19 Moving Contact Line Problem in Electrowetting Relevance to Tribological Phenomenon

Ya-Pu Zhao and Ying Wang

CONTENTS

19.1	Introduction	492
19.2	Characteristic Time and Length Scales Relevant to EWOD	
	Phenomenon	495
	19.2.1 Characteristic Timescales	495
	19.2.2 Characteristic Length Scales	496
19.3	Electrowetting Theories	498
	19.3.1 Classical Electrowetting Theory: The Lippmann–Young	
	Equation	498
	19.3.1.1 Thermodynamic Approach	498
	19.3.1.2 Energy Minimization Approach	499
	19.3.1.3 Electromechanical Approach	501
	19.3.2 Extended Lippmann–Young Equations	504
	19.3.2.1 Electrowetting on Rough Surfaces	504
	19.3.2.2 Electrowetting on Curved Surfaces	507
	19.3.2.3 Electrowetting under High Voltage	509
	19.3.2.4 Electrowetting at Micro- and Nanoscales	511
	19.3.3 Contact Angle Hysteresis and Droplet Actuation	513
	19.3.3.1 Contact Angle Hysteresis	513
	19.3.3.2 Minimum Actuation Voltage	515
	19.3.4 Marangoni Convection	516
	19.3.5 Precursor Film	517
	19.3.5.1 Huh–Scriven Paradox	517
	19.3.5.2 Possible Explanations for Huh–Scriven Paradox	518
	19.3.5.3 Molecular Kinetic Theory and Properties of Precursor	
	Film	518
	19.3.6 Spontaneous Electrowetting	521
19.4	Experiments and Molecular Dynamics Simulations	526
	19.4.1 Electrowetting Experiments on Surfaces with	
	Various Configurations	526

19.4.1.1 Electrowetting on Planar Surfaces	527
19.4.1.2 Electrowetting on Rough Surfaces	527
19.4.1.3 Electrowetting on Curved Surfaces	530
19.4.2 Breakdown of the Dielectric Film	532
19.4.3 Voltage-Induced Droplet Actuation	534
19.4.3.1 Droplet Transportation	534
19.4.3.2 Voltage-Induced Droplet Actuation on a Lotus Leaf	536
19.4.3.3 All-Terrain Droplet Actuation	538
19.4.4 In Situ Observation of Thermal Marangoni Convection	539
19.4.5 Electro-Elastocapillarity: Electrowetting on Flexible Substance	541
19.4.6 Electrowetting in a Hydrophilic Interior Corner	542
19.4.7 Electrowetting as a Tool for Suppressing the Coffee Stain	545
19.5 Summary and Conclusions	
Acknowledgments	
Symbols	
References	549

Electrowetting (EW) or electrowetting-on-dielectric (EWOD) has been widely used as a tool for the manipulation of microfluidics in microelectromechanical systems, and there have been rapid developments in the last two decades. In EW, when an external voltage is applied, the contact line of the droplet on solid surface moves until the droplet reaches a new equilibrium. The moving contact line (MCL) phenomenon in EW is a matter of the solid–liquid interface, in which tribology works. This chapter focuses on the MCL problem for EW or EWOD, in which the "Huh–Scriven paradox" is also valid. As a matter of fact, the MCL problem has remained an issue of controversy and debate for more than 40 years since the famous paper by Huh and Scriven in 1971. The difficulty stems partly from the fact that classical hydrodynamic equations coupled with the conventional no-slip boundary condition predict a singularity for the stress that results in a nonphysical logarithmically singular energy dissipation rate at the triple contact line.

After a concise review of the classical EW fundamental theories, we pay special attention to the nanoscale EW, electro-elasto-capillarity and EW on curved surfaces, which are currently being investigated in our group both experimentally and numerically. Precursor film (PF) for planar EW and precursor chain (PC) for EW in an interior corner, together with molecular kinetic theory analysis, are discussed in depth. Both PF and PC are the effective mechanisms to eliminate the nonphysical singular stress distribution and the logarithmically singular energy dissipation rate for the MCL problem under electric field.

19.1 INTRODUCTION

Along with the decreasing system size, properties of microelectromechanical systems (MEMS) and nanoelectromechanical systems (NEMS) will become different

from that of macroscopic systems. Especially, the large surface-area-to-volume ratio raises serious adhesive and frictional problems for their operation, dictating that surface properties are of paramount importance in these miniaturized systems.

The manipulation of a liquid droplet in MEMS and NEMS has been developed rapidly in recent decades, owing to its wide potential use in various fields like biomedicine. Electrowetting (EW) or electrowetting-on-dielectric (EWOD), which alters wettability of a liquid droplet on a solid substrate by introducing a voltage, can be used as one useful method to manipulate individual droplets. Since individual droplets can be handled independently and more easily, which is better than conventional microfluidic devices that are based on continuous flow, EW or EWOD in MEMS and NEMS could provide more chances to application and open wider vistas. In EW, when an external voltage is applied, the contact line of the droplet on the solid surface moves until the droplet reaches a new equilibrium. This moving contact line (MCL) phenomenon in EW is a matter of solid–liquid interface, which is relevant to tribology. A good understanding of the MCL problems in EW will help in better design of MEMS and NEMS based on the EW principle.

Modern EW or EWOD was developed from electrocapillarity, which was first studied and described in detail by Gabriel Lippmann [1], who won the Nobel Prize for physics in 1908 for his method of reproducing colors photographically based on the phenomenon of interference. He carried out experiments to study the electrocapillarity of mercury in contact with electrolyte solutions, finding that the capillary depression of mercury could be influenced by the applied voltage between mercury and the electrolyte solutions. The explanation of this phenomenon was that the induced residual charge altered the solid–liquid interfacial tension γ_{sl} , and the Lippmann equations were put forward:

$$\sigma = -\frac{\partial \gamma_{\rm sl}}{\partial V},\tag{19.1}$$

$$c = \frac{\partial \sigma}{\partial V},\tag{19.2}$$

where σ is the surface charge density, V is the value of the applied voltage, and c is the capacitance per unit area. Lippmann's PhD thesis, presented to Sorbonne University on July 24, 1875, was on electrocapillarity.

Following Lippmann's study, subsequent researches [2,3] concentrated on this voltage-influenced phenomenon, from electrocapillarity to EW, for more than a century. In early EW studies, the droplet was in direct contact with the electrode surface. This made it hard to put it into application because the electrolytic decomposition of water took place when the applied voltage exceeded a few hundred millivolts [4]. This problem was solved by placing a thin insulating layer on the substrate to separate it from the liquid droplet [5,6], which is called EWOD. In this situation, the applied voltage can be increased to hundreds of volts, and the variation in wettability

is reversible over a very large range of contact angles, and thus made it possible to put it into real application. Since EWOD is superior to EW in application, current studies almost concentrate on EWOD rather than EW. Actually, the concepts of EWOD and EW are currently without strict distinction, and EWOD is often called as EW for short, except in special cases.

