# Wetting Tension Due to Coulombic Interaction in Charge-Related Wetting Phenomena

Kwan Hyoung Kang,*,† In Seok Kang,‡ and Choung Mook Lee†

*Department of Mechanical Engineering and Department of Chemical Engineering, Pohang University of Science and Technology, San 31, Hyoja-dong, Pohang 790-784, Republic of Korea*

*Received January 30, 2003. In Final Form: April 16, 2003*

The influence of Coulombic interaction on wetting is elucidated within the framework of electromechanics. The Maxwell stress and osmotic pressure acting on a meniscus are integrated to obtain a concise analytical expression for the Coulombic contribution to wetting tension. The results are verified alternatively by using a thermodynamic approach. The method is applied to three important charge-related wetting configurations in which droplets are placed on a solid substrate. First, when the constant-potential boundary condition is applied at the substrate surface, only the electrocapillary term which represents the electrostatic free energy of the electrical double layer contributes to the wetting tension. Second, in the case of the constant-charge condition, the wetting tension includes an additional edge-effect term. It is found that the wetting tension in this case is dependent on the interface profile near the three-phase contact line. Third, in the case of electrowetting on dielectrics, the wetting tension also includes the edge-effect term. The wetting-tension term appearing in the Lippmann−Young equation is recovered as a special case of the third case.

## Introduction

The macroscopic contact angle of liquid layers (film or droplet) is significantly influenced by externally applied electric potential (Figure 1a, case I),[1−3] degree of surface charge on substrates,[4] and the pH value of the solution[5] (Figure 1b, case II). These electrical modifications of wettability have important consequences on the behavior of liquid layers such as spreading, film instability, adhesion and subsequent spreading of biological cells and membranes,[6] and mineral separation by flotation.[7]

The electrical control of contact angle on dielectric substrates or on self-assembled monolayers (Figure 1c, case III), which is sometimes called electrowetting or more distinctly electrowetting on dielectrics, has drawn much attention recently for its potential applications in microfluidic control. By use of electrowetting on dielectrics, nano- or microliter volumes of (nearly any kinds of) electrolyte liquids can be controlled very quickly and reversibly with low power consumption (refs 8−11 and references therein).

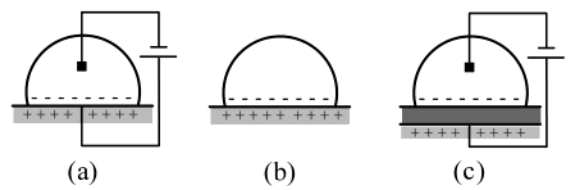


**Figure 1.** Three typical cases of the electrical effect on wetting. (a) Droplet on an electrode (case I). (b) Droplet on a charged substrate (case II). (c) Droplet on a dielectric substrate (case III). Droplets are assumed to be two-dimensional based on the axisymmetric condition.

Here, we call all the aforementioned three configurations *charge-related wetting phenomena*.[12] These charge-related wetting phenomena have been regarded by many investigators as a branch of the electrocapillary phenomenon, that is, as a consequence of electrical modification of interfacial energy (Lippmann effect, primary electrocapillary effect). Recently, Digilov[13] suggested that the charge-related wetting phenomena (especially of cases I and II) are a result of the electrical force acting on the three-phase contact line (TCL). He designated it as the secondary electrocapillary effect in contrast to the Lippmann effect. The main difference between the Lippmann (primary electrocapillary) effect and the secondary electrocapillary effect is that the secondary electrocapillary effect is not directly associated with interfacial energy.

The theory of Digilov[13] on the electrical effect on wetting is rather qualitative, and to assess the effect quantitatively, the Coulombic interaction at TCL should be analyzed, for instance, as was done by Kang.[14] Without detailed analysis of the electrostatic field, Chou[15] showed

* To whom correspondence should be addressed. E-mail: khkang@postech.edu.

† Department of Mechanical Engineering.

‡ Department of Chemical Engineering.

(1) Nakamura, Y.; Kamada, K.; Katoh, Y.; Watanbe, A. *J. Colloid Interface Sci.* **1973**, *44*, 517−524.

(2) Nakamura, Y.; Matsumoto, M.; Nishizawa, K.; Kamada, K.; Watanbe, A. *J. Colloid Interface Sci.* **1977**, *59*, 201−210.

(3) Hato, M. *J. Colloid Interface Sci.* **1989**, *130*, 130−136.

(4) Gil'man, A. B.; Drachev, A. I.; Kuznetsov, A. A.; Lopukhova, G. V.; Pavlov, S. A.; Potapov, V. K. *High Energy Chem.* **1996**, *30*, 335−338.

(5) Xu, Z.; Liu, Q.; Ling, J.; Summers, A. *Langmuir* **1996**, *12*, 547−554.

(6) Bernard, A.-L.; Guedeau-Boudeville, M.-A.; Jullien, L.; di Meglio, J.-M. *Langmuir* **2000**, *16*, 6809−6820.

(7) Preuss, M.; Butt, H.-J. *Langmuir* **1998**, *14*, 3164−3174.

(8) Quilliet, C.; Berge, B. *Curr. Opin. Colloid Interface Sci.* **2001**, *6*, 34−39.

