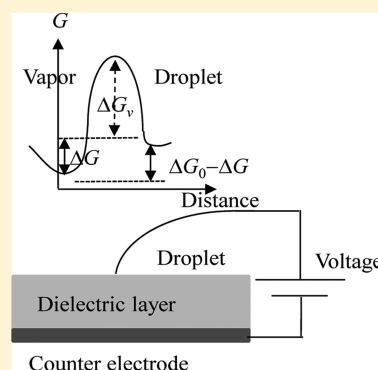


Analysis of Electrowetting of a Conducting Droplet on a Dielectric Layer

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S Supporting Information

ABSTRACT: Electrowetting has been used to actuate and control the motion of droplets on solid surfaces. An analysis based on the theories of thermodynamics and thermal activation processes is presented for the electrowetting of a conducting droplet on a dielectric layer. The concept of release rate of electric energy is proposed. The release rate of electric energy is proportional to the square of the applied electric voltage and the derivative of electric capacitance with respect to the surface area of the corresponding electric system. The velocity of a contact line under the action of an electric voltage is a hyperbolic sine function of the release rate of electric energy. Using the release rate of electric energy and introducing line tension in the analysis, the contact angle of a droplet at a stationary state under the action of a constant electric voltage is found to be a linear function of the release rate of electric energy and the line tension. The line tension introduces the droplet-size effect on the contact angle. A critical contact angle as a function of the applied electric voltage, the thickness of the dielectric layer, and the radius of the contact area is obtained. There exist stable and unstable zones, depending on the relative value of the contact angle and the critical contact angle. There exists an upper bound of electric voltage with the corresponding contact angle of 65.89° between 60 and 70° of the saturated contact angle reported for electrowetting of conducting droplets. This result suggests that the saturation of contact angle likely is related to the condition determining the field-induced stability of the contact line.



1. INTRODUCTION

Electrowetting is referred to as the field-induced change of the wetting of a liquid on a solid. Using electrowetting to control the shape and motion of liquid droplets has attracted great attention in microfluidics,^{1–3} drug delivery,³ and micro-optics.^{4–6} Electrowetting is related to electrocapillarity, which was first observed by Lippmann⁴ in studying the effect of electric voltage on the capillary rise of mercury. Lippmann⁴ introduced the concepts that the surface tension is a function of electric voltage and the change of surface tension with applied voltage induces surface charges on the surface of a liquid droplet.

Various approaches have been used to analyze the dependence of contact angle on applied voltage, including thermodynamics,^{7–9} energy minimization,¹⁰ and electromechanics.^{11,12} All of these studies have found that the contact angle under the action of an electric voltage is a linear function of the square of the applied voltage. Recently, Wang and Zhao¹³ used the method of energy minimization to analyze electrowetting on curved surfaces and discussed the effect of line tension. They obtained a similar result; i.e., the contact angle is a linear function of the square of the applied voltage.

Generally, most of the studies have been focused on the equilibrium state of the contact line under the action of an electric voltage. There is little study addressing the effect of

electric field on the stability and motion of the contact line. In this work, the stability of the contact line of a conducting droplet on a dielectric layer under the action of an electric field is analyzed. The effect of electric field and line tension on the spreading parameter is also discussed.

2. RELEASE RATE OF ELECTRIC ENERGY

It is known that one can introduce the potential energy of a solid body, Π , in the calculation of strain energy release rate¹⁴ as

$$\Pi = \int_V \left(\int_0^{\epsilon_{ij}} \sum_{i,j=1}^3 \sigma_{ij} d\epsilon_{ij} \right) dV - \int_{\Xi} \mathbf{t} \cdot \mathbf{u} d\Xi - \int_V \mathbf{F} \cdot \mathbf{u} dV \quad (1)$$

where σ_{ij} and ϵ_{ij} are the components of stress tensor and strain tensor, respectively, \mathbf{t} and \mathbf{F} are the surface force and body force applied to the material, respectively, \mathbf{u} is the displacement vector, Ξ is the surface area, and V is the volume of the solid body. The first term in eq 1 represents the strain energy stored in the solid, and the second and third terms represent the

Received: September 9, 2014

Revised: October 24, 2014

Published: October 25, 2014

mechanical work done to the solid by the surface force and body force, respectively. For linearly elastic materials, eq 1 can be reduced to

$$\Pi = \int_V \frac{1}{2} \sum_{i,j=1}^3 \sigma_{ij} \varepsilon_{ij} dV - \int_{\Xi} \mathbf{t} \cdot \mathbf{u} d\Xi - \int_V \mathbf{F} \cdot \mathbf{u} dV \quad (2)$$

Consider a droplet of a conducting liquid placed on a smooth surface of a linear dielectric solid, as shown in Figure 1. The