EWOD has attracted much attention, and relevant investigations have developed fast in recent decades. Lab-on-a-chip (LOC), which has been used in biomedical [7-10] and chemical [11-13] devices, is one of the most popular applications of EWOD. Such EWOD-based devices can be used to manipulate aqueous droplets ranging from nanoliters to microliters in volume [14]. Droplet motions such as dispensing, mixing, merging, splitting, and transport can be realized without the use of conventional pumps, valves, or channels. Transport of droplets is rapid and repeatable, and was demonstrated with well over 100,000 cycles of transfer for a single droplet [14]. Owing to its high level of integration and operational flexibility, LOC devices are promising for use in biomedical instruments, and considerable progress has been made in such applications as sample collection and preparation, DNA analysis and repair, protein recognition, and cell sorting [15]. Microlens is another example of EWOD-controlled application, where the drop is used as an optical lens. Compared with solid lenses, liquid lenses are more flexible with adjustable curvature and focal length, which can be controlled via EWOD. Berge and Peseux [16] pioneered this work by designing an optical system with variable focal length controlled merely by an external voltage. Their results showed that their optical systems were with high quality, speed, and reversibility, demonstrating the possibility of fabricating cheap electrically controllable lenses. More investigations [17-21] on microlens were carried out following their study, including an attempt to develop better conductive liquid droplet and to use liquid lens arrays, intending to optimize the devices and expand their applications. Besides, EWOD can also be used in electronic display technology (such as portable devices). "Droplet-on-a-wristband" for electric signal and droplet connections, which was put forward recently by Fan and coworkers [22], is a promising use of EWOD. Recently, the concept of electronic paper (e-paper) was proposed, and considerable attentions have been paid to such a substrate [23–25] owing to its advantages of flexibility, versatility, and low cost. Electronic devices can be readily fabricated on paper substrate, as was demonstrated by Kim and Steckl [26] who investigated several types of paper. E-paper provides more opportunities to improve the existing electronic display devices and develop new ones.

Scientifically speaking, EW or EWOD can be included into the broader MCL problem, in which the "Huh–Scriven paradox" is also valid. As a matter of fact, the MCL problem has remained an issue of controversy and debate for more than 40 years, ever since the famous paper by Huh and Scriven [27] in 1971. The difficulty stems partly from the fact that classical hydrodynamic equations coupled with conventional no-slip boundary condition predict a singularity for the stress that results in a nonphysical logarithmically singular energy dissipation rate at the triple contact line (TCL).

In this chapter, we will give a brief overview of the fundamentals of EWOD, in conjunction with our group's work. Before delving into a detailed discussion, EWOD-relevant characteristic time and length scales will be presented in Section 19.2. In

Section 19.3, EWOD theories, including the basic and extended equations, droplet actuation principles, and precursor films (PFs), will be introduced. The corresponding experiments and molecular dynamics (MD) simulations will be discussed subsequently in Section 19.4 before the conclusion section.

Note that EWOD is actually a very complex phenomenon, and we do not aim to cover all of the issues in this chapter. We will focus on the MCL problem in EW. PF for planar EW and precursor chain (PC) for EW in an interior corner, together with molecular kinetic theory (MKT) analysis, are discussed in depth. Both PF and PC are effective mechanisms to eliminate nonphysical singular stress distribution and the logarithmically singular energy dissipation rate for the MCL problem under an electric field. We hope that this chapter will help in better understanding of EWOD phenomenon and inspire new investigations and more applications, particularly for the MCL problem in EW.

19.2 CHARACTERISTIC TIME AND LENGTH SCALES RELEVANT TO EWOD PHENOMENON

EWOD-based devices have been used in various fields and applications, as was discussed in the preceding section. Along with the decreasing system size, micro- and nanosystems will perform differently from macroscopic systems. The forces that dominate in macroscopic systems may become unimportant in micro- and nanosystems, whereas others that can be neglected in macrosystems become significant. Surface tension effect is one such example that dominates at micro- and nanoscales due to increase in the surface-to-volume ratio with decreasing size. A clear understanding of relevant characteristic time and length scales would assist the study of the surface effects and help to design new micro- and nanosystems.

19.2.1 CHARACTERISTIC TIMESCALES

The period of a free droplet in free oscillation T_{LR} was given by Lord Rayleigh in 1879 [28], which is called Lord Rayleigh's period:

$$T_{\rm LR} = \frac{\pi}{4} \sqrt{\frac{\rho D^3}{\gamma_{\rm lv}}},\tag{19.3}$$

where γ_{lv} is the liquid–vapor surface tension, ρ is the mass density of the droplet, and *D* is the droplet diameter. In conventional EWOD experiment, where $D \approx 2 \times 10^{-3}$ m, $\gamma_{lv} = 72 \times 10^{-3}$ N/m (at room temperature 25°C), and $\rho \approx 10^3$ kg/m³, then Lord Rayleigh's period $T_{LR} \approx 8.3 \times 10^{-3}$ s.

Another often used characteristic time is the capillary characteristic time T_c , which is based on the mass of the droplet and is defined as follows:

$$T_{\rm c} = \sqrt{\frac{m}{\gamma_{\rm lv}}},\tag{19.4}$$

where *m* is the droplet mass. Combining Equation 19.3 with Equation 19.4, the relationship between the two characteristic timescales can be obtained: $T_{\rm c} = \sqrt{(8/3\pi)}T_{\rm LR} \approx 0.92T.$

Taking the viscosity of the liquid into account, viscous characteristic time T_{vis} can be derived from the capillary number *Ca* (the definition of *Ca* is $Ca = (\eta v / \gamma_{1v}) = (\eta l / \gamma_{1v} t)$, where *v* is the characteristic velocity and *t* is the characteristic time), and its expression is [29]

$$T_{\rm vis} \sim \frac{\eta l}{\gamma_{\rm lv}}$$
 (19.5)

where η is the viscosity of the liquid droplet and *l* is the characteristic length.

The magnitudes of some characteristic times relevant to EWOD are

- 1. The Maxwell relaxation time of bulk water $t \sim 10^{-12}$ s [30,31].
- 2. The characteristic timescale for dipolar reorientation in an uncharged nanotube is in the range of nanoseconds [32].
- The response time of EWOD-based display devices at millimeter level is about 10 ms.

19.2.2 CHARACTERISTIC LENGTH SCALES

There are many characteristic length scales related to surface effects, and it is not possible to list all of them. Only those relevant to EWOD are given here.