(9) Moon, H.; Cho, S. K.; Garrell, R. L.; Kim, C.-J. *J. Appl. Phys.* **2002**, *92*, 4080−4087.

(10) Quinn, A.; Sedev, R.; Ralston, J. *J. Phys. Chem. B* **2003**, *107*, 1163−1169.

(11) Gorman, C. B.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1995**, *11*, 2242−2246.

(12) The terminology of *electrowetting* has been widely used to represent the change of wettability of liquid layers due to externally *applied* electric potential. In this context, it is improper to include case II within the category of electrowetting. Therefore, we use here a more general terminology of *charge-related wetting phenomenon* to represent the (electrical) charge-induced modification of wettability of liquid layers.

(13) Digilov, R. *Langmuir* **2000**, *16*, 6719−6723.

(14) Kang, K. H. *Langmuir* **2002**, *18*, 10318−10322.

(15) Chou, T. *Phys. Rev. Lett.* **2001**, *87*, 106101.

10.1021/la034163n CCC: $25.00 
Published on Web 05/15/2003

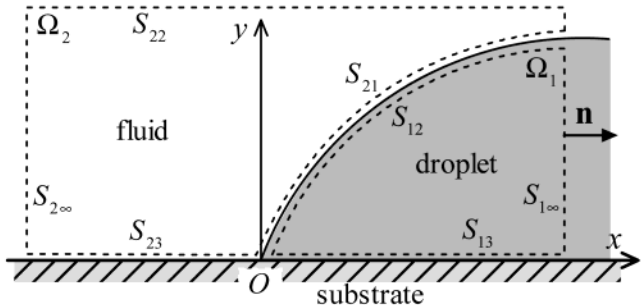


**Figure 2.** Coordinate systems and definition of variables.

(by considering the free energy of Coulombic interaction near TCL) that some useful information can be deduced. The thermodynamic approach, on the other hand, is somewhat indirect in offering a specific understanding of the detailed physics associated with the electrical effect on wetting. Furthermore, the approach is based on the equilibrium assumption, and therefore, it cannot be applied to analyze the dynamical problems. In that sense, a more direct complementary approach is necessary, and the electromechanical approach can be a good candidate.

The electromechanical approach in many cases can provide more detailed information, and it can constitute a potential backbone for direct analysis and understanding on charge-related wetting problems. As a first attempt in this direction, Jones[16] and Kang[14] analyzed a simple problem of a special case with the electromechanical approach and showed that it produces an equivalent result to that obtained by the thermodynamic approach.

In this paper, we show how the Coulombic interaction at TCL generates wetting tension ($W_{el}$) which enforces a liquid layer to spread and is related with the (apparent) contact angle ($\theta$) as[17,18]

$$\cos\theta = \cos\theta_0 + \frac{W_{el}}{\gamma}$$

where $\theta_0$ is the contact angle without the electrical effect and $\gamma$ is the interfacial tension at the interface of droplet and surrounding fluid. Attention is focused on the electrostatic interaction at TCL, anticipating a significant electrostatic interaction there, contributed by the long-range nature of the Coulombic interaction. Concrete analytical expressions of wetting tension for the three practically important cases shown in Figure 1 are derived (eqs 9, 11, and 17), and the wetting tensions are compared with those of the thermodynamic counterpart.

## Analysis

**Coulombic Contribution to Wetting Tension.** Let us consider a two-dimensional droplet of electrolyte in stable equilibrium on a horizontal solid substrate, being immersed in another fluid (air or liquid) (see Figure 2). A cross section of the droplet shown in Figure 2 can be imagined to continue normal to the page. We introduce two control surfaces $\Sigma_1 = S_{12} \cup S_{13} \cup S_{1\infty}$ and $\Sigma_2 = S_{21} \cup S_{22} \cup S_{23} \cup S_{2\infty}$ which enclose the droplet and the surrounding fluid regions, respectively. Hereafter, the indices 1, 2, and 3 indicate the variables associated with droplet, surrounding fluid, and substrate. The double indices in $S_{ij}$ indicate the surface in the $i$th medium facing the $j$th medium. The surrounding fluid will be called the *fluid* for brevity. All the surfaces such as $S_{12}$, $S_{13}$, and $S_{23}$ have unit depth normal to the page. Note that the two surfaces $S_{12}$ and $S_{21}$ indicate the droplet−fluid interfaces in $\Sigma_1$ and $\Sigma_2$, respectively. $S_{1\infty}$ and $S_{2\infty}$ indicate the surfaces vertical to the substrate surface located at a sufficiently large distance from TCL. A Cartesian ($x$, $y$) coordinate system is introduced in which the origin is placed at TCL. The $x$- and $y$-axes are parallel and normal to the substrate surface, respectively.

The electrostatic force **F** acting on the droplet−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 droplet−fluid interface:[19]

$$\mathbf{F} = -\int_{S_{12}+S_{21}} \mathbf{T}\cdot\mathbf{n}\, \mathrm{d}S \qquad (1)$$

Here, $\mathbf{T} = -(\Pi + (1/2)\epsilon E^2)\mathbf{I} + \epsilon\mathbf{EE}$ is the *sum* of the Maxwell stress tensor and the osmotic pressure ($\Pi$) tensor, **n** is the outward unit normal vector at the surfaces, $\mathbf{E} = -\nabla\varphi$ is the electric field, $E = |\mathbf{E}|$, $\varphi$ is the electrostatic potential, $\epsilon$ is the electric permittivity, and **I** is the second-order isotropic tensor. The Coulombic contribution to the wetting tension ($W_{el}$) is the horizontal component of **F**, here in the negative $x$-direction, that is,

$$W_{el} = -\mathbf{F}\cdot\mathbf{e}_x \qquad (2)$$

where $\mathbf{e}_x$ represents the unit vector in the positive $x$-direction.