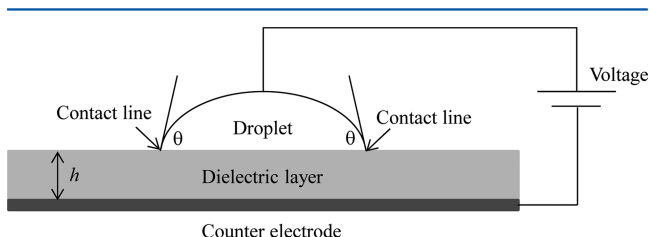


Figure 1. Schematic of electrowetting of a conducting droplet on a dielectric layer.

droplet is under the action of an electric field with the potential difference between the droplet and the counter electrode being φ . The solid is inert and homogeneous, and the mechanical deformation of the solid under the action of the electric field and the droplet is assumed to be negligible. Similarly, one can define a potential energy, U_e , of the electromechanical system as

$$U_e = \int_{\varphi_1}^{\varphi_2} Q d\varphi - \frac{1}{2} \int_{\Omega} \sum_{i=1}^3 E_i D_i d\Omega \quad (3)$$

where Q is the electric charge on the surface/interface of the droplet, φ is the electric voltage applied to the droplet, E_i and D_i ($i = 1, 2, 3$) are the components of electric field intensity and electric displacement vector, respectively, and Ω is the total volume of the system. Note that there is a sign difference between eq 2 and eq 3. Obviously, the electric charge is analogous to mechanical force, and the potential to displacement. The first term on the right side of eq 3 represents the work done by changing the electric voltage between the droplet and the counter electrode, and the second term represents the electric energy stored in the system. There are two limiting cases for electric loading; one is constant voltage, and the other is constant charge. The release rate of electric energy can be calculated as

$$G_e = -\frac{1}{2} Q \left(\frac{\partial \varphi}{\partial A} \right)_Q \quad \text{for constant charge} \quad (4)$$

$$G_e = \frac{\partial U_e}{\partial A} = \frac{1}{2} \varphi \left(\frac{\partial Q}{\partial A} \right)_{\varphi} \quad \text{for constant voltage} \quad (5)$$

For the derivation of eq 4, see the Supporting Information. For the general case, there is

$$G_e = \frac{\partial U_e}{\partial A} = -\frac{1}{2} Q^2 \frac{\partial}{\partial A} \left(\frac{\varphi}{Q} \right) \quad \text{for the general case} \quad (6)$$

where A is the area of the interface between the droplet and the environment. Obviously, eqs 4 and 5 can be easily derived from eq 6.

The electric capacitance of an electrical system, C , can be calculated as

$$C = \frac{Q}{\varphi} \quad (7)$$

Substituting eq 7 in eq 6, one obtains

$$G_e = \frac{1}{2} \varphi^2 \frac{\partial C}{\partial A} \quad (8)$$

The release rate of electric energy is proportional to the square of electric voltage and the derivative of the electric capacitance with respect to the area of interface between the droplet and the environment.

3. ELECTROWETTING EQUATION

As used by Digilov⁹ and Wang and Zhao,¹³ one can approximate the shape of a droplet on a solid surface as a spherical cap. The contact line, depicted in Figure 1, can start to move under the action of an electric voltage. Although the droplet will retain the shape of spherical cap, the motion of the contact line leads to the change of free energy and causes the system to move to the equilibrium state.

For a system which is isolated thermally and mass-conservatively, chemical potential has no effect on the equilibrium state of the system. The free energy of the system, F , with the dimensions of the droplet smaller than the capillary length is

$$F = \gamma A_{lv} + \pi r^2 (\gamma_{sl} - \gamma_{sv}) + 2\pi r \tau + \frac{1}{2} \int_{\Omega} \sum_{i=1}^3 E_i D_i d\Omega \quad (9)$$

where γ is the surface energy of the liquid/vapor interface, γ_{sl} is the surface energy of the solid/liquid interface, γ_{sv} is the surface energy of the solid/vapor interface, A_{lv} is the area of the liquid/vapor interface, r is the contact radius between the droplet and the solid surface, and τ is the line tension of the contact line. Note that the line tension is the specific free energy of the three-phase contact line,^{15,16} as first suggested by Gibbs,¹⁵ who stated that "We may here remark that a nearer approximation to the theory of equilibrium and stability might be obtained by taking special account, in our general equations, of the lines in which surfaces of discontinuity meet. These lines might be treated in a manner entirely analogous to that in which we have treated surfaces of discontinuity. We might recognize linear densities of energy, of entropy, and of the several substances which occur about the line, also a certain linear tension."

Using the relation among the droplet volume, the area of the liquid/vapor interface, the contact angle, and the contact radius and Young's relation for the contact angle without the action of an electric field,¹⁶ eq 9 can be rewritten as

$$F = \gamma \pi r^2 \left(\frac{2}{1 + \cos \theta} - \cos \theta_0 \right) + 2\pi r \tau + \frac{1}{2} \int_{\Omega} \sum_{i=1}^3 E_i D_i d\Omega \quad (10)$$

where θ is the contact angle of the droplet under the action of an electric voltage, and θ_0 is the contact angle without electric field.