1. EW number. The Lippmann-Young (L-Y) equation is the basis for EWOD:

$$\cos \theta = \cos \theta_0 + \frac{\varepsilon V^2}{2d\gamma_{\rm lv}},\tag{19.6}$$

where θ_0 is the contact angle described by the Young equation $\cos \theta_0 = (\gamma_{sv} - \gamma_{sl}/\gamma_{lv})$, that is, contact angle without voltage. \boxtimes is the dielectric constant, *d* is the thickness of the dielectric film, γ_{lv} is the liquid–vapor surface tension, and *V* is the applied voltage. The last term of the L–Y equation is a dimensionless number, which is called the EW number:

$$Ew = \frac{\varepsilon V^2}{2\gamma_{\rm lv} d}.$$
(19.7)

It represents the ratio of electrostatic energy to interfacial energy. The larger the EW number, the bigger is the change in contact angle due to applied voltage.

2. *The characteristic time of line tension effect.* The Young equation, which is the basis of wetting, can be regarded as a special case of the L–Y equation, that is, it describes EW without applied voltage. It does not take the three-phase

molecular interactions at the contact line into account. Considering the line tension effect, the Young equation should be modified for planar surface [33]:

$$\cos\theta = \cos\theta_0 - \frac{\tau}{\gamma_{\rm lv}R} \tag{19.8}$$

where *R* is the radius of the contact line and τ is the line tension. The line tension can be positive or negative, depending on the properties of the droplet and the substrate material. It can be expressed approximately as [33]

$$\tau \approx 4\delta \sqrt{\gamma_{\rm sv} \gamma_{\rm lv}} \cot \theta_0, \qquad (19.9)$$

in which δ stands for the average distance between the liquid and the solid molecules. The order of magnitude of the line tension is in the range from ~10⁻¹¹ N to ~10⁻⁶ N [34]. From Equation 19.8, a characteristic length $l_{\rm B}$ can be derived:

$$l_{\rm B} = \frac{|\tau|}{\gamma_{\rm lv}}.\tag{19.10}$$

It measures the strength of the line tension relative to liquid–vapor surface tension. From the above equation, it can be inferred that the line tension effect should be considered only when the droplet size is below the micrometer level.

3. *Debye screening length (or Debye shielding length).* When a particle that carries +*q* charge is deposited in a continuous medium, the electrons in the medium will be attracted to form an electron sphere, outside of which charges are screened. A Debye sphere is such a volume in which there is a sphere of influence inside the volume while the influence vanishes outside. The Debye length is the radius of such a sphere [35,36], which is defined as

$$\lambda_{\rm D} = \sqrt{\frac{\varepsilon \varepsilon_0 k_{\rm B} T}{e^2 N_{\rm A} \sum_i z_i^2 M_i}},$$
(19.11)

where \mathbb{A}_0 is the permittivity of the medium (e.g., vacuum), $k_{\rm B}$ is the Boltzmann's constant, *T* is the absolute temperature, *e* is the charge of an electron, $M_{\rm i}$ is the molar concentration, and $z_{\rm i}$ is the valency. Debye screening length is an important characteristic length scale in EW. In conventional macroscopic EW, the diameter of the droplet is of the order of millimeters, which is much larger than the Debye screening length, that is, $D \gg \lambda_{\rm D}$, so that the liquid is insulating. However, for EW at nanoscale, the droplet size *D* is much smaller than the Debye screening length [37], that is, $D \ll \lambda_{\rm D}$. Thus, at nanoscale, the droplet becomes a conductor. Actually, in most macroscopic EW experiments, the droplet liquid is a conducting solution (e.g., 0.1 mol/L KCl solution) instead of just pure water.

19.3 ELECTROWETTING THEORIES

Classical EWOD theories were initially based on the ideal model, such as the system is macroscopic, the surface is planar and smooth, and the liquid droplet is a perfect conductor. Owing to its great application potential, EWOD has drawn much attention from various fields. With the development of EWOD, more intensive studies are conducted, concentrating on different aspects. For instance, the real surface configurations (such as curvature, roughness, etc.), EWOD under high voltage and below micrometer level are taken into consideration. Contact angle hysteresis is an accompanying phenomenon that always affects EWOD as well as wetting. It can be caused by many factors, and will affect droplet actuation by influencing the minimum actuation voltage. Temperature-induced effect should also be considered, which is related to Marangoni convection, because the introduction of voltage may cause uneven heat distribution in the droplet and at the liquid–vapor interface. At a microscopic level, many phenomena and properties may be different from those at macroscopic level. The properties of the molecular PF will be discussed in this section. At the end of this section, compared with classical EWOD, another form called spontaneous EW will be discussed.

19.3.1 CLASSICAL ELECTROWETTING THEORY: THE LIPPMANN–YOUNG EQUATION

The L–Y equation, which describes the relationship between contact angle and applied voltage, is the basis of EWOD:

$$\cos\theta = \cos\theta_0 + \frac{\varepsilon V^2}{2d\gamma_{\rm lv}}.$$
(19.6)

A typical curve from an EWOD experiment is shown in Figure 19.1. It can be seen that the L–Y equation correctly predicts the experimental results under low voltage. However, it fails under high voltage. Contact angle saturation under high voltage will be discussed in detail in Section 19.3.2.2.

The L–Y equation can be derived from different approaches. Here, we will give three main approaches, which have also been discussed by Mugele [4] and Berthier [15]: thermodynamic approach, energy minimization approach, and electromechanical approach.

19.3.1.1 Thermodynamic Approach

The droplet directly contacted the metal surface in Lippmann's original work. In this case, when voltage is introduced, all of the counterions are assumed to be located at a fixed distance $d_{\rm H}$ from the surface based on the Helmholtz model, and an electrical double layer (EDL) forms at the solid–liquid interface. As was mentioned above, modern EW is EWOD by introducing a thin dielectric film to separate the droplet and the metal. The thickness of the EDL $d_{\rm H}$ (of the order of a few nanometers) is far less than that of the dielectric film, so that the effect of the EDL can be neglected. Taking the dielectric film as a component of the solid–liquid interface, the reduction of the effective interfacial tension $\gamma_{\rm sl}^{\rm eff}$ is



FIGURE 19.1 A typical curve of cosine of the contact angle (θ) versus applied voltage in electrowetting-on-dielectric (EWOD). The points are experimental results whereas the solid line is the theoretical prediction following the Lippmann–Young equation 19.6. (From F. Mugele and J. C. Baret, Electrowetting: From basics to applications, *J. Phys.: Condens. Matter*, 17, 705, 2005. With permission.)

$$d\gamma_{\rm sl}^{\rm eff} = -\sigma_{\rm sl}dV. \tag{19.12}$$

When a voltage is introduced, the electric energy is mainly stored in the dielectric film, very little of which is available to change the solid–liquid interfacial tension. σ_{sl} is the surface charge density at the solid–liquid interface and is given by

$$\sigma_{\rm sl} = \frac{\varepsilon_0 \varepsilon_{\rm d}}{d} V. \tag{19.13}$$

From Equation 19.12 and 19.13, the effective interfacial tension can be obtained:

$$\gamma_{\rm sl}^{\rm eff} = \gamma_{\rm sl} - \frac{\varepsilon_0 \varepsilon_{\rm d}}{2d} V^2. \tag{19.14}$$

Using the Young equation, by substituting γ_{sl}^{eff} for $\gamma_{sl},$ the L–Y equation can be derived.

