How Electrostatic Fields Change Contact Angle in Electrowetting

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The electrowetting phenomenon is investigated in the viewpoint of the classical electrostatics. Special attention is devoted to excavating the influence of excess charge induced at the edge region of a droplet. For this, the electrostatic field around an infinite wedge is analyzed, assuming the droplet as a perfect conductor. It is shown that the Maxwell stress is concentrated on the small region comparable to the thickness of the thin dielectric film beneath the liquid droplet. On the basis of the macroscopic balance condition of the horizontal-force components at the three-phase contact line, the conventional electrowetting equation is derived. This result suggests that macroscopic changes of contact angle originated from the electrostatic force, rather than from the change of the interfacial tension at the droplet–dielectric interface. Moreover, as the apparent contact angle becomes small, the vertical component of the electrostatic force, which would oppose the reduction of contact angle, increases significantly. This can be another possible cause of the limited validity of the conventional electrowetting equation and subsequent occurrence of contact-angle saturation phenomenon.

Introduction

The electrical control of wettability of liquids on a dielectric solid, which is called electrowetting, draws much attention nowadays as a microfluidic actuation mechanism in integrated microfluidic devices. The electrowetting can be used as a very fast and efficient means to deliver and mix micro- or nanoliter volumes of liquid droplets with a relatively low electrical potential and power consumption.[1,2] Furthermore, the fluid motion can be controlled reversibly over hundreds of thousands of cycles by changing the magnitude of the applied potential.[1] A lens of variable focal length,[3] electrically addressable operations of aqueous liquids,[2,4] and electrowetting-assisted coating process[5] demonstrate the various potential applications of such useful characteristics of the electrowetting (see also, Quilliet and Berge[6]).

The electrowetting equation which relates the change of contact angle with externally applied electrical potential can be derived from the Lippmann equation employing the parallel-capacitor approximation for the droplet–dielectric interface.[7] It can be alternatively derived by way of the minimum free-energy requirement for ther-modynamic equilibrium conditions,[8] as follows

$$\cos \theta = \cos \theta_{o} + \frac{\epsilon V^{2}}{2\gamma_{12}d} \tag{1}$$

Here, θ_{o} is the contact angle without externally applied electrical potential, θ is the contact angle under the electrical potential of V, ϵ is the electric permittivity of the dielectric layer beneath the droplet, γ_{12} is the interfacial tension between liquid droplet and surrounding fluid, and d is the thickness of dielectric layer.

The above equation has been successfully implemented by many investigators in correlating empirical results on contact angles within a moderate change of contact angle.[8,9] Such a success has made the electrowetting phenomenon to be understood, by many investigators, within the category of the electrocapillarity. That is, the reduction of contact angle due to external electrical potential is regarded as originating from the change of liquid–dielectric interfacial tension due to the induced electrical charge at the interface. It is a more or less dubious reasoning, however, considering that the free-energy contribution of the electrical double layer in the liquid phase is not likely to be significant enough to drive such a large change of contact angle.[10] A few other deficiencies of the Lippmann phenomenon as a governing mechanism of the electrowetting phenomena were mentioned by Digilov.[11]

In contrast with the interpretation relying on the Lippmann phenomenon, Digilov[11] suggested, based on a thermodynamic analysis, that the change of contact angle is due to the line tension. Here, the line tension is in fact an electrostatic force originating from the excess electrical

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(1) Prins, M. W. J.; Welters, W. J. J.; Weekamp, J. W. Fluid control in multichannel structures by electrocapillary pressure. *Science* **2001,** *291,* 277–280.

(2) Lee, J.; Moon, H.; Fowler, J.; Schoellhammer, T.; Kim, C.-J. Electrowetting and electrowetting-on-dielectric for microscale liquid handling. *Sens. Actuators* **2002,** *95,* 259–268.

(3) Berge, B.; Peseux, J. Variable focal lens controlled by an external voltage: An application of electrowetting. *Eur. Phys. J.* **2000,** *E3,* 159–163.