Assume that the contribution of viscous dissipation to the change of the system energy is negligible in the analysis, since the motion of a contact line generally is much slower. The change of the free energy of the system then can be calculated as

$$dF = \pi \left[\gamma r^2 \left(\frac{2}{1 + \cos \theta} - \cos \theta_0 \right) \right] + 2\pi \, d(\tau r) + d \left(\frac{1}{2} \int_{\Omega} \sum_{i=1}^3 E_i D_i \, d\Omega - \int_{V_1}^V Q \, dV \right) \quad (11)$$

If the surface energies and the line tension are independent of the droplet size, eq 11 can be simplified as

$$\frac{dF}{dr} = 2\pi\gamma r(\cos \theta - \cos \theta_0) + 2\pi\tau - G_e \frac{dA}{dr} \quad (12)$$

for the motion of the contact line maintaining the concentricity of the contact area and the constraint of constant volume. For the derivation of eq 12, see the Support Information.

At the equilibrium state, there is $dF = 0$. Equation 12 gives

$$\cos \theta = \cos \theta_0 - \frac{\tau}{\gamma r} + \frac{G_e}{2\pi\gamma r} \frac{dA}{dr} \quad (13)$$

The contact angle of the droplet under the action of an electric voltage is a linear function of the release rate of electric energy. Substituting eq 8 in eq 13, one has

$$\cos \theta = \cos \theta_0 - \frac{\tau}{\gamma r} + \frac{\varphi^2}{4\pi\gamma r} \frac{\partial C}{\partial A} \frac{dA}{dr} \quad (14)$$

The contact angle of the droplet under the action of an electric voltage is a quadratic function of the electric voltage applied to the conducting droplet, similar to the results given by Berge¹⁰ and Wang and Zhao;¹³ it is also a linear function of the derivative of the electric capacitance with the surface area. For $\varphi = 0$, eq 14 reduces to the modified Young's equation¹⁶ of the equilibrium condition for any point at the three-phase contact line, which considers the contribution of line tension. The line tension introduces the droplet-size effect on the contact angle for the electrowetting of a droplet, which differs from the typical electrowetting relationship.

It is worth mentioning that, for the electrowetting of a liquid between two parallel electrodes, the contribution of electric energy to the equilibrium condition of the contact line, i.e., the last term on the right side of eq 12, becomes $-G_e$. Using eq 8 and the definition of z direction (which is the opposite of the outward normal of the liquid/vapor interface) given by Jones,¹² one has

$$-G_e = -\frac{1}{2}\varphi^2 \frac{\partial C}{\partial A} = \frac{\varphi^2}{2} \frac{\partial C}{\partial z} \quad (15)$$

which gives the same result as eq 5 of Jones' work¹² per unit length of the contact line. Note that the right side of eq 15 represents the force required to counterbalance the electric force due to the change of the capacitance.

For a conducting droplet of spherical cap placed on the surface of a dielectric layer, the electric capacitance consists of two portions: one is associated with air, and the other is associated with the dielectric solid. Using the solid angle corresponding to the surface area of the droplet and the electric capacitance of a conducting sphere, the electric capacitance, C_a , associated with air can be approximately calculated as

$$C_a \approx C_s \Omega_d = \frac{2\pi\epsilon_0}{1 + \cos \theta} \frac{r^2}{a} = \frac{2\pi\epsilon_0 r \sin \theta}{1 + \cos \theta} \quad (16)$$

where ϵ_0 is the dielectric constant of air. See the Supporting Information for the derivation of eq 16.

For the electric capacitance associated with the dielectric layer, the conducting droplet can be approximated as a circular disk. Considering the effect of electric fringe field, the electric capacitance to the second order approximation of h/r for $h/r < 1$ can be expressed as¹⁷

$$C_s \approx \frac{\pi\epsilon r^2}{h} \left[1 + \frac{2h}{\pi r} \ln \left[\frac{8\pi r}{eh} \right] + \left(\frac{h}{\pi r} \ln \left[\frac{h}{8\pi r} \right] \right)^2 \right] \quad (17)$$

with ϵ being the dielectric constant of the dielectric solid and h being the thickness of the dielectric layer. Thus, the electric capacitance of the droplet/solid system is

$$C = C_s + C_a \approx \frac{2\pi\epsilon_0 r \sin \theta}{1 + \cos \theta} + \frac{\pi\epsilon r^2}{h} \left[1 + \frac{2h}{\pi r} \ln \left[\frac{8\pi r}{eh} \right] + \left(\frac{h}{\pi r} \ln \left[\frac{h}{8\pi r} \right] \right)^2 \right] \quad (18)$$

which is dependent on the contact radius and the contact angle.

For $h/r < 1$, the contribution of the electric capacitance from air is much smaller than that from the dielectric solid. The electric capacitance of the droplet/solid system then can be calculated from eq 17, and the release rate of electric energy of the droplet/solid system is

$$G_e \approx \frac{1}{2}\varphi^2 \frac{\partial C_s}{\partial A} = \frac{\pi\epsilon r \varphi^2}{h} \left(1 + \frac{h}{\pi r} \ln \left[\frac{8\pi r}{h} \right] + \frac{h^2}{\pi^2 r^2} \ln \left[\frac{8\pi r}{h} \right] \right) \frac{dr}{dA} \quad (19)$$

Substituting eq 19 into eq 13, one obtains the relationship between the equilibrium contact angle, θ_{eq} , and the applied electric voltage as

$$\cos \theta_{eq} = \cos \theta_0 - \frac{\tau}{\gamma r} + \frac{\epsilon \varphi^2}{2\gamma h} \left(1 + \frac{h}{\pi r} \ln \left[\frac{8\pi r}{h} \right] + \frac{h^2}{\pi^2 r^2} \ln \left[\frac{8\pi r}{h} \right] \right) \quad (20)$$

which reduces to

$$\cos \theta_{eq} = \cos \theta_0 - \frac{\tau}{\gamma r} + \frac{\epsilon \varphi^2}{2\gamma h} \quad (21)$$

for $h \ll r$. For $\tau = 0$, eq 21 is the same as the result given by Berge,¹⁰ who ignored the effect of the fringe field. The dimensionless parameter, Θ_{eq} , is defined as

$$\Theta_{eq} = \left(\cos \theta_{eq} - \cos \theta_0 + \frac{\tau}{\gamma r} \right) \left(\frac{\epsilon \varphi^2}{2\gamma h} \right)^{-1} \quad (22)$$

Figure 2 shows the dependence of the parameter of Θ_{eq} on the ratio of h/r . The parameter of Θ_{eq} increases with the increase of the ratio of h/r . This result suggests that the contact angle of the droplet under the action of an electric voltage is dependent on the ratio of the film thickness to the contact radius as well as the dielectric constant of the dielectric material. There exists a size effect on the behavior of electrowetting.

Chevalliot et al.¹⁸ had examined the thickness effect on the electrowetting of conducting droplets. The liquid used was 0.02 wt % NaCl aqueous solution with 0.028 wt % Triton X102; the dielectric film was Parylene C (chlorinated). The film thicknesses of the dielectric films were 0.43, 1.3, and 5.5 μm . They coated a Fluoropel film of 50 nm in thickness on the

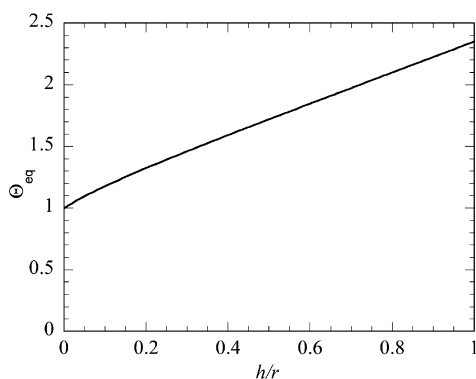


Figure 2. Dependence of the parameter of Θ_{eq} on the ratio of h/r .

surface of the Parylene C films to make the surface hydrophobic and used a droplet of 1 μL in volume in their study.

It is assumed that the droplets were in the shape of a spherical cap. From the volume of the droplets, one can calculate the contact radius of the droplets with substrates under the action of electric voltage. Table 1 lists the contact radius of the droplets on Parylene C films under the action of electric voltages of 20 and 25 V. Obviously, $r > h$, which satisfies the condition of eq 20. χ is defined as

$$\chi = 1 + \frac{h}{\pi r} \ln \left[\frac{8\pi r}{h} \right] + \frac{h^2}{\pi^2 r^2} \ln \left[\frac{8\pi r}{h} \right] \quad (23)$$

which gives

$$\cos \theta_{eq} - \cos \theta_0 = \frac{\varepsilon \varphi^2 \chi}{2\gamma h} \quad (24)$$

for $\tau = 0$. Figure 3 shows the variation of $(\cos \theta_{eq} - \cos \theta_0)$ with χ/h for the experimental results given by Chevalliot et al.¹⁸ For comparison, the experimental results ($\chi = 1$) are also included in Figure 3. It is clear that, for the experimental conditions, the new model of eq 24 gives approximately the same results as the classical electrowetting relationship because of $r \gg h$.

4. STABILITY ANALYSIS OF THE MOTION OF CONTACT LINE

The condition for the onset of the motion of a contact line may be formulated from the concept of the energy balance. A state of equilibrium is reached when the total potential energy of the system has a stationary value with respect to any virtual change in the contact size between the droplet and the solid surface; i.e., $dF = 0$. Define the following quantity, R ,

$$R = \frac{d}{dA_{sl}} (\gamma A_{lv} + A_{sl}(\gamma_{sl} - \gamma_{sv}) + \tau l) \quad (25)$$

which represents the change in the potential energy from the surface energy and the line energy. Here, A_{sl} is the contact area between the droplet and the solid surface and l is the perimeter of the contact edge. The equation at a stationary state is