19.3.1.2 Energy Minimization Approach

Consider the droplet, the dielectric film, the metal counter electrode, and the voltage source as a thermodynamic system. When a voltage is applied, the droplet will spread until its free energy F reaches a minimum value:

$$dF = \gamma_{\rm sl} dA - \gamma_{\rm sv} dA + \gamma_{\rm lv} dA \cos\theta + dU - dW_{\rm B} = 0$$
(19.15)

where γ_{sl} , γ_{sv} , and γ_{lv} are the solid–liquid, solid–vapor, and liquid–vapor interfacial energy, respectively. *U* is the electric energy, W_B is the work that the voltage source performs, and *A* is the droplet base area (see Figure 19.2). Dividing both sides of Equation 19.15 by *dA* gives

$$\gamma_{\rm sl} - \gamma_{\rm sv} + \gamma_{\rm lv}\cos\theta + \frac{dU}{dA} - \frac{dW_{\rm B}}{dA} = 0.$$
(19.16)

In order to get the contact angle θ , we need the values of dU/dA and dW_B/dA . According to electromagnetics, U is defined by the formula $dU = (1/2)\boxtimes E^2 d\Omega$, where E is the electric field intensity and Ω is the volume filled with electric field. The predominant effect in EWOD process is the distribution of the electric field, which is very complicated near the three-phase contact line. For simplicity but without loss of generality, the area with electric field singularity is supposed to be much smaller compared with the uniform field, so that the singularity within the vicinity of the contact line can be neglected and the electric field is taken as a uniform field. The electrostatic energy per unit area under the droplet base is

$$\frac{U}{A} = \int_0^d \frac{1}{2} \varepsilon_0 \varepsilon_{\rm d} E^2 dz.$$
(19.17)

Hence, the increase of electrostatic energy upon an infinitesimal increment of the droplet base area can be given by

$$\frac{dU}{dA} = \frac{1}{2}\varepsilon_0\varepsilon_d E^2 d = \frac{1}{2}\frac{\varepsilon_0\varepsilon_d}{d}V^2.$$
(19.18)



FIGURE 19.2 Schematic of the variation of contact angle with applied voltage. When the voltage increases, the droplet base area increases with an infinitesimal value *dA* to reach a new equilibrium. (With permission from H.J.J. Verheijen and M.W.J. Prins, Reversible electrowetting and trapping of charge model and experiments, *Langmuir*, 15, 6616. Copyright 1999, American Chemical Society.)

In the droplet spreading process, the work per unit area $dW_{\rm B}/dA$ done by the voltage source to redistribute the charge can be written as

$$\frac{dW_{\rm B}}{dA} = V\sigma_{\rm sl} = \frac{\varepsilon_0\varepsilon_{\rm d}}{d}V^2.$$
(19.19)

Substitution of Equations 19.18 and 19.19 in Equation 19.16 gives the L–Y equation 19.6.

19.3.1.3 Electromechanical Approach

The droplet, which is deposited symmetrically on a planar thin dielectric solid, is assumed to be perfectly conductive and is surrounded by an immiscible, perfectly insulating fluid (for instance, vapor). Consider the right-half plane of the droplet (see Figure 19.3). The bottom electrode is grounded and an external potential of *V* is applied, so that $\Phi = V$ on S_{12} (the liquid–fluid interface) and S_{13} (the solid–liquid interface), $\Phi = 0$ on S_e , where Φ is the electrostatic potential and $E = -\nabla \Phi$. Within the surrounding fluid and dielectric field, the electrostatic potential satisfies the Laplace equation $\nabla^2 \Phi = 0$. The electric field *E* is perpendicular to the surface of the droplet on the surrounding fluid side, and vanishes in the conducting droplet. Neglecting the osmotic contribution, the electrostatic force acting on the droplet surface is

$$F_{d} = \int_{S_{12}+S_{13}} T \cdot n dS, \qquad (19.20)$$

where *T* is the Maxwell stress tensor:

$$\boldsymbol{T} = -\frac{1}{2} \boldsymbol{\varepsilon} E^2 \boldsymbol{I} + \boldsymbol{\varepsilon} \boldsymbol{E} \otimes \boldsymbol{E}, \qquad (19.21)$$



FIGURE 19.3 Schematic of interface domain to be studied in electrowetting (EW). θ is the contact angle, S_{12} is the liquid–fluid interface, S_{13} is the liquid–dielectric film interface, and S_{∞} is the surface which is at an infinitely remote distance from the droplet.

where I is the second-order isotropic tensor and \otimes is the tensor product. There is no tangential electric field on the surface of the conducting droplet on the fluid side, so that $E = E_n$ and $E = E \cdot n$. The electrostatic force in Equation 19.20 becomes

$$F_{\rm d} = \int_{S_{12}+S_{13}} \frac{1}{2} \varepsilon E^2 n dS.$$
(19.22)

The solution to Equation 19.22 requires calculation of the electric field (or charge) distribution along the droplet surface. The normal stress on the dielectric film surface, which is caused by the electrostatic force at the solid–liquid interface, can be balanced by elastic stress. Therefore, what we are concerned most with is the electrostatic force at the liquid–fluid interface. As the three-phase contact line is approached, both the charge density and the electric field increase sharply owing to sharp-edge effects. Hence, the field within the vicinity of the contact line will mainly contribute to the electrostatic force at the liquid–fluid interface.

Taking the edge region of the droplet as an infinite planar wedge, Vallet et al. [38] and Kang [39] analyzed the electrostatic field within the vicinity of the edge region by using Schwarz–Christoffel conformal mapping:

$$Z = \int_{i\pi}^{w} (e^{w'} + 1)^{\beta} dw' + i\pi, \qquad (19.23)$$

where the parameter β is defined as $\beta = 1 - \theta/\pi$. Equation 19.23 transforms the plane Z = x + iy to the plane w = u + iv, and the transformed coordinates u and v are scaled by d/π and V/π (see Figure 19.4). For simplicity, the electric permittivities of the surrounding fluid and the dielectric film are assumed to be the same, so that the electric field is uniform in the transformed plane w and $E = V/\pi$. Then, the electric field in the original plane can be obtained:

$$E = E_{\rm n} = \frac{V/\pi}{d/\pi} \frac{1}{dZ/dw} = \frac{V}{d} \frac{1}{|e^u - 1|^{\beta}}.$$
 (19.24)



FIGURE 19.4 Schwarz–Christoffel transformation of the droplet edge region. The *Z* plane $(Z = x + iy, x \text{ and } y \text{ are the complex coordinates of the original plane) is transformed into the$ *w*plane (<math>w = u + iv, *u* and *v* are the complex coordinates of the transformed plane). (Left figure: With permission from K.H. Kang, How electrostatic fields change contact angle in electrowetting, *Langmuir*, 18, 10318. Copyright 2002, American Chemical Society.)