We assume that the electrical double layer inside the droplet and in the fluid satisfies the following Poisson−Boltzmann equation:

$$\nabla^2\varphi = \frac{\kappa_j^{\,2}}{\beta}\sinh\beta\varphi$$

Here, $\kappa_j^{-1} = (2n_{jb}z^2e^2/\epsilon_j kT)^{-1/2}$ (where $j$ = 1, 2) represents the Debye length in the $j$th medium, $n_{jb}$ 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 subscripts 1, 2, or $j$ which are used to indicate each medium may be dropped for brevity. Then, the osmotic pressure is given by[17]

$$\Pi = 2n_b kT[\cosh\beta\varphi - 1]$$

The osmotic pressure term in eq 1 vanishes for a perfect dielectric (or conducting) medium.

The evaluation of the force can be simplified by using the following mechanical equilibrium condition of the system in consideration (see the Appendix).

$$\int_\Sigma \left\{-\left(\Pi + \frac{1}{2}\epsilon E^2\right)\mathbf{I} + \epsilon\mathbf{EE}\right\}\cdot\mathbf{n}\, \mathrm{d}S \left(=\int_\Sigma \mathbf{T}\cdot\mathbf{n}\, \mathrm{d}S\right) = 0 \qquad (3)$$

Now, we apply the above result to cases I, II, and III to obtain the force acting on the droplet−fluid interface. It is assumed that the Debye length is much smaller than the dimension of the droplet, so that the electrical double layer is localized within a small region near the substrate surface.

(16) Jones, T. B. *Langmuir* **2002**, *18*, 4437−4443.
(17) Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*, 6th ed.; John Wiley & Sons: New York, 1997; Chapter 13.
(18) Yaminsky, V.; Nylander, T.; Ninham, B. *Langmuir* **1997**, *13*, 1746−1757.
(19) Russel, W. B.; Saville, D. A.; Schowalter, W. R. *Colloidal Dispersions*; Cambridge University Press: Cambridge, 1989; Chapter 4.

**Constant-Potential Case (Case I).** In this case, the electrostatic potential is constant over the substrate surface, that is, $\varphi = V$ on $S_{13}$ and $S_{23}$. The force acting on the droplet–fluid interface in eq 1 can be decomposed to the forces acting on the droplet side ($\mathbf{F}_1$) and the fluid side ($\mathbf{F}_2$), respectively:

$$\mathbf{F} = \mathbf{F}_1 + \mathbf{F}_2 = -\int_{S_{12}} \mathbf{T}\cdot\mathbf{n}\ \mathrm{d}S - \int_{S_{21}} \mathbf{T}\cdot\mathbf{n}\ \mathrm{d}S \quad (4)$$

The integration domains in the above equation can be converted to more convenient surfaces to integrate by using eq 3, so that

$$\mathbf{F}_1 + \mathbf{F}_2 = \int_{S_{1\infty}+S_{13}} \mathbf{T}\cdot\mathbf{n}\ \mathrm{d}S + \int_{S_{2\infty}+S_{23}+S_{22}} \mathbf{T}\cdot\mathbf{n}\ \mathrm{d}S$$

We consider these two force components separately. At a sufficiently far distance from TCL ($S_{1\infty}$), there is no electrostatic field normal to the control surface, such that $\mathbf{E}\cdot\mathbf{n}|_{S_{1\infty}} = 0$, and therefore the force acting on the droplet side ($\mathbf{F}_1$) becomes

$$\mathbf{F}_1 = -\int_{S_{1\infty}}\left(\Pi + \frac{1}{2}\epsilon_1 E^2\right)\mathbf{n}\ \mathrm{d}S + \int_{S_{13}}\left[-\left(\Pi + \frac{1}{2}\epsilon_1 E^2\right)\mathbf{n} + \epsilon_1(\mathbf{n}\cdot\mathbf{E})\mathbf{E}\right] \mathrm{d}S \quad (5)$$

Since $W_{\mathrm{el}} = -\mathbf{F}\cdot\mathbf{e}_x$, we are here interested only in the horizontal component of $\mathbf{F}_1$, that is, $f_{1x} = \mathbf{F}_1\cdot\mathbf{e}_x$. At the horizontal substrate surface, $\mathbf{n}\cdot\mathbf{e}_x|_{S_{13}} = 0$. Thus, from the foregoing equation, we obtain

$$f_{1x}^{(\mathrm{I})} = -\int_{S_{1\infty}}\left(\Pi + \frac{1}{2}\epsilon_1 E^2\right)\mathbf{n}\cdot\mathbf{e}_x\ \mathrm{d}S + \int_{S_{13}} \epsilon_1(\mathbf{n}\cdot\mathbf{E})\mathbf{E}\cdot\mathbf{e}_x\ \mathrm{d}S \quad (6)$$