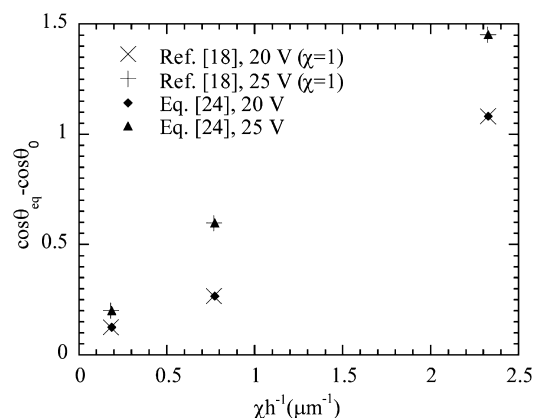


Figure 3. Comparison of numerical results with Chevalliot et al.'s experimental results.¹⁸

$$R = G_e \quad (26)$$

which is the same as $dF = 0$. R characterizes the resistance force associated with the morphological evolution of the droplet. Of the parameters of R and G_e , only R relates directly to intrinsic properties of the droplet/solid system. If the electric energy stored in air is much smaller than that stored in the dielectric layer, eq 8 can be approximated as

$$G_e \approx \frac{1}{2} \varphi^2 \frac{\partial C_s}{\partial A_{sl}} \quad (27)$$

and eq 26 gives

$$\frac{d}{dr} (\gamma A_{lv} + A_{sl}(\gamma_{sl} - \gamma_{sv}) + \tau l) \approx \frac{1}{2} \varphi^2 \frac{\partial C_s}{\partial r} \quad (28)$$

for maintaining the concentricity of the contact area at the stationary state.

Equation 26 can predict the condition for the contact line being stationary, while it is not a condition for continuous spreading of the contact line under the action of electric voltage. For the contact line to continuously move under the action of an electric voltage, the stationary state must be unstable; i.e., any small disturbance to the contact line will lead to the motion of the contact line. To determine the nature, one needs to consider the second derivative of the free energy: i.e., d^2F/dr^2 , for a circular contact area. Whether the system is stable or unstable under the action of an electric voltage depends on whether the second derivative is less than or greater than zero. In terms of R and G_e , one has

$$\frac{dG_e}{dA} > \frac{dR}{dA_{sl}} \quad (\text{unstable}) \quad \frac{dG_e}{dA} < \frac{dR}{dA_{sl}} \quad (\text{stable}) \quad (29)$$

At the stationary state of $dF = 0$, one can obtain a criterion by using the Taylor series expansion to the second term if the contribution of the electric energy stored in air is negligible. This criterion can be written as

Table 1. Contact Radius of Droplets on Parylene C Dielectric Films under the Action of Two Electric Voltages

electric voltage (V)	20			25		
thickness of dielectric film (μm)	0.43	1.3	5.5	0.43	1.3	5.5
contact radius (μm)	850	489	390	1022	657	447

$$\frac{d^2F}{dr^2} > 0 \quad (\text{stable}) \quad \frac{d^2F}{dr^2} < 0 \quad (\text{unstable}) \quad (30)$$

Thus, the critical state is determined by the following equation

$$\frac{d^2F}{dr^2} = 0 \quad (31)$$

Under the condition of constant voltage applied to the droplet, the critical angle, θ_{cr} , can be found from the following equation,

$$\begin{aligned} \cos \theta_{cr} + (2 + \cos \theta_{cr}) \sin^2 \theta_{cr} \\ = \cos \theta_0 + \frac{\varepsilon \varphi^2}{2h\gamma} \left(1 + \frac{h}{\pi r} + \frac{2h^2}{\pi^2 r^2} \log \left[\frac{8\pi r}{eh} \right] - \frac{h^2}{\pi^2 r^2} \left(\log \left[\frac{8\pi r}{eh} \right] \right)^2 \right) \end{aligned} \quad (32)$$

which reduces to

$$\cos \theta_{cr} + (2 + \cos \theta_{cr}) \sin^2 \theta_{cr} = \cos \theta_0 + \frac{\varepsilon \varphi^2}{2h\gamma} \quad (33)$$

for $h \ll r$. The line tension has no effect on the stability of the electrowetting of a conducting droplet on a dielectric layer under the action of an electric voltage. For $h \ll r$, eq 33 suggests that the critical angle is independent of the radius of the contact area, while it is a linear function of $\varepsilon \varphi^2 / 2h\gamma$.

Φ is defined as

$$\Phi = \cos \theta + (2 + \cos \theta) \sin^2 \theta \quad (34)$$

For a droplet of spherical cap with a height of H , there is

$$\sin \theta = \frac{2rH}{H^2 + r^2} \quad \cos \theta = \frac{|H^2 - r^2|}{H^2 + r^2} \quad (35)$$

Substituting eq 35 into eq 34 yields

$$\Phi = \frac{|H^2 - r^2|}{H^2 + r^2} + \left(2 + \frac{|H^2 - r^2|}{H^2 + r^2} \right) \left(\frac{2rH}{H^2 + r^2} \right)^2 \quad (36)$$

which can be readily calculated from the parameters measured in electrowetting tests.

Figure 4 shows the variation of Φ with θ . The function of Φ increases with the increase of θ , reaches the maximum of 2.42 at $\theta_{\max} = 1.15$ (65.89°), and decreases with the increase of θ for θ in the range of 0 to π . For $\theta_{eq} < \theta_{cr} < \theta_{\max}$ or $\theta_{\max} < \theta_{cr} < \theta_{eq}$, the system is unstable. The droplet may spread over the solid surface and become a thin film under the action of an electric voltage for $\theta_{eq} < \theta_{cr} < \theta_{\max}$. For $\theta_{cr} < \theta_{eq} < \theta_{\max}$ or $\theta_{\max} < \theta_{eq} <$

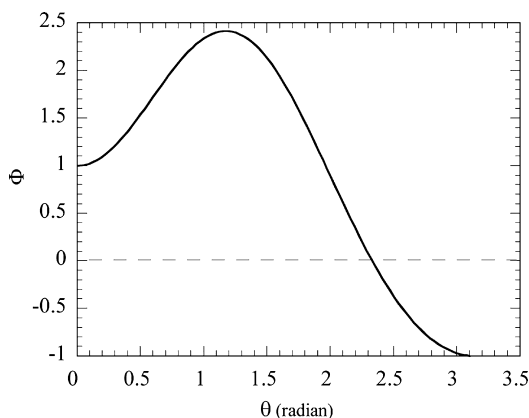


Figure 4. Variation of Φ with θ .

θ_{cr} , the system is stable. Note that Φ must be positive and there is a maximum value of Φ . The maximum value of Φ suggests that there is a maximum electric voltage, corresponding to the upper bound of electric voltage, below which the system may reach a stationary electrowetting state. For an electric voltage larger than the upper bound, there is no solution of eq 32. It is interesting to note that the value of θ_{\max} (65.89°) is between 60 and 70° of the saturated contact angle for electrowetting of conducting droplets.¹⁸ The saturation of contact angle likely is related to the condition determining the field-induced stability of the contact line.

Yeo and Chang¹⁹ suggested that electrowetting behavior can be classified into static electrowetting and spontaneous electrowetting, depending on the electrode configuration adopted. The preceding analysis provides the possible condition for the presence of static electrowetting and spontaneous electrowetting of a conducting droplet on a dielectric substrate. The static electrowetting corresponds to the stable state of the contact line, and spontaneous electrowetting corresponds to the unstable state. Note that the geometrical configuration of the electric system of Yeo and Chang²⁰ is different from the one analyzed in this work.

5. FIELD EFFECT ON THE KINETICS OF ELECTROWETTING

There are two approaches to analyze the motion of a contact line. One is based on hydrodynamic analysis, and the other is based on thermal activation processes (molecular kinetic theory, MKT) as developed by Eyring et al.^{21–23} Cherry and Holmes²⁴ were the first to use the MKT theory to analyze the kinetics of wetting of surfaces and obtained the rate constant for the wetting process which is related to the change of the contact angle. Following an approach similar to that of Cherry and Holmes,²⁴ Blake and Hayes²⁵ derived the velocity of the contact line which is a hyperbolic sine function of $(\cos \theta - \cos \theta_0)$. Their result can reduce to the result of Cherry and Holmes²⁴ if one uses the Taylor series expansion of hyperbolic sine function to the first term. Considering the interaction between liquid molecules and solid molecules and using the MKT theory, Yang²⁶ found that there exists a critical shear stress for the onset of slip flow that is dependent upon the bonding strength between the molecules of liquid and the molecules of solid. Recently, Yuan and Zhao,²⁷ following the same approach as Blake and Hayes,²⁵ obtained the wetting rate under the action of electric voltage simply by adding the contribution from electric voltage.

Considering the importance of electrowetting in micro- and nanofluidics, we analyze the field effect on the wetting kinetics in detail. From a microscopic point of view, the wetting of a droplet on a solid surface occurs when a molecule jumps from inside the droplet to outside the droplet. Generally, the energy state of a molecule inside the droplet is different from that outside the droplet, as shown schematically in Figure 5. There exists an energy barrier that molecules need to overcome in order to escape from the droplet, i.e., desorption. Similarly, molecules need to overcome an energy barrier for them to jump into the droplet, i.e., adsorption. The energy barrier for desorption is different from that for adsorption, and the difference between the energy barrier of inside the droplet and the energy barrier of outside the droplet is ΔG_0 .

The resultant flux for molecules to cross the liquid/vapor interface on the solid surface can be calculated as

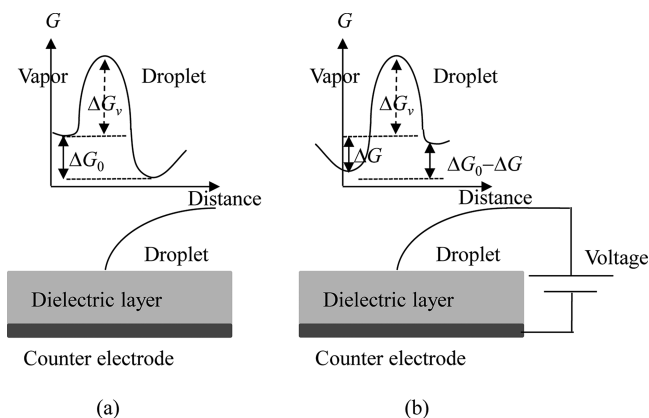


Figure 5. Energy diagram of a molecule near the contact line: (a) without the action of an electric voltage and (b) with the action of an electric voltage.

$$J = \frac{N^+ kT}{\hbar} e^{-(\Delta G_v + \Delta G_0)/kT} - \frac{N^- kT}{\hbar} e^{-\Delta G_v/kT} \quad (37)$$

where N^- and N^+ are the number of molecules per unit volume on the left and right sides of the liquid/vapor interface, respectively, \hbar is the Planck constant, ΔG_v is the energy barrier that molecules need to overcome to jump from the vapor phase to the droplet, k is the Boltzmann constant, and T is absolute temperature. Assume that the average jump distance of molecules is λ . The velocity of the contact line, v , is

$$v = J\lambda = \frac{kT\lambda}{\hbar} (N^+ e^{-(\Delta G_v + \Delta G_0)/kT} - N^- e^{-\Delta G_v/kT}) \quad (38)$$

At the equilibrium state, there is no change of the droplet morphology and the contact line is at a dynamic “stick” state, i.e. $v = 0$. Equation 38 gives

$$N^- e^{-\Delta G_v/kT} = N^+ e^{-(\Delta G_v + \Delta G_0)/kT} \quad (39)$$

As discussed previously, the contact line will move when $R \neq G_e$. The driving force is related to the magnitude of $|R - G_e|$, which results in the change of the energy barrier for the jump of molecules across the contact line. Under the condition that the contact area maintains concentricity and the contribution of the electric energy stored in air is negligible during the motion of the contact line, the change in the energy barrier can be calculated as

$$\Delta G = (R - G_e)\Xi = \left(\gamma(\cos \theta - \cos \theta_0) + \frac{\tau}{r} - G_e \right) \Xi \quad (40)$$

where Ξ is the activation area for the rate process. The energy barriers become $\Delta G_v + \Delta G$ for the jump to the droplet and $\Delta G_v + \Delta G_0 - \Delta G$ for the jump to outside the droplet, and the velocity of the contact line becomes

$$\begin{aligned} v &= \frac{kT\lambda}{\hbar} (N^+ e^{-(\Delta G_v + \Delta G_0 - \Delta G)/kT} - N^- e^{-(\Delta G_v + \Delta G)/kT}) \\ &= \frac{kT\lambda}{\hbar} N^+ e^{-(\Delta G_v + \Delta G_0)/kT} \sinh \left(\gamma(\cos \theta - \cos \theta_0) + \frac{\tau}{r} - G_e \right) \frac{\Xi}{kT} \end{aligned} \quad (41)$$

which is similar to the result given by Blake and Hayes²⁵ for $\tau = 0$ and $G_e = 0$.

The diffusivity of molecules, D , in an isotropic liquid can be calculated as

$$D = \frac{1}{6} \lambda^2 N^+ \frac{kT}{\hbar} e^{-\Delta G^*/kT} \quad (42)$$

with ΔG^* being the energy barrier (activation energy) for the diffusion of molecules. The diffusivity and the viscosity, η , of a liquid can be correlated with the diffusivity by Einstein's relation,^{28,29}

$$\frac{D\eta}{kT} = \frac{1}{2\pi} \left(\frac{1}{\tilde{\Omega}} \right)^{1/3} \quad (43)$$

where $\tilde{\Omega}$ is the molecular volume. Substituting eqs 42 and 43 into eq 41, one obtains

$$\begin{aligned} v &= \frac{3kT}{\pi\eta\lambda} \left(\frac{1}{\tilde{\Omega}} \right)^{1/3} e^{(\Delta G^* - (\Delta G_v + \Delta G_0))/kT} \\ &\quad \times \sinh \left(\gamma(\cos \theta - \cos \theta_0) + \frac{\tau}{r} - G_e \right) \frac{\Xi}{kT} \end{aligned} \quad (44)$$

The value of $\Delta G^* - (\Delta G_v + \Delta G_0)$ ($\equiv -\Delta G^\pm$) represents the difference of the energy barrier between the diffusion inside the droplet and the desorption from the droplet. For $[\gamma(\cos \theta - \cos \theta_0) + \tau/r - G_e]\Xi \ll kT$, eq 44 simplifies to

$$v = \frac{3kT}{\pi\eta\lambda} \left(\frac{1}{\tilde{\Omega}} \right)^{1/3} e^{-\Delta G^\pm/kT} \left(\gamma(\cos \theta - \cos \theta_0) + \frac{\tau}{r} - G_e \right) \frac{\Xi}{kT} \quad (45)$$

The velocity of the contact line is a linear function of $\cos \theta$ and G_e . If $[\gamma(\cos \theta - \cos \theta_0) + \tau/r - G_e]\Xi \gg kT$, there is

$$v = \frac{3kT}{\pi\eta\lambda} \left(\frac{1}{\tilde{\Omega}} \right)^{1/3} e^{-\Delta G^\pm/kT} \exp \left\{ \frac{\Xi}{kT} \left(\gamma(\cos \theta - \cos \theta_0) + \frac{\tau}{r} - G_e \right) \right\} \quad (46)$$

which gives

$$\ln(v) = \ln \left[\frac{3kT}{\pi\eta\lambda} \left(\frac{1}{\tilde{\Omega}} \right)^{1/3} \right] - \frac{\Delta G^\pm}{kT} + \left(\gamma(\cos \theta - \cos \theta_0) + \frac{\tau}{r} - G_e \right) \frac{\Xi}{kT} \quad (47)$$

The logarithm of the velocity of the contact line is a linear function of $\cos \theta$ and G_e .

Substituting eq 19 into eq 44 for a conducting droplet of spherical cap on the surface of a dielectric layer, one obtains

$$\begin{aligned} v &= \frac{3kT}{\pi\eta\lambda} \left(\frac{1}{\tilde{\Omega}} \right)^{1/3} e^{-\Delta G^\pm} \sinh \left(\frac{\Xi}{kT} \right) \left(\gamma(\cos \theta - \cos \theta_0) + \frac{\tau}{r} \right. \\ &\quad \left. - \frac{\varepsilon\varphi^2}{2h} \left(1 + \frac{h}{\pi r} \ln \left[\frac{8\pi r}{h} \right] + \frac{h^2}{\pi^2 r^2} \ln \left[\frac{8\pi r}{h} \right] \right) \right) \end{aligned} \quad (48)$$

which simplifies to

$$v = \frac{3kT}{\pi\eta\lambda} \left(\frac{1}{\tilde{\Omega}} \right)^{1/3} e^{-\Delta G^\pm} \sinh \left(\frac{\Xi}{kT} \right) \left(\gamma(\cos \theta - \cos \theta_0) + \frac{\tau}{r} - \frac{\varepsilon\varphi^2}{2h} \right) \quad (49)$$

for $h \ll r$. The velocity of the contact line is dependent on the size of the droplet and the thickness of the dielectric layer and is a function of the electric voltage applied to the droplet.

Considering the effect of disjoining pressure for a thin liquid film of nanoscale, Yuan and Zhao²⁷ modified the equation of Blake and Hayes²⁵ by adding the related terms. The effect of disjoining pressure represents the contribution of intermolecular interaction. For the wetting/dewetting of ultrathin films, the contribution of intermolecular interaction can be included in the difference of the energy barrier between the adsorption to the film and the desorption from the film. Accordingly, one

obtains the wetting/dewetting rate with an exponential dependence instead of the hyperbolic sine dependence.

6. SUMMARY

Electrowetting has the potential of controlling the motion of liquid droplets and fluid flow for the applications of “lab-on-a-chip”. Considering the important role of electric energy and electric work in manipulating the motion of droplets on solid surfaces, the concept of the release rate of electric energy was proposed in this work. For a conducting droplet on the surface of a dielectric solid layer under the action of an electric voltage, the release rate of electric energy was found to be proportional to the square of the applied voltage and the derivative of electric capacitance with respect to the surface area of the droplet, which is independent of the condition of electric loading. Under the action of electric loading, the contact angle of a conducting droplet at the equilibrium state is a linear function of the release rate of electric energy.

The stability analysis of the wetting of a droplet on a dielectric layer under the action of an electric voltage was analyzed. A critical contact angle as a function of the applied electric voltage, the thickness of the dielectric layer, and the radius of the contact area was obtained. There exist stable and unstable zones, i.e., static electrowetting and spontaneous electrowetting, and there exists an upper bound of electric voltage with the corresponding contact angle of 65.89° between 60 and 70° of the saturated contact angle for electrowetting of conducting droplets on dielectric films.¹⁸ The saturation of contact angle likely is related to the condition determining the field-induced stability of the contact line.

Using the theory of thermal activation processes, the velocity of a contact line under the action of an electric voltage was found to be a hyperbolic sine function of the release rate of electric energy. The velocity of the contact line is dependent on the size of the droplet and the thickness of the dielectric layer and is a function of the electric voltage applied to the droplet. For the radius of the contact area much larger than the thickness of the dielectric layer, the velocity of the contact line is dependent on $\varepsilon\varphi^2/2h$.

■ ASSOCIATED CONTENT

■ Supporting Information

Text describing the derivation of the release rate of electric energy for the condition of constant charge, the derivation of the change of the free energy of the system as a function of the release rate of electric energy, and the calculation of the electric capacitance of the droplet associated with air and a figure showing the potential difference–charge curves under varying conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by the “Opening fund of State Key Laboratory of Nonlinear Mechanics (LNM)”.

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