The surface charge density ($\sigma = \boxtimes E$) that is related to the field is

$$\frac{\sigma}{\sigma_0} = \begin{cases} \frac{1}{(e^u - 1)^{\beta}}, & \text{on } S_{12} \\ \\ \frac{1}{(1 - e^u)^{\beta}}, & \text{on } S_{13} \end{cases}$$
(19.25)

where $\sigma_0 = \varepsilon V/d$ is the charge density at the solid–liquid interface far from the contact line. The Maxwell stress tensor, which is calculated by Equation 19.21, can be expressed in the *n*-, *t*-, and *z*-axis system (*n*-axis is aligned with the normal liquid–fluid surface) using the following equation:

$$[\mathbf{T}] = \varepsilon \begin{bmatrix} \frac{1}{2}E_n^2 & 0 & 0\\ 0 & -\frac{1}{2}E_n^2 & 0\\ 0 & 0 & -\frac{1}{2}E_n^2 \end{bmatrix}.$$
 (19.26)

On the wedge surface, where $w = u + i\pi$, the mapping equation becomes

$$\frac{dZ}{dw} = \frac{dZ}{du} = \frac{dx + idy}{du} = \frac{dx}{du} + i\frac{dy}{du}.$$
(19.27)

Then, the distance from the wedge apex l can be obtained:

$$\frac{dl}{du} = \frac{d}{\pi} \frac{\sqrt{(dx)^2 + (dy)^2}}{du} = \frac{d}{\pi} \left| \frac{dZ}{dw} \right| = \frac{d}{\pi} \left| e^u - 1 \right|^{\beta},$$
(19.28)

$$l = \frac{d}{\pi} \int_0^u |e^{u'} - 1|^\beta \ du'.$$
(19.29)

For a droplet with a small contact angle, that is, $\theta \to 0$ and $\beta = 1 - \theta/\pi \to 1$, we can obtain the relationship between the electric field and the distance [40]:

$$E_{\rm n} \sim \frac{1}{|l|^{1/2}}.$$
 (19.30)

The field singularity occurs near the wedge region, especially at the wedge tip. In fact, from Equation 19.24, it can be seen that the field is always singular near the wedge tip (where u = 0) for the contact angle ranging from 0 to π . Studies [38–41] show that this singularity effect occurs in a very confined region with a length scale of magnitude *d*. Since the charge density and the Maxwell stress are both related

to the electric field, both will be singular within the region of O(d). The electrostatic stress will therefore be confined within the vicinity of the edge region. With Equations 19.25 and 19.28, the net electrostatic force acting on the upper side of the wedge can be calculated:

$$F_{\rm e} = \frac{\varepsilon V^2}{2\pi d} \int_0^\infty \frac{1}{(e^u - 1)^\beta} du = \frac{\varepsilon V^2}{2d} \operatorname{cosec} \theta.$$
(19.31)

The horizontal and vertical components of this force are

$$F_{\text{ex}} = \frac{\varepsilon V^2}{2d}, \quad F_{\text{ey}} = \frac{\varepsilon V^2}{2d} \cot \theta.$$
 (19.32)

Divided by the liquid–vapor surface tension γ_{lv} , the horizontal part is exactly the EW number in the L–Y equation. Actually, the L–Y equation can be obtained from the balance of forces in the horizontal direction at the contact line.

The thermodynamic and electromechanical approaches discussed in Sections 19.3.1.1 and 19.3.1.3, respectively, represent two different interpretations of the EWOD phenomenon. While one regards the reduction of the contact angle as originating from the change of the solid–liquid interfacial tension, the other considers it as the Maxwell tensor that "drags" the droplet to spread out. It is still dubious which mechanism is the reason, though the two interpretations seem to be related in a sense. The possible interpretations to EW are summarized in Figure 19.5. More investigations are required to clarify the phenomenon. However, regardless of which interpretation is responsible for the phenomenon, the L–Y equation always works and is the basis of EW.

19.3.2 EXTENDED LIPPMANN-YOUNG EQUATIONS

19.3.2.1 Electrowetting on Rough Surfaces

Real surfaces are always rough with topography patterns [41,42], such as the configuration of lotus leaves. While the L–Y equation is for EWOD on ideal smooth surfaces, new models need to be established to describe the contact angle variation on rough surfaces.

The Cassie and Baxter method for a composite surface was used to extend the classical EW equations to microstructured surfaces [43]. For simplicity, the rough surface is represented by hemispherically topped cylindrical asperities (see Figure 19.6). By using the energy minimization approach, an extended equation is derived:

$$\cos\theta_{\rm c} = f_1 \left(\cos\theta_0 + \frac{1}{2} \frac{\varepsilon_0 \varepsilon_{\rm d} V^2}{d\gamma_{\rm lv}} \right) - f_2, \tag{19.33}$$

where θ_c is the contact angle on rough surface, θ_0 is the contact angle described by the Young equation, $f_1 = dA_{s11}/dA_{s1}$ and $f_2 = dA_{s12}/dA_{s1}$ are the surface roughness factors shown in Figure 19.6. The contact area on the rough surface is divided into two parts at the composite interface: one part is for the solid–liquid interface A_{s11} while



FIGURE 19.5 Possible interpretations (a) through (e) to the reduction of the contact angle (CA) as a result of the applied voltage: primary electrocapillarity, secondary electrocapillarity, repulsion of like-charges at the triple line, effective capacitance and electromechanics. (a) Primary electrocapillarity means that the solid-liquid interfacial energy changes by applying a voltage, that is, $\gamma_{sl}(V) = \gamma_{sl} - (\epsilon V^2/2d)$, thus leading to the reduction of CA. (b) Secondary electrocapillarity indicates that the applied voltage causes polarization of the triple line, leading to change in the line tension and as thereby in CA, that is, $\partial \cos \theta / \partial \Phi_{slv} = \chi_{slv} / R \gamma_{lv}$, where χ_{slv} is the line density of the electric charges and Φ_{slv} is the electrostatic potential on the triple line. (c) Repulsion of like charges at the triple line shows that it is repulsion that may cause the contact line moves and droplet spreads. (d) Effective capacitance shows that the dielectric film is taken as part of the solid-liquid interface. The effective solid-surface energy changes as the voltage is applied, that is, $\gamma_{sl}^{\text{eff}}(V) = \gamma_{sl} - (\varepsilon V^2/2d)$. The dielectric film works as a capacitor and almost all of the electric energy is stored in it. (e) Electromechanics illustrates that the reduction of CA is a result of Maxwell stress tension or the electrostatic force. (Y. Wang and Y.P. Zhao, Electrowetting on curved surfaces, Soft Matter, 8, 2599, 2012. By permission of The Royal Society of Chemistry.)

the other is for the liquid–air interface A_{sl2} . Using the dimensionless EW number $E_W = \varepsilon_0 \varepsilon_d V^2 / 2d\gamma_{1v}$, Equation 19.33 can be rewritten as

$$\cos\theta_{\rm c} = f_1 (\cos\theta_0 + Ew) - f_2. \tag{19.34}$$

Equation 19.33 or Equation 19.34 is the extended L–Y equation based on the Cassie–Baxter model. Without applied voltage, that is, V = 0, Equation 19.34 reduces to the Cassie–Baxter equation.



FIGURE 19.6 Electrowetting on an optimized rough surface with hemispherically topped cylindrical asperities. The air remains in the grooves. The roughness factor in the solid–liquid area is $R_1 \cdot f_1 = dA_{sl1}/dA_{sl}$ and $f_2 = dA_{sl2}/dA_{sl}$.

Using the same method, another extended L–Y equation based on the Wenzel model can be established [44]:

$$\cos\theta_{\rm c} = R_1 \left(\cos\theta_0 + Ew \right) \tag{19.35}$$

where $R_1 = A_{sl1(actual)}/A_{sl1(apparent)}$ is the roughness factor [45], which is defined as the ratio of the actual-to-apparent (geometric) solid–liquid contact areas.

It was found that during the EW process on rough surfaces, the contact angle might display a step change [46,47] (see Figure 19.7). This is because wetting on rough surfaces is initially in the Cassie–Baxter state; but after a threshold value of



FIGURE 19.7 Cosine of the contact angle as a function of the applied voltage squared for molten salt on nanostructured and planar substrates. The one line (the dotted one) is the variation of $\cos \theta$ on a planar substrate. The other two lines (solid ones) represent the variation of $\cos \theta$ on nanostructured surfaces, with pitch 4.0 and 1.05 µm, respectively, both of which display a step change in $\cos \theta$ at a certain value of voltage. (With permission from T.N. Krupenkin et al., From rolling ball to complete wetting: The dynamic tuning of liquids on nanostructured surfaces, *Langmuir*, 20, 3824. Copyright 2004, American Chemical Society.)

TABLE 19.1 Influence of Electrowetting Number on Droplet States on Rough Electrowetted Surfaces

EW Number	Stable State	Comments
$\eta < -\cos\theta_0 - \left[(1-\phi)/(r_{\rm m} - \phi) \right]$	Cassie	Finite energy barrier for Cassie–Wenzel transition. Barrier for reverse transition lower.
$\eta > -\cos\theta_0 - \left[(1 - \phi)/(r_{\rm m} - \phi) \right]$	Wenzel	Finite energy barrier for Cassie–Wenzel transition. Barrier for reverse transition higher.
$\eta > -\cos \theta_0$	Wenzel	No energy barrier for Cassie–Wenzel transition. Reverse transition disallowed.

Source: From V. Bahadur and S.V. Garimella, Langmuir, 23, 4918, 2007. With permission.

voltage, EW would be in the Wenzel state. An intermediate state occurs during transition from the Cassie–Baxter to the Wenzel state, where the droplet partially wets the grooves, and the contact angle is [43,44]

$$\cos\theta_{\rm c} = R_1 f_1 \left(\cos\theta_0 + \frac{1}{2} \frac{\varepsilon_0 \varepsilon_d V^2}{d\gamma_{\rm lv}} \right) - f_2.$$
(19.36)

The droplet state on a rough surface is related to the EW number Ew and the initial contact angle θ_0 . The influence of these two factors is summarized in Table 19.1 [44].

19.3.2.2 Electrowetting on Curved Surfaces

Since EW on planar surfaces is a specific and relatively simple situation, structured surfaces with curved features are more common, such as liquid lenses with curved contact surfaces, flexible paper-like substrate, and lotus leaf. The L–Y equation is derived from and applicable for EW on planar surfaces under low voltage. However, it does not take the surface curvature effect into consideration.

Considering the surface curvature effect, by using the principle of energy minimization, an extended L–Y equation on spherical surfaces (Figure 19.8) was derived [48]:

$$\cos\theta(V) = \cos\theta_0 + \frac{\varepsilon V^2}{2\gamma_{\rm b}d} \cdot \frac{1}{1\pm\xi},\tag{19.37}$$

where $\xi = d/R_s$. Equation 19.37 means that for convex surface

$$\cos\theta(V) = \cos\theta_0 + \frac{\varepsilon V^2}{2\gamma_{\rm lv}d} \cdot \frac{1}{1+\xi},$$
(19.38a)



FIGURE 19.8 Schematic of EWOD on curved surfaces: (a) EWOD on a convex surface; (b) EWOD on a concave surface. A conducting liquid droplet is placed on a metal counter electrode coated with a dielectric film. The contact angle θ changes when a voltage is introduced. (Y. Wang and Y.P. Zhao, Electrowetting on curved surfaces, *Soft Matter*, 8, 2599, 2012. By permission of The Royal Society of Chemistry.)

and for concave surface

$$\cos\theta(V) = \cos\theta_0 + \frac{\varepsilon V^2}{2\gamma_{\rm lv}d} \cdot \frac{1}{1-\xi}.$$
(19.38b)

Comparing with the EW number, a curvature-modified EW number was introduced:

$$Ew^* = \frac{\varepsilon V^2}{2\gamma_{\rm lv} d} \cdot \frac{1}{1 \pm \xi}.$$
(19.39)

The curvature-modified EW number can be expressed as a function of Ew and ξ :

$$Ew^* = Ew \cdot \frac{1}{1 \pm \xi}.$$
(19.40)

The surface curvature has an influence on the contact angle; especially with decrease of the system size, the effect becomes even more significant. At the present experimental condition, ξ or the ratio of *d* to R_s is small, which makes the modified term of the EW number close to 1. In this case, the variation of the contact angle on curved surfaces is close to that on planar surfaces, and the surface curvature effect is not obvious. However, when R_s becomes very small or EWOD is on and below microscale, such as EW in carbon nanotubes (CNTs) or on a graphene substrate, the surface curvature effect cannot be neglected. Nevertheless, there are few experiments on and below microscale in the published work, and further investigation

is necessary. Besides, since a curved surface can be either convex or concave, the variation of the contact angle is different. While the variation of the contact angle on convex surfaces decreases compared with that on planar surfaces, it increases on concave surfaces. This means that concave surfaces can enhance wettability better than convex surfaces when applying the same voltage.

As the capacitance of a spherical capacitor per unit area is $c = \varepsilon/d(1 \pm \xi)$, Equation 19.37 can be simplified as

$$\cos\theta(V) = \cos\theta_0 + \frac{1}{2} \cdot \frac{cV^2}{\gamma_{\rm lv}}.$$
(19.41)

where *c* is the capacitance per unit area. Actually, Equation 19.41 is always applicable for EW on surfaces with various curvatures. For EW on a planar surface, substituting the capacitance of a parallel-plate capacitor per unit area $c = \varepsilon/d$ into Equation 19.41, we get $\cos \theta(V) = \cos \theta_0 + (cV^2/2\gamma_{1v})$. This is exactly the classical L–Y equation. Therefore, the L–Y equation can be seen as a degenerate equation considering the surface curvature effect in a sense. For EW on curved surfaces under low voltage, once the capacitance per unit area is known, the variation of the contact angle can be predicted. However, it should be noted that although the extended EW equation can be simplified as the form of capacitance, it is not just simply a problem of capacitor, since the mechanism of EW is still debatable.

Considering that the line tension works on and below microscale, a uniform expression of EW on various geometrical surfaces was given [48]:

$$\cos\theta(V) = \cos\theta_{\rm Y} - \frac{\tau\chi}{\gamma_{\rm lv}} + \frac{1}{2} \cdot \frac{cV^2}{\gamma_{\rm lv}}, \qquad (19.42)$$

where θ_{Y} is the Young contact angle, τ is the line tension, χ is the geodesic curvature, and *c* is the capacitance per unit area.

19.3.2.3 Electrowetting under High Voltage

According to the L–Y equation, complete wetting would be achieved at $V = \sqrt{2d\gamma_{1v}(1 - \cos\theta_0)/\epsilon_0\epsilon_d}$. However, complete wetting has never been observed experimentally [4]. Experiments [4,5,49,50] found that the contact angle saturated around 30°–80° under high voltages, and electrical breakdown of the dielectric film would happen when the voltage is high enough [50,51]. The factors that were identified as influencing critical voltage for breakdown include physical properties of the dielectric film, the contact time between the wire electrode and the droplet, and the electrode–dielectric film distance [51]. This means that the L–Y equation fails to describe EWOD under high voltages. New theories need to be established to explain the phenomenon. However, the mechanism of the phenomenon is still ambiguous and no consistent theory has been set up so far. Researchers have never stopped exploring the high-voltage phenomenon and various mechanisms have been proposed.

One of the most broadly accepted explanations was proposed by Verheijen and Prins [52]. They indicated that above a threshold voltage, almost all charges would

get trapped in or on the insulating layer. By using the principle of virtual displacement, they derived the equation for EW:

$$\cos\theta = \cos\theta_0 + \frac{1}{2} \frac{\varepsilon_0 \varepsilon_d \left(V - V_T \right)^2}{d\gamma_{1v}},$$
(19.43)

where $V_{\rm T}$ is the voltage of the trapped charge, which is induced by the trapped charge $\sigma_{\rm T} = \epsilon_0 \epsilon_{\rm d} V_{\rm T} / d_{\rm T}$ (see Figure 19.9). Below the threshold voltage, there is no trapped charge and the variation of the contact angle is proportional to V^2 . When the applied voltage *V* exceeds the threshold value, trapped charges are generated so that the variation of the contact angle will be proportional to $(V - V_{\rm T})^2$. Equation 19.43 corresponded well with their experimental data. However, since the trapped charge is associated with the insulator properties, the model fails to establish the relation between the threshold voltage and the known material properties.

Another modified L–Y equation considering the saturation effect was proposed by Berthier et al. [53]. They used the Langevin function $L(\cdot)$ that is defined as

$$L(X) = \coth(3X) - \frac{1}{3X},$$
(19.44)

and verified that the function fit well with the experimental results:

$$\frac{\cos\theta - \cos\theta_0}{\cos\theta_{\rm s} - \cos\theta_0} = L \left[\frac{\varepsilon_0 \varepsilon_{\rm d} V^2}{2d\gamma_{\rm lv} \left(\cos\theta_{\rm s} - \cos\theta_0\right)} \right],\tag{19.45}$$

where θ_s is the saturation angle.



FIGURE 19.9 Schematic representation of contact angle saturation phenomenon. A sheet of trapped charge does not generate until the voltage is above a threshold value. *d* is the thickness of the dielectric film, and $d_{\rm T}$ is the distance between the sheet of trapped charge and the bottom of the dielectric film. (With permission from H.J.J. Verheijen and M.W.J. Prins, Reversible electrowetting and trapping of charge model and experiments, *Langmuir*, 15, 6616. Copyright 1999, American Chemical Society.)

Electrical breakdown of the dielectric film will happen when the voltage is high enough. It was pointed out [50,51,54] that the critical voltage for breakdown was proportional to the thickness of the dielectric film. A whole process of breakdown was recorded with a high-speed camera in 200 Hz by Feng and Zhao [51]. In this experiment, a spark was seen as the start of breakdown, at which stage the dielectric film was destroyed and there was an instant current between the wire and the counter electrodes. The heat generated by the instant current generated bubbles by electrolysis of the electrolyte, which swelled dramatically, like an explosion, and electrical energy was converted to dynamic energy of conductive liquids. Droplet ejection is a common phenomenon occurring under high voltages, which has also been observed and reported by other groups [38,55].

Many other studies have been carried out trying to explore EW under high voltage [38,55–58]. However, none of these existing explanations can fully explain the phenomenon and the mechanism is still unclear. More intensive work is needed to fully understand and explain EW under high voltage.

19.3.2.4 Electrowetting at Micro- and Nanoscales

Owing to a variety of applications, such as micro- and nanofluidic manipulation and LOC, EW at a small scale has attracted considerable attention. However, the L–Y equation was derived from and is applicable for EW in macroscopic systems. It neglects some effects such as line tension, which play a major role and cannot be neglected at a microscopic scale. Besides, the assumptions in the derivation may fail due to scale effect. For instance, the size of a nanodroplet is well below the Debye screening length, in which case the treatment of the charge distribution in droplets will be different from macroscopic droplets. Therefore, the study for EW at microand nanoscales is of great importance, both for understanding the mechanisms and for application.

19.3.2.4.1 Line Tension Effect

It has been recognized for a long time that the Young equation does not account for three-phase molecular interactions at the contact line. A number of studies have been conducted to consider this effect [33,59,60]. A modified Young equation that takes into account line tension is given by [61]

$$\cos\theta_{\rm ac} = \cos\theta_{\rm Y} - \frac{\tau H}{\gamma_{\rm lv}} - \frac{\nabla\tau \cdot \nabla H + (\nabla\tau \times \nabla w) \cdot (\nabla w \times \nabla H)}{R\gamma_{\rm lv} \sqrt{|\nabla H|^2 + |\nabla H \times \nabla w|^2}}, \quad (19.46)$$

where τ is the line tension, χ is the geodesic curvature at a certain point, *H* is the thickness of the liquid at each point, and *w* is the elevation of the solid surface. Generally, the last term in Equation 19.46 can be neglected and simplifies to

$$\cos\theta_{\rm ac} = \cos\theta_{\rm Y} - \frac{\tau\chi}{\gamma_{\rm lv}}.$$
(19.47)

Especially, $\chi = 1/R$ for planar surfaces (*R* is the radius of the three-phase contact line) and $\chi = \sqrt{1 - (R/R_S)^2}/R$ for spherical surfaces (R_s is the radius of the solid surface). Values of reported line tension [34,62,63] range from 10⁻¹⁰ to 10⁻⁶ N in order of magnitude, which means it will apply when the system is at and below microscale.

While a great deal of work has been done to modify the Young equation considering the line tension effect, far fewer studies exist about the line tension correction for EW. Using the Gibbs–Johnson–Neimann (GJN) approach, which assumes that a free liquid drop automatically takes the shape that minimizes the total system energy, Digilov considered the line tension effect and the presence of charges on the threephase contact line and gave the modified equation [64]

$$\cos\theta = \cos\theta_{\rm Y} - \frac{\tau}{\gamma_{\rm lv}R} + \chi_{\rm slv}U_{\rm slv}, \qquad (19.48)$$

where χ_{slv} is the excess line charge and U_{slv} is the excess energy of the three-phase contact line. Equation 19.48 can be rewritten as

$$\left(\frac{\partial\cos\theta}{\partial\Phi_{\rm slv}}\right)_{T,u} = \frac{1}{\gamma_{\rm lv}R}\chi_{\rm slv},\tag{19.49}$$

where Φ_{slv} is the potential at the three-phase contact line. Equation 19.49 illustrates that the change in the cosine of the contact angle under an applied potential is governed by the electric charges on the three-phase contact line. This result is similar to the explanation that it is the Maxwell tension on the contact line that changes the contact angle to some extent.

19.3.2.4.2 Electrowetting (EW) at Nanoscale

In macroscopic EWOD systems, the conducting liquid will spread under a weak electric field, or the apparent contact angle will decrease with an applied voltage. The diameter of the droplet *L* is at millimeter level, which is much larger than the Debye screening length λ_D , that is, $L \gg \lambda_D$. For pure water, whose ionic concentration is on the order of 10⁻⁷ M, an EDL, on the order of a few nanometers that follows the Helmholtz model, will generate at the insulator–liquid interface. The electric field will then be confined in this interface layer. In this case, the contact angle can be described by the L–Y equation $\cos\theta = \cos\theta_0 + \langle \epsilon\epsilon_1 |E|^2 \rangle d_E / 2\gamma_{\rm lv}$, where the brackets $\langle \cdot \rangle$ denote the average over $d_E (d_E$ is the thickness of the EDL) and $\boxtimes_{\rm l}$ is the dielectric constant of the liquid. Note that in conventional EWOD, since the thickness of the EDL is much less than that of the dielectric film (on the order of several μ m), the EDL effect can be neglected.

Unlike macroscopic drops, nanodroplets with size well under the Debye screening length when placed on a parallel-plate capacitor will essentially behave as conductors [37]. The electric field permeates the whole droplet, and polarization is strongest at the liquid surfaces, which may cause the dipolar molecules to be attracted to the interface [37,65]. The average interaction *w* between a free dipole μ and an applied electric field *E* is [37]:

$$w \approx -|\mathbf{E}||\mathbf{m}| L\left(\frac{|\mathbf{E}||\mathbf{m}|}{k_{\rm B}T}\right)$$
(19.50)

where $L(\cdot)$ is the Langevin function and $k_{\rm B}$ is the Boltzmann's constant. Under a weak electric field

$$w \approx -\frac{|\mathbf{m}|^2 |\mathbf{E}|^2}{3k_{\rm B}T}.$$
 (19.51)

When the electric field gets stronger, the problem will become different and more complicated.

Here, we discussed only the line tension and dipole effects. Actually, while a continuum picture is still applicable, EW at micro- and nanoscales may become different from the macroscopic situation due to scale effect. Forces or other effects that are less important in macrofluidics may play critical roles in microfluidics, for instance, van der Waals (vdW) forces or double-layer forces [66] will become significant and should be considered as the system becomes smaller. At present, relevant research is not far enough, further studies are needed.

19.3.3 CONTACT ANGLE HYSTERESIS AND DROPLET ACTUATION

19.3.3.1 Contact Angle Hysteresis

EWOD has been widely used to manipulate and control microliter or nanoliter quantity of liquids in micro-total-analysis systems (μ -TAS) and LOC. It was found that the droplet did not move immediately when the voltage was applied, but started to move when the voltage exceeded a threshold value [67–69]. Different threshold values were required to initiate movement of the droplet [69,70] in different systems. Once the threshold was exceeded, movement would be both rapid and repeatable. The contact angle hysteresis was believed to be the mechanism responsible for the threshold effect [69].

The contact angle of a droplet advancing on a solid surface is usually different from that receding on the surface. This difference between advancing and receding angles is known as contact angle hysteresis. It can be caused by such factors as surface roughness, surface physical, and chemical heterogeneity [71–73]. The mechanism of contact angle hysteresis is not fully clear. Theoretical [73] and experimental [67,74] studies have been conducted to measure contact angle hysteresis. Figure 19.10a shows the experimental results for a microdroplet of deionized water immersed in silicone oil and placed on a SiOC substrate [67]. The vertical shift between the two curves in Figure 19.10b defines the EW contact angle hysteresis. Contact angle hysteresis is undesirable in EWOD devices due to its influence



FIGURE 19.10 (a) Experimental results for a microdrop of deionized water immersed in silicone oil and placed on a SiOC substrate. (b) Local amplification of (a). The vertical shift between the two curves in (b) is the EW contact angle hysteresis. (From *Sens. Actuators A: Phys.*, 134, J. Berthier et al., Actuation potentials and capillary forces in electrowetting based microsystems, 471. Copyright 2007, with permission from Elsevier.)

on the minimum actuation potential. Different measures [68,73] were proposed to minimize hysteresis, such as using known-good dice (dice that show good repeatability after preliminary EWOD testing) to circumvent the inconsistent coating effect [68]. As contact angle hysteresis is closely dependent on the properties of the substrate, such studies will provide indications for optimizing the design of EWOD devices.

19.3.3.2 Minimum Actuation Voltage

Prior knowledge of the minimum actuation potential is important for the estimation and design of an EW system. Berthier et al. [67] established a model to estimate the minimum actuation voltage, assuming that the static advancing and receding contact angles were $\theta_0 + \alpha$ and $\theta - \alpha$, where θ is the actuated contact angle, θ_0 the nonactuated contