Both linear and nonlinear analyses clearly show that the contact-angle dependence of the wettability is pronounced for small contact angles.

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Appendix: Numerical Analysis of the Electrostatic Field

Substituting the approximated potential (eq 18) into the free energy functional, one can obtain the discretized functional for an element as

$$G_{\text{el}}^{(e)}(\varphi^{(e)}) = \sum_{i=1}^m \varphi_i \int_{S^{(e)}} \sigma N_i \, dS^{(e)} - \frac{1}{2} \sum_{i=1}^m \sum_{j=1}^m \varphi_i \varphi_j \int_{\Omega^{(e)}} \epsilon \nabla N_i \cdot \nabla N_j \, d\Omega^{(e)} - \sum_{i=1}^m \int_{\Omega^{(e)}} \Pi_i(\varphi) N_i \, d\Omega^{(e)} \quad (\text{A1})$$

Here, $\Pi = (\epsilon \kappa^2 / \beta^2) [\cosh \beta \varphi - 1]$ is again the osmotic pressure at the i th node point. This can be rewritten in a matrix form as

$$G_{\text{el}}^{(e)}(\varphi^{(e)}) = \{\varphi\}^T \{R\} - \frac{1}{2} \{\varphi\}^T [S] \{\varphi\} - \{\Pi(\varphi)\}^T \{Q\}$$

where $\{\cdot\}$ and $[\cdot]$ represent $1 \times m$ and $m \times m$ matrices, and the elements of $\{R\}$, $[S]$, and $\{Q\}$ become, respectively,

$$R_i = \int_{S^{(e)}} \sigma N_i \, dS^{(e)} \quad (\text{A2a})$$

$$S_{ij} = \int_{\Omega^{(e)}} \epsilon \nabla N_i \cdot \nabla N_j \, d\Omega^{(e)} \quad (\text{A2b})$$

$$Q_i = \int_{\Omega^{(e)}} N_i \, d\Omega^{(e)} \quad (\text{A2c})$$

The total electrical contribution to the free energy of the domain is the sum of the free energy of the individual elements, that is $G_{\text{el}} = \sum_e G_{\text{el}}^{(e)}$. This can be represented in a matrix form as

$$G_{\text{el}} = \sum_e \left[\{\varphi\}^T \{R\} - \frac{1}{2} \{\varphi\}^T [S] \{\varphi\} - \{\Pi(\varphi)\}^T \{Q\} \right] \quad (\text{A3})$$

At an equilibrium condition, G_{el} should be minimized with respect to the variation of electrostatic potential, that is, $\partial G_{\text{el}}^{(e)} / \partial \varphi_i = 0$, for $i = 1, 2, \dots, m$. This requirement results in the following matrix equation:

$$[S] \{\varphi\} = \{R\} - \{Q\} \quad (\text{A4})$$

where

$$Q'_i = \int_{\Omega^{(e)}} (\partial \Pi / \partial \varphi)_i N_i \, d\Omega^{(e)} = \frac{\epsilon \kappa^2}{\beta} \int_{\Omega^{(e)}} \sinh(\varphi_i) N_i \, d\Omega^{(e)}$$

(32) There exist explicit forms of π_e for simple electrical boundary conditions at interfaces (see, e.g., refs 6 and 16).

(33) Tsao, H.-K. *Langmuir* **2000**, *16*, 7200–7209.

(34) Pompe, T.; Herminghaus, S. *Phys. Rev. Lett.* **2000**, *85*, 1930–1933.

(35) de Gennes, P. G. *Rev. Mod. Phys.* **1985**, *57*, 827–863; p 840.

The computational domain is shown in Figure 5. The constant charge boundary condition at S_{13} is imposed by way of R_i in eq A2a. At other boundary surfaces, the insulating boundary condition is applied. In the finite element method, this condition is automatically satisfied if it is not specified at a boundary surface. The surfaces

S_a and S_b in Figure 5 are set at sufficiently far distance from the origin. The distance from the origin (L_x) is at least 10 times the Debye length. Then the set of algebraic equations in eq A4 is solved iteratively for given values of σ , ϵ , κ , and β .

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