(4) Pollack, M. G.; Fair, R. B.; Shenderov, A. D. *Appl. Phys. Lett.* **2000,** *77,* 1725–1726.

(5) Blake, T. D.; Clarke, A.; Stattersfield, E. H. An investigation of electrostatic assist in dynamic wetting. *Langmuir* **2000,** *16,* 2928–2935.

(6) Quilliet, C.; Berge, B. Electrowetting: a recent outbreak. *Curr. Opin. Colloid Interface Sci.* **2001,** *6,* 34–39.

(7) Vallet, M.; Vallade, M.; Berge, B. Limiting phenomena for the spreading of water on polymer films by electrowetting. *Eur. Phys. J.* **1999,** *B11,* 583–591.

(8) Verheijen, H. J. J.; Prins, M. W. J. Reversible electrowetting and trapping of charge: model and experiments. *Langmuir* **1999,** *15,* 6616–6620.

(9) Welters, W. J. J.; Fokkink, L. G. J. Fast electrically switchable capillary effects. *Langmuir* **1998,** *14,* 1535–1538.

(10) Peykov, V.; Quinn, A.; Ralston, J. Electrowetting: a model for contact-angle saturation. *Colloid Polym. Sci.* **2000,** *278,* 789–793.

(11) Digilov, R. Charge-induced modification of contact angle: the secondary electrocapillary effect. *Langmuir* **2000,** *16,* 6719–6723.

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charge at the three-phase contact line. His assertion was disputed by Quilliet and Berge[6] because the excess capacitance of the edge region was estimated to be very small compared to that of the parallel capacitor region.[7,8] The past experience that there is little dependency of contact angle on the system size also has made it difficult to regard the line tension as a driving mechanism of the electrowetting phenomenon.
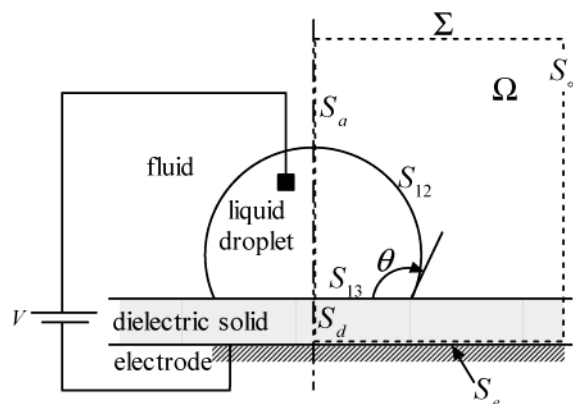
Jones[12] insisted that the electrostatic driving force could be obtained within the electromechanical framework for the case of capillary-rise system. Due to the macroscopic nature of his derivation method, however, the electrostatic force could not be localized as to where it acts on the liquid.

As described above, there is not any convincing theory to draw a firm conclusion on which mechanism does play a dominant role in the contact-angle change in electrowetting, not to mention of any reliable explanations for the occurrence of contact-angle saturation and edge instability.[6-10,13,14] The main cause of such uncertainties seems to come from the deficiency in systematic analysis, concerned with the electrowetting phenomenon, on the force which intervenes between the external work and the change of contact angle. In this paper, mechanical origin of still ambiguous electrowetting phenomena is pursued, relying on the classical electrostatics. Following the notion of Quilliet and Berge,[6] the role of excess charge present at the three-phase contact line is specifically illuminated.

The potential-dependent wetting of aqueous liquids on self-assembled monolayers (SAMs) shares common features in some part with the conventional electrowetting.[15,16] However, the electrowetting on SAMs is significantly influenced by electrochemical reactions of surface species, such as the adsorption/desorption and oxidation/reduction processes.[17-19] For the time being, therefore, the scope of the present investigation will, rather, be limited to the case of electrochemically inert substrates having ideal dielectric properties.

Analysis

Let us consider the right-hand half plane of the droplet placed on an infinite size of planar thin dielectric solid having the electric permittivity of ϵ_3 (see Figure 1). There is an electrode in contact with the dielectric layer. The droplet is assumed to be a perfect conductor and is surrounded by an immiscible, perfectly insulating fluid having the electric permittivity of ϵ_2. Hereafter, the subscripts 1, 2, and 3 indicate the variables associated

(12) Jones, T. B. On the relationship of dielectrophoresis and electrowetting. *Langmuir* **2002**, *18*, 4437−4443.

(13) Janocha, B.; Bauser, H.; Oehr, C.; Brunner, H.; Göpel, W. Competitive electrowetting of polymer surfaces by water and decane. *Langmuir* **2000**, *16*, 3349−3354.

(14) Seyrat, E.; Hayes, R. A. Amorphous fluoropolymers as insulators for reversible low-voltage electrowetting. *J. Appl. Phys.* **2001**, *90*, 1383−1386.
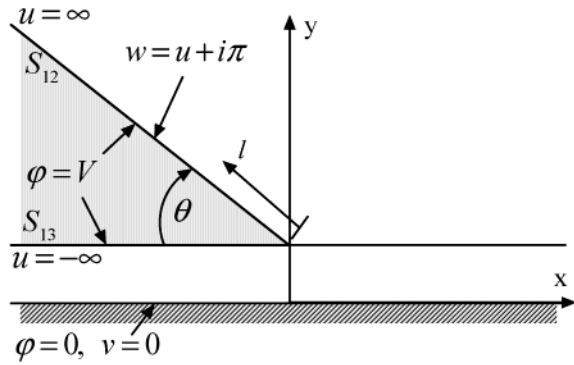
(15) Sondag-Huethorst, J. A. M.; Fokkink, L. G. J. Potential-dependent wetting of octadecanethiol-modified polycrystalline gold electrodes. *Langmuir* **1992**, *8*, 2560−2566.

(16) Sondag-Huethorst, J. A. M.; Fokkink, L. G. J. Electrical double layers on thiol-modified polycrystalline gold electrodes. *J. Electroanal. Chem.* **1994**, *367*, 49−57.

(17) Sondag-Huethorst, J. A. M.; Fokkink, L. G. J. Potential-dependent wetting of electroactive ferrocene-terminated alkanethiolate monolayers on gold. *Langmuir* **1994**, *10*, 4380−4387.

(18) Abbott, N. L.; Whitesides, G. M. Potential-dependent wetting of aqueous solutions on self-assembled monolayers formed from 15-(ferrocenylcarbonyl)pentadecanethiol on gold. *Langmuir* **1994**, *10*, 1493−1497.

(19) Gorman, C. B.; Biebuyck, H. A.; Whitesides, G. M. Control of the shape of liquid lenses on a modified gold surface using an applied electrical potential across a self-assembled monolayer. *Langmuir* **1995**, *11*, 2242−2246.

Figure 1. Schematic sketch of domain of interest. The surface S_∞ is taken at an infinitely remote distance from the droplet.

with the droplet, surrounding fluid, and dielectric layer, respectively. The overall results of the present investigation are also applicable to the capillary rise situation,[1,9,12] although it will not be specifically dealt with here.

Within the surrounding fluid and dielectric layer, the electrostatic potential (φ) satisfies the following Laplace equation

$$\nabla^2 \varphi = 0$$

An external potential of V is applied to the droplet, so that $\varphi = V$ on S_{12} and S_{13}. The bottom electrode is grounded, so that $\varphi = 0$ on S_e. On the dielectric-fluid interface, $\|\epsilon \mathbf{E} \cdot \mathbf{n}\| = 0$ and $\|\mathbf{E} \cdot \mathbf{t}\| = 0$, which result from the Gauss law and Stokes law, respectively.[20] Here, $\|f\|$ denotes the difference of a function (f) across the interface, $\mathbf{E} = \nabla \varphi$, $\mathbf{n}$ denotes the unit normal vector, and $\mathbf{t}$ denotes the unit tangential vector on interfaces.

The electrostatic force acting on the droplet surface becomes, neglecting the osmotic contributions,[21]

$$\mathbf{F}_d = \int_{S_{12}+S_{13}} \mathbf{T} \cdot \mathbf{n} \, dS \tag{2}$$

Here, $\mathbf{T}$ is the Maxwell stress tensor which is written as

$$\mathbf{T} = -\frac{1}{2} \epsilon E^2 \mathbf{I} + \epsilon \mathbf{E}\mathbf{E} \tag{3}$$

where $\mathbf{I}$ denotes the second-order isotropic tensor, and $E = |\mathbf{E}|$. On a surface of a conductor, there is no tangential electric field and the surface charge density (σ) is related with the electric field as $\sigma = \epsilon \mathbf{E} \cdot \mathbf{n}$. On the surface of the droplet, therefore, $\sigma = \epsilon \mathbf{E} \cdot \mathbf{n}$, $\mathbf{E} = E\mathbf{n}$, and $E = \mathbf{E} \cdot \mathbf{n}$. The force acting on the droplet becomes

$$\mathbf{F}_d = \int_{S_{12}+S_{13}} \frac{1}{2} \epsilon (\mathbf{E} \cdot \mathbf{n}) \mathbf{E} \, dS = \int_{S_{12}+S_{13}} \frac{1}{2} \epsilon \mathbf{n} E^2 \, dS =$$
$$\int_{S_{12}+S_{13}} \frac{1}{2} \sigma \boldsymbol{E} \, dS \tag{4}$$

It is evident from the above equation that the electric field exerts a nonvanishing net force on the droplet surface, which is normal to the surface and directed outward with respect to the droplet, i.e., a negative pressure force. The magnitude and direction of the net force vector are

(20) Landau, L. D.; Lifshitz, E. M. *Electrodynamics of Continuous Media*; Pergamon Press: Sydney, 1960; Chapter 2.

(21) Russel, W. B.; Saville, D. A.; Schowalter, W. R. *Colloidal Dispersions*; Cambridge University Press: Cambridge, 1989; Chapter 4.

Figure 2. Edge of a droplet for electrostatic analysis.

dependent on the electrostatic potential distribution which is a function of geometry of the droplet.

Vallet et al.[7] analyzed the electrostatic field near the edge region, regarding the edge region of the droplet as an infinite planar wedge as shown in Figure 2. They assumed that the electric permittivities of the dielectric layer and the fluid phase are the same. This is not an unrealistic assumption because the relative permittivity of polymeric substrates which have been used in the previous experiments is actually about 2. In the present investigation, the result of Vallet et al.[7] is used to obtain the surface-charge distribution.

The following Schwarz−Christoffel transformation is introduced for the analysis of the potential problem

$$Z = \int_{i\pi}^{w} (e^{w'} + 1)^{\alpha} \, dw' + i\pi \qquad (5)$$

where $Z = x + iy$, $i = \sqrt{-1}$, and $w = u + iv$ are the complex coordinates of the transformed plane. The transformed coordinates u and v are scaled by d/π and V/π, respectively. The parameter $\alpha = p/q$, in which p and q are positive integers, is related with the contact angle as $\alpha = 1 - \theta/\pi$. On the wedge surface, where $w = u + i\pi$, the distance from the apex of the wedge (l) becomes, from eq 5,

$$dl/du = d/\pi \, |e^{u} - 1|^{\alpha} \qquad (6)$$

Thus,

$$l = d/\pi \int_{0}^{u} |e^{u'} - 1|^{\alpha} \, du' \qquad (7)$$

Vallet et al.[7] obtained the charge density as follows, due to the Schwarz−Christoffel transformation of eq 5,

$$\frac{\sigma}{\sigma_o} = \frac{1}{|(e^{w} + 1)^{\alpha}|} \qquad (8)$$

where $\sigma_o = \epsilon V/d$ denotes the charge density at the droplet−dielectric interface, far from the three-phase contact line. On the surface of the wedge, it becomes

$$\frac{\sigma}{\sigma_o} = \begin{cases} 1/(e^{u} - 1)^{\alpha}, & \text{on } S_{12} \\ 1/(1 - e^{u})^{\alpha}, & \text{on } S_{13} \end{cases} \qquad (9)$$

Figure 3 shows the calculated charge density on the wedge surface for a typical case of $\theta = 60°$. The charge density near the apex becomes very high relative to that at the parallel capacitor region in which $\sigma/\sigma_o = 1$. Most of the excess charges induced by the edge effect are distributed within the region of $O(d)$. Since the Maxwell stress is related with the surface-charge density as σ^2/ϵ, the electrostatic stress will be confined within the edge region.
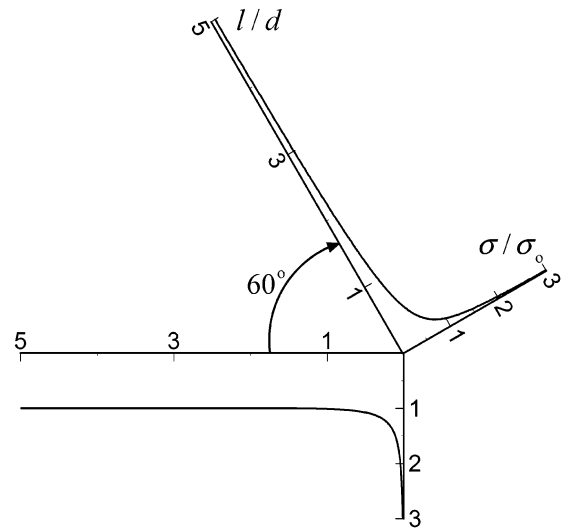
Figure 3. Charge distribution around the wedge for $\theta = 60°$.
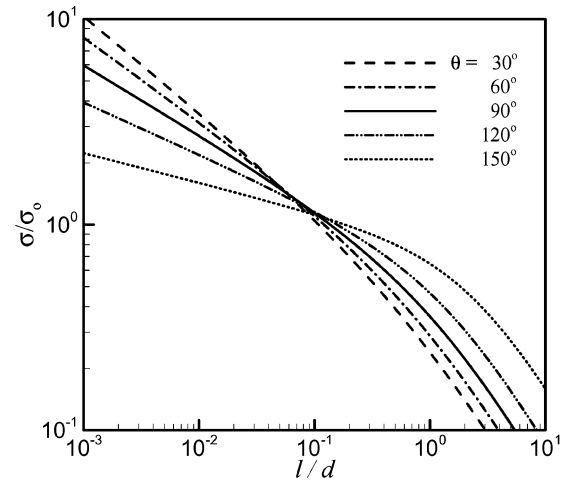
Figure 4. Charge distribution on the upper surface of the wedge.

Figure 4 shows the charge density on S_{12} for different contact angles, with respect to the distance from the apex. When the wedge becomes sharper, the degree of charge concentration on the apex region becomes more apparent.

Figure 5 shows a horizontal component of the Maxwell stress, i.e., $(\sigma/\sigma_o)^2 \sin \theta$, with respect to the vertical distance measured from the fluid−dielectric interface. It is reconfirmed that most of the horizontal component of the stress acting on the surface is concentrated on a thin region of $O(d)$.
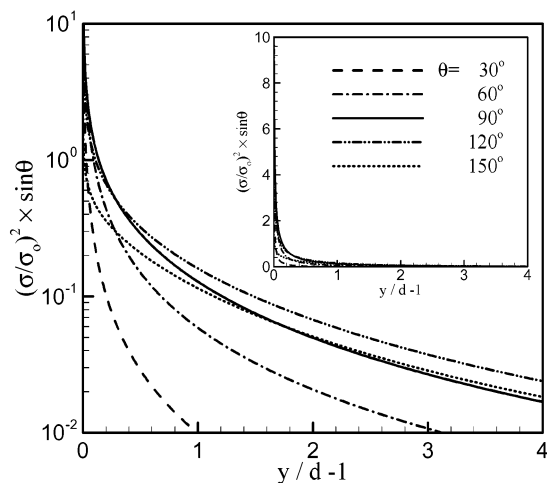
The net electrostatic force acting on the upper side of the wedge due to the Maxwell stress (F_e) becomes, from eq 4,

$$F_e = \int_{S_{12}} \frac{\sigma^2}{2\epsilon} \, dl = \frac{\epsilon V^2}{2d^2} \int_{S_{12}} \frac{1}{(e^{u} - 1)^{2\alpha}} \, dl \qquad (10)$$
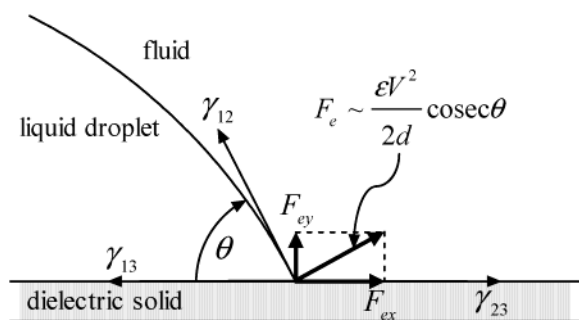
By using the differential relation between the length along the droplet surface and the complex coordinate u, eq 6, the above equation can be rewritten as

$$\frac{\epsilon V^2}{2\pi d} \int_{0}^{\infty} \frac{1}{(e^{u} - 1)^{\alpha}} \, du$$

The integral in the above equation becomes, by changing

Figure 5. Distribution of horizontal component of the Maxwell stress on the upper surface of the wedge.

Figure 6. Electrostatic force and its influence on horizontal balance of forces acting on the three-phase contact line.

the variables as $t = e^u - 1$, as follows[22]

$$\int_0^\infty \frac{\mathrm{d}u}{(e^u - 1)^\alpha} = \int_0^\infty \frac{t^{\theta/\pi - 1}}{t + 1}\,\mathrm{d}t = \frac{\pi}{\sin\theta}$$

Therefore, the net electrostatic force acting on S_{12}, which is always directed outward with respect to the droplet, can be obtained as

$$F_e = \frac{\epsilon V^2}{2d}\operatorname{cosec}\theta \qquad (11)$$

This force can be decomposed into horizontal (F_{ex}) and vertical parts (F_{ey}), respectively, as

$$F_{ex} = \frac{\epsilon V^2}{2d}, \quad F_{ey} = \frac{\epsilon V^2}{2d}\cot\theta \qquad (12a,b)$$

It is very interesting that the horizontal force component is independent of the contact angle. This force would pull the three-phase contact line until the force balance with the dragging force of surface tensions is attained (see Figure 6). On the other hand, as shown in Figure 5, the Maxwell stress is concentrated within a very small region of the droplet edge, which is comparable to the thickness of the dielectric layer. The thickness of the dielectric layer is typically in the order of micrometers while the size of the droplet is typically in the order of millimeters. Thus, in the macroscopic sense, the stress can be represented with point force acting on the three-phase contact line.

(22) Gradshteyn, I. S.; Ryzhik, I. M. *Table of Integrals, Series, and Products*; Academic Press: London, 1965; p 289.

The macroscopic balance of horizontal force components for a very small volume of liquid at the contact point results in the following relation which is actually identical to the conventional electrowetting equation (see, eq 1).

$$\gamma_{12}\cos\theta = \gamma_{23} - \gamma_{13} + \frac{\epsilon V^2}{2d} \qquad (13)$$

This consistency of the present results with the conventional electrowetting equation is an encouraging one. It should be noted that the last term in the above equation comes from the Maxwell stress. This term, in fact, corresponds to the so-called *electrocapillary pressure*.[1,12]

The effect of the present electrostatic force shares common features with the line-tension effect suggested by Digilov.[11] It should be noted, however, that there is a clear distinction in their origin. The line tension of Digilov arises due to the excess free energy at the three-phase contact line, with separate consideration of the contribution from the electrostatic pressure. It is reasonable to think that his generalized Young's equation (eq 33 of Digilov[11]) corresponds to the case of microscopic contact angle, while eq 13 corresponds to the case of macroscopic, or apparent contact angle.

The vertical component of the electrostatic force seems to have very important implications. The vertical force acting on liquid surface sharply increases with $\cot\theta$ when the contact angle decreases. In the mechanical viewpoint, this upward electrostatic stress resists the decrease of the contact angle which is driven by the horizontal component of the electrostatic force. This can be another possible cause of contact-angle-saturation phenomenon, together with the electron-discharge mechanism of Vallet et al.,[7] the charge-trapping mechanism of Verheijen and Prins,[8] and the material-defect mechanism of Seyrat and Hayes.[14]

To make a firm conclusion on the interplay of these electrostatic force components, it is necessary to take into consideration of the microscopic deformation of interface in the analysis. However, it is evident that to reduce the contact angle for a small θ, a considerable amount of excess work should be done to overcome the vertical force component. The electrical work done on the system can be stored in the form of curvature energy.

Concluding Remarks

The electrowetting phenomenon is illuminated within the framework of the classical electrostatics. The present model suggests that the phenomenon originated from the electrostatic pressure, which is a direct consequence of the excess charge at the three-phase contact line, rather than from the change of apparent interfacial tension at the droplet−dielectric interface.

The Maxwell stress exerts an outward normal force of eq 11 on the edge of the contact line and is confined to a small region comparable to the thickness of dielectric layer. The force is responsible for the spreading of a droplet and subsequent change of contact angle. Thus, according to the present model, the change of contact angle and the net driving force of spreading are not independent, which is evidently opposed to the notion of Jones,[12] and are closely linked each other.

From the balance condition of horizontal forces, the conventional electrowetting equation of eq 1 is derived. However, the upward vertical force, which resists the reduction of contact angle, increases as $\cot\theta$, with the reduction of contact angle. It means, therefore, a considerable amount of excess work should be done, to reduce

the contact angle when the contact angle is small. This result suggests that the validity of eq 1 is limited within a certain range of contact angles around 90°. Moreover, the resisting role of the vertical force against the decrease of contact angle may be related with the occurrence of contact-angle-saturation phenomenon and potentially with the subsequent edge instability which occurs at even higher voltages.

The electrowetting on SAMs involves more complicated electrochemical processes; however, it shows some common features with the conventional electrowetting for chemically stable monolayers. These are, for instance, the pronounced wettability change for thinner monolayers[16] and negligible contribution of diffuse electrical double layers to the overall capacitance.[15,16] This strongly suggests that the mechanism discussed in this paper will take on an important role in the potential-dependent wetting on SAMs also (together with other electrochemical processes and short-ranged interactions).

A few important simplifications are made to obtain a closed form of solution. One of them is the negligence of the contribution of the electrical double layer, by assuming the droplet as a perfect conductor. The suppression of edge instability by salt addition[7] appears to manifest the influence of the electrical double layer. The electrical double layer will perturb the electrostatic field near the three-phase contact line to some extent. The author is now performing an investigation to excavate this aspect. Second, the electric permittivity of the substrate layer and surrounding fluid are assumed to be the same. Although the results of the thermodynamic analysis of eq 1 strongly suggest that the dependency should not be strong, clear evidence is not obtained by the present investigation, which also requires further studies.

Furthermore, it should be noted that the validity of the results of the present investigation is rather limited to the case of substrates having ideal dielectric properties. Other physical and chemical properties of substrate material, such as piezoelectricity,[13] charge-trapping characteristic,[8] and material defect,[14] can have significant influences on the electrowetting phenomenon. Further investigation is necessary to excavate the influence of such parameters on electrowetting.

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