Since the electrostatic potential is constant over the substrate surface (i.e., $\varphi|_{S_{13}} = V$), $\mathbf{E}\cdot\mathbf{e}_x|_{S_{13}} = -(\partial\varphi/\partial x)|_{S_{13}} = 0$. Therefore, the second integral in eq 6 vanishes. On the other hand, the first integral in eq 6 corresponds to the free energy (per unit surface area) of the plane electrical double layer. Consequently,[21]

$$f_{1x}^{(\mathrm{I})} = -8\frac{n_{1b}kT}{\kappa_1}\left[\cosh\frac{\beta V}{2} - 1\right] \quad (7)$$

With a similar procedure to obtain $f_{1x}^{(\mathrm{I})}$, the horizontal component of the force acting on the fluid side ($S_{21}$) can be obtained as

$$f_{2x}^{(\mathrm{I})} = 8\frac{n_{2b}kT}{\kappa_2}\left[\cosh\frac{\beta V}{2} - 1\right] \quad (8)$$

Therefore, the net horizontal component of the force acting on the droplet–fluid interface toward the *negative x*-direction, which is the wetting tension $W_{\mathrm{el}}^{(\mathrm{I})} = -f_{1x}^{(\mathrm{I})} - f_{2x}^{(\mathrm{I})}$, becomes

$$W_{\mathrm{el}}^{(\mathrm{I})} = 8kT\left(\frac{n_{1b}}{\kappa_1} - \frac{n_{2b}}{\kappa_2}\right)\left[\cosh\frac{\beta V}{2} - 1\right] \quad (9)$$

The wetting tension in this constant-potential case is identical to the surface-tension renormalization term of electrocapillarity. No extra terms which represent the local electrostatic interaction at TCL arise except for the (primary) electrocapillary terms. Consequently, the wetting tension in this case is independent of the droplet profile near TCL although the electric field near TCL will be significantly perturbed due to its interaction with the droplet surface.

**Constant-Charge Case (Case II).** In this case, the surface charge densities on $S_{13}$ and $S_{23}$ are kept constant with $\sigma_1$ and $\sigma_2$, respectively. In this case too, the net force acting on the droplet–fluid interface can be represented as a sum of the force acting on $S_{12}$ and $S_{21}$ as shown in eq 4. By noting that $\mathbf{n}\cdot\mathbf{e}_x|_{S_{13}} = 0$ again, the force acting on $S_{12}$, $f_{1x}^{(\mathrm{II})}$, can be written in the identical form to eq 6 as

$$f_{1x}^{(\mathrm{II})} = -\int_{S_{1\infty}}\left(\Pi + \frac{1}{2}\epsilon_1 E^2\right)\mathbf{n}\cdot\mathbf{e}_x\ \mathrm{d}S + \int_{S_{13}} \epsilon_1(\mathbf{n}\cdot\mathbf{E})\mathbf{E}\cdot\mathbf{e}_x\ \mathrm{d}S \quad (10)$$

The first integral in eq 10 becomes identical to eq 7. The difference with case I comes from the second term of eq 10. On the substrate surface, $\epsilon_1\mathbf{E}\cdot\mathbf{n}|_{S_{13}} = -\sigma_1$, and therefore,

$$\int_{S_{13}} \epsilon_1(\mathbf{n}\cdot\mathbf{E})\mathbf{E}\cdot\mathbf{e}_x\ \mathrm{d}S = \sigma_1\int_0^\infty \frac{\partial\varphi}{\partial x}\,\mathrm{d}x = \sigma_1(\varphi_{1\infty} - \varphi_0)$$

where $\varphi_0$ represents the electrostatic potential at TCL and $\varphi_{1\infty}$ denotes the electrostatic potential far from TCL. Therefore, the force acting on $S_{12}$ becomes

$$f_{1x}^{(\mathrm{II})} = -8\frac{n_{1b}kT}{\kappa_1}\left[\cosh\frac{\beta\varphi_{1\infty}}{2} - 1\right] + \sigma_1(\varphi_{1\infty} - \varphi_0)$$

A similar result is obtained for the force acting on $S_{21}$, as was done in case I, as follows:

$$f_{2x}^{(\mathrm{II})} = 8\frac{n_{2b}kT}{\kappa_2}\left[\cosh\frac{\beta\varphi_{2\infty}}{2} - 1\right] + \sigma_2(\varphi_0 - \varphi_{2\infty})$$

Thus, the wetting tension in eq 2, which is $W_{\mathrm{el}}^{(\mathrm{II})} = -f_{1x}^{(\mathrm{II})} - f_{2x}^{(\mathrm{II})}$ in this case, becomes

$$W_{\mathrm{el}}^{(\mathrm{II})} = \left\{\frac{8n_{1b}kT}{\kappa_1}\left[\cosh\frac{\beta\varphi_{1\infty}}{2} - 1\right] - \sigma_1\varphi_{1\infty}\right\} - \left\{\frac{8n_{2b}kT}{\kappa_2}\left[\cosh\frac{\beta\varphi_{2\infty}}{2} - 1\right] - \sigma_2\varphi_{2\infty}\right\} + (\sigma_1 - \sigma_2)\varphi_0 \quad (11)$$

The first and second terms in eq 11 come from the electrostatic free energy (per unit surface area) of the electrical double layer having constant charge density.[21] That is, the two terms represent the normal electrocapillary force. An edge-effect term of $(\sigma_1 - \sigma_2)\varphi_0$ appears in addition to the electrocapillary term, as a result of Coulombic interaction near TCL, which is distinct from the earlier constant-potential case (case I).

In the constant-potential case, the wetting tension $W_{\mathrm{el}}^{(\mathrm{I})}$ in eq 9 is independent of the geometry of the interface. However, in the present case (case II), $\varphi_0$ (the electrostatic potential at TCL) is evidently anticipated to depend on the contact shape of the droplet with the substrate. To determine the wetting tension, therefore, the electrostatic field around TCL should be analyzed. The solution of the Poisson–Boltzmann equation should rely on a numerical method, which is not carried out in the present work, and will be a subject to be pursued in a future investigation.

(20) Landau, L. D.; Lifshitz, E. M. *Electrodynamics of Continuous Media*; Pergamon Press: Sydney, 1960; Chapter 2.
(21) Overbeek, J. T. G. *Colloids Surf.* **1990**, *51*, 61–75.

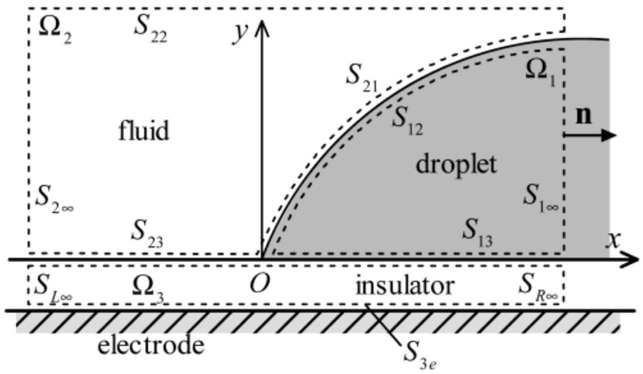


**Figure 3.** Control surfaces for case III.

**Electrowetting on Dielectrics (Case III).** A procedure similar to that of cases I and II can be adopted to obtain the wetting tension in this case. There is a thin dielectric region beneath the droplet and the fluid region, which requires a special consideration (see Figure 3). The domain of integration for the force acting on droplet−fluid interface in this case is transformed as follows:

$$f_x^{(\mathrm{III})} = \mathbf{e}_x\cdot\int_{S_{13}+S_{1\infty}} \mathbf{T}\cdot\mathbf{n}\ \mathrm{d}S + \mathbf{e}_x\cdot\int_{S_{23}+S_{22}+S_{2\infty}} \mathbf{T}\cdot\mathbf{n}\ \mathrm{d}S \quad (12)$$

As in eqs 7 and 8 of case I, the integrals become at the control surfaces far from TCL ($S_{1\infty}$, $S_{2\infty}$)

$$\mathbf{e}_x\cdot\int_{S_{1\infty}} \mathbf{T}\cdot\mathbf{n}\ \mathrm{d}S = -8\frac{n_{1b}kT}{\kappa_1}\left[\cosh\frac{\beta\varphi_{1\infty}}{2} - 1\right]$$

$$\mathbf{e}_x\cdot\int_{S_{2\infty}} \mathbf{T}\cdot\mathbf{n}\ \mathrm{d}S = 8\frac{n_{2b}kT}{\kappa_2}\left[\cosh\frac{\beta\varphi_{2\infty}}{2} - 1\right]$$

Here, $\varphi_{1\infty}$ and $\varphi_{2\infty}$ are the potentials at the droplet−substrate and the fluid−substrate interfaces far from TCL. On the horizontal substrate surfaces, $\mathbf{n}\cdot\mathbf{e}_x|_{S_{13},S_{23}} = 0$, and consequently $\mathbf{e}_x\cdot\int_{S_{13},S_{23}}(\Pi + (1/2)\epsilon E^2)\mathbf{n}\ \mathrm{d}S = 0$. Therefore, eq 12 is reduced to

$$f_x^{(\mathrm{III})} = -8\frac{n_{1b}kT}{\kappa_1}\left[\cosh\frac{\beta\varphi_{1\infty}}{2} - 1\right] + 8\frac{n_{2b}kT}{\kappa_2}\left[\cosh\frac{\beta\varphi_{2\infty}}{2} - 1\right] + \int_{S_{13}+S_{23}} \epsilon(\mathbf{E}\cdot\mathbf{e}_x)\mathbf{E}\cdot\mathbf{n}\ \mathrm{d}S \quad (13)$$

The integrals at $S_{13}$ and $S_{23}$ in eq 13 can be converted to the boundary integrals in the insulator region ($\Omega_3$) beneath the droplet. For this, it will be shown that the integral on $S_{13}$ and $S_{23}$ in eq 13 can be converted to that at the adjacently facing surface of $S_{31}$ and $S_{32}$. Since $\mathbf{e}_x\cdot\mathbf{n}|_{S_{31}} = \mathbf{e}_x\cdot\mathbf{n}|_{S_{32}} = 0$, it becomes

$$\mathbf{e}_x\cdot\int_{S_{31}+S_{32}}\left[-\frac{1}{2}\epsilon E^2\mathbf{n} + \epsilon\mathbf{E}(\mathbf{E}\cdot\mathbf{n})\right]\mathrm{d}S = \int_{S_{31}+S_{32}} \epsilon(\mathbf{E}\cdot\mathbf{e}_x)\mathbf{E}\cdot\mathbf{n}\ \mathrm{d}S$$

The normal electric flux at the vertically adjacent points on the liquid−substrate and the fluid−substrate interfaces should be continuous; therefore,

$$\epsilon\mathbf{E}\cdot\mathbf{n}|_{S_{13},S_{23}} = -\epsilon\mathbf{E}\cdot\mathbf{n}|_{S_{31},S_{32}}$$

Here, we assume that there is no specifically adsorbed ionic species on the droplet−substrate and fluid−substrate interfaces.[22] The tangential component of the electric field should also be continuous, so that

$$\mathbf{E}\cdot\mathbf{e}_x|_{S_{13},S_{23}} = \frac{\partial\varphi}{\partial x}\Big|_{S_{13},S_{23}} = \frac{\partial\varphi}{\partial x}\Big|_{S_{31},S_{32}} = \mathbf{E}\cdot\mathbf{e}_x|_{S_{31},S_{32}}$$

Therefore, it becomes

$$\int_{S_{13}+S_{23}} \epsilon(\mathbf{E}\cdot\mathbf{e}_x)\mathbf{E}\cdot\mathbf{n}\ \mathrm{d}S = -\int_{S_{31}+S_{32}} \epsilon(\mathbf{E}\cdot\mathbf{e}_x)\mathbf{E}\cdot\mathbf{n}\ \mathrm{d}S \quad (14)$$

In $\Omega_3$, the following relation holds, due to the mechanical equilibrium condition of eq 1:

$$\mathbf{e}_x\cdot\int_{S_{31}+S_{32}} \mathbf{T}'\cdot\mathbf{n}\ \mathrm{d}S = -\mathbf{e}_x\cdot\int_{S_{L\infty}+S_{R\infty}+S_{3e}}\left(-\frac{1}{2}\epsilon E^2\mathbf{n} + \epsilon\mathbf{E}\mathbf{E}\cdot\mathbf{n}\right)\mathrm{d}S \quad (15)$$

where $\mathbf{T}' = -(1/2)\epsilon E^2\mathbf{I} + \epsilon\mathbf{E}\mathbf{E}$. At the point far from TCL in $\Omega_3$, the equipotential line is parallel to the substrate. Thus, the electrostatic field has only a vertical component, that is, $\mathbf{E}\cdot\mathbf{n}|_{S_{R\infty},S_{L\infty}} = 0$, and

$$\mathbf{E}_{1,2} = -\frac{\partial\varphi}{\partial y}\mathbf{e}_y \cong \frac{V - \varphi_{1,2\infty}}{d}\mathbf{e}_y$$

for a small thickness of the dielectric substrate $d$. Here, $V$ is the externally applied electric potential at the electrode, $\epsilon_3$ is the electric permittivity of the insulating layer, and $\mathbf{e}_y$ is the unit vector in the vertical direction. On the horizontal electrode surface ($S_{3e}$), $\mathbf{n}\cdot\mathbf{e}_x = 0$ and $\mathbf{E}\cdot\mathbf{e}_x = -\partial\varphi/\partial x = 0$, so there is no contribution from $S_{3e}$ to the integral in eq 15. It follows, then, that

$$\int_{S_{L\infty}+S_{R\infty}+S_{3e}} \mathbf{e}_x\cdot(\mathbf{T}'\cdot\mathbf{n})\ \mathrm{d}S = \frac{\epsilon_3}{2d}[(V - \varphi_{1\infty})^2 - (V - \varphi_{2\infty})^2] \quad (16)$$

Substitution of eq 16 into eq 13 by using eqs 14 and 15 leads to the wetting tension

$$W_{\mathrm{el}}^{(\mathrm{III})} = -f_x^{(\mathrm{III})} = \frac{\epsilon_3}{2d}[(V - \varphi_{1\infty})^2 - (V - \varphi_{2\infty})^2] + 8\frac{n_{1b}kT}{\kappa_1}\left[\cosh\frac{\beta\varphi_{1\infty}}{2} - 1\right] - 8\frac{n_{2b}kT}{\kappa_2}\left[\cosh\frac{\beta\varphi_{2\infty}}{2} - 1\right] \quad (17)$$

The second and third terms on the right-hand side of eq 17 are again the normal electrocapillary terms which originated from the electrical double layer.

It would be interesting to consider the case in which the surrounding fluid is air. Assuming air as a perfect dielectric, $\varphi_{2\infty} = V$ and $\kappa_2^{-1} = 0$, we find that the second term inside the first bracket and the third term of eq 17 vanish. Furthermore, if the droplet phase is a perfect conductor, $\varphi_{1\infty} = 0$. Then the term appearing in the conventional electrowetting equation[8,14,16] of

$$\cos\theta = \cos\theta_0 + \frac{\epsilon_3 V^2}{2d\gamma}$$

(22) The case with specific adsorption of ionic species on substrate surface can be analyzed in a similar fashion. In that case, however, the contribution from that to the wetting tension includes an integral form of, for instance, $\int_0^\infty \sigma(\partial\varphi/\partial x)|_{S_{13}}\ \mathrm{d}x$ which cannot be simplified further. Here, we neglect the influence of specifically adsorbed ionic species for brevity of formula and more clear comparison with the thermodynamic result.

is recovered as a special case of eq 17 as

$$W_{\mathrm{el}}^{(\mathrm{III})} = \frac{\epsilon_3 V^2}{2d} \tag{18}$$

Jones[16] was first to use the Maxwell stress tensor to show the correspondence of the electromechanical force (per unit perimeter of a droplet) to the wetting tension appearing in the electrowetting equation. Later, Kang[14] obtained the result of eq 18 by direct integration of the Maxwell stress using the solution of the electrostatic field around a perfectly conducting droplet. To obtain an analytical expression of the electrostatic field, the electric permittivity of the surrounding fluid was assumed to be the same as that of the insulating layer. Moreover, the shape of the droplet edge was assumed to be a perfect wedge. The result of eq 17 clearly shows that the result of Kang is valid, irrespective of the shape of the droplet edge and the electric permittivity of the surrounding fluid.

**Thermodynamic Derivation.** It will be briefly shown here that the thermodynamic approach generates the same wetting tensions obtained by the electromechanical approach. The electrostatic free energy ($G_{\mathrm{el}}^{(i)}$) of the present system is written as[21]

$$G_{\mathrm{el}}^{(i)} = \int_{\Sigma_{\mathrm{tot}}} \sigma\varphi \, \mathrm{d}S - \int_{\Omega_{\mathrm{tot}}} \left(\frac{1}{2}\epsilon E^2 + \Pi\right) \mathrm{d}\Omega + \Delta G_{\mathrm{el,res}}^{(i)} \tag{19}$$

in which $i$ = I, II, and III. Here $\Sigma_{\mathrm{tot}}$ and $\Omega_{\mathrm{tot}}$ represent the total surfaces and volumes throughout the system, and $\Delta G_{\mathrm{el,res}}^{(i)}$ represents the free-energy change of the charge reservoir with respect to a reference value.

The thermodynamic definition of electrostatic wetting tension becomes

$$\delta G_{\mathrm{el}}^{(i)} = -W_{\mathrm{Th}}^{(i)} \delta S_{13} \tag{20}$$

The electric field near TCL is independent of the displacement of the contact line ($\delta S_{13}$), for a fixed droplet profile close to TCL.[23] As in the case of surface tension, therefore, we have to consider only the change of the surface area of each region. However, the volume integral term in $G_{\mathrm{el}}^{(i)}$ also varies with $\delta S_{13}$. It is because the integral domain of each region in $\Omega_{\mathrm{tot}}$ in eq 19 changes in conjunction with $\delta S_{13}$.

In cases I and III, there exists a net flux of charge from the charge reservoir to satisfy the constant-potential condition on the electrode surface, which is represented by[21]

$$\Delta G_{\mathrm{el,res}}^{(\mathrm{I,III})} = -\int_{\Sigma_{\mathrm{tot}}} \sigma\varphi \, \mathrm{d}S$$

It follows, then, that

$$G_{\mathrm{el}}^{(\mathrm{I,III})} = -\int_{\Omega_{\mathrm{tot}}} \left(\frac{1}{2}\epsilon E^2 + \Pi\right) \mathrm{d}\Omega$$

The change of free energy of the system in this case comes from the change of the volume of each region due to the incremental change of $S_{13}$, that is,

$$\delta G_{\mathrm{el}}^{(\mathrm{I})} = -8kT\left(\frac{n_{1b}}{\kappa_1} - \frac{n_{2b}}{\kappa_2}\right)\left[\cosh\frac{\beta V}{2} - 1\right]\delta S_{13}$$

in case I. Thus

$$W_{\mathrm{Th}}^{(\mathrm{I})} = 8kT\left(\frac{n_{1b}}{\kappa_1} - \frac{n_{2b}}{\kappa_2}\right)\left[\cosh\frac{\beta V}{2} - 1\right] \tag{21}$$

This is equal to that obtained by the mechanical approach of eq 9. In case III, an additional free energy contribution from the parallel capacitor region formed by the insulating layer should be considered. It can be shown that $W_{\mathrm{Th}}^{(\mathrm{III})}$ is also identical to that obtained by the electromechanical approach.

In case II, there certainly exists a net flux of charge from the charge reservoir to the present system in consideration to satisfy the constant-charge condition at the substrate surface corresponding to $\delta S_{13}$, which amounts to $(\sigma_1 - \sigma_2)\varphi_0\delta S_{13}$. To be compatible with eq 11 for the wetting tension, the change of free energy of the charge reservoir should be written as $\Delta G_{\mathrm{el,res}}^{(\mathrm{II})} = -\int_{\Sigma\mathrm{tot}} \sigma\varphi_0 \, \mathrm{d}S + c$, in which $c$ is a constant. Then, we obtain from eq 19

$$G_{\mathrm{el}}^{(\mathrm{II})} = \int_{\Sigma_{\mathrm{tot}}} \sigma(\varphi - \varphi_0) \, \mathrm{d}S - \int_{\Omega_{\mathrm{tot}}} \left(\frac{1}{2}\epsilon E^2 + \Pi\right) \mathrm{d}\Omega + c \tag{22}$$

It can be shown that $W_{\mathrm{Th}}^{(\mathrm{II})}$ is also the same as the wetting tension given in eq 11.[24]

## Concluding Remarks

In the present investigation, the Coulombic contribution to the wetting tension for the three representative charge-related wetting configurations is analyzed by invoking the electromechanical approach. The wetting tension is obtained by integrating the Maxwell stress and osmotic pressure acting on the droplet surface. They are alternatively derived by using the thermodynamic approach, which validates the results of the electromechanical approach. The two approaches are in fact complementary to each other. However, the electromechanical approach is beneficial in that it can provide more direct insight on the nature of the electrical effects on wetting.

The wetting tension is composed of the electrocapillary term which results from the interfacial energy of the droplet−substrate interface and the additional edge-effect term. In case I (constant-potential case), it is revealed that only the electrocapillary term, which is independent of the interface shape of the TCL region, contributes to the wetting tension. In case II (constant-charge case), in addition to the normal electrocapillary term, the edge-effect term also contributes to the wetting tension. This edge-effect term can be determined by analyzing the electrostatic field around TCL, and therefore, the wetting tension is certainly dependent on the interface shape of the TCL region.

In case III (electrowetting on dielectrics), the wetting tension includes the edge-effect term as well as the electrocapillary term. The edge-effect term can also be identified as the Lippmann effect by considering the

(23) The change of the interface shape around TCL can give rise to an additional change of the (excess) electrostatic free energy of the system. This should be accounted for on the basis of the *line tension* effect, which is beyond the scope of the present investigation.

(24) Case II of the present investigation is identical to the case considered by Chou (ref 15) by using a thermodynamic approach. The wetting tension in Chou's modified equation of Young (eq 3 in ref 15) corresponds to $W_{\mathrm{el}}^{(\mathrm{II})} = -(\sigma_1 - \sigma_2)\varphi_0$ which is equivalent to the last term of eq 11, but with different sign.

electrostatic free energy of the insulating layer. Since the terms are not directly related with the free energy of the droplet–substrate interface, it may be more suitable to be considered as the edge-effect term.

On the basis of the present analysis, it can be stated that the charge-related wetting phenomenon is primarily a consequence of stress acting on the droplet surface. The stress will certainly change the microscopic profile of a droplet surface. Then, the free energy of the system due to van der Waals interaction which is dependent on the microscopic shape of the interface will change. In the present analysis, only the direct influences of the Coulombic interaction are considered and any other secondary effects which may arise in conjunction with the interface deformation are neglected. An ultimate assessment of the complete Coulombic interaction effect should include the resolution of the secondary effects, and the present investigation may form a beginning theoretical basis toward such investigations.

**Acknowledgment.** The present investigation was supported by the Brain Korea 21 Program in 2002 and by the Pohang Steel Company (POSCO) Technology Development Fund in 2002 (Contract No. 1UD02013) administered by the Pohang University of Science and Technology. I.S.K. was also supported by a grant from the Korea Science and Engineering Foundation (KOSEF) (Contract No. R01-2001-00410).

## Appendix: Mechanical Equilibrium Condition

From the divergence theorem and a vector identity, it becomes for the volume Ω (having a uniform electric permittivity) enclosed by the surface Σ

$$\int_\Sigma \epsilon(\mathbf{n}\cdot\mathbf{E})\mathbf{E}\,\mathrm{d}S = \int_\Omega \epsilon\nabla\cdot(\mathbf{E}\mathbf{E})\,\mathrm{d}\Omega = \int_\Omega \epsilon\left[\mathbf{E}(\nabla\cdot\mathbf{E}) + \frac{1}{2}\nabla(\mathbf{E}\cdot\mathbf{E})\right]\mathrm{d}\Omega$$

Then, by using the Poisson–Boltzmann equation [$\nabla\cdot\mathbf{E} = -\nabla^2\varphi = -(\kappa^2/\beta)\sinh\beta\varphi$] and the definition of the Debye length ($\kappa^2 = 2n_b kT\beta^2/\epsilon$), the foregoing relation can be rewritten as

$$\int_\Sigma \epsilon(\mathbf{n}\cdot\mathbf{E})\mathbf{E}\,\mathrm{d}S = \int_\Omega \nabla\left\{2n_b kT[\cosh\beta\varphi - 1] + \frac{1}{2}\epsilon\mathbf{E}\cdot\mathbf{E}\right\}\mathrm{d}\Omega$$

If the volume integral of the foregoing relation is converted to a surface integral by using the divergence theorem, the following relation can be derived.

$$\int_\Sigma \left\{-\left(\Pi + \frac{1}{2}\epsilon E^2\right)\mathbf{I} + \epsilon\mathbf{E}\mathbf{E}\right\}\cdot\mathbf{n}\,\mathrm{d}S \;(= \int_\Sigma \mathbf{T}\cdot\mathbf{n}\,\mathrm{d}S) = 0$$

The above equation in fact states that the electrostatic force acting on a volume Ω is balanced by the electrostatic pressure force acting on the enclosing surface Σ,[20] that is, the mechanical equilibrium condition.

LA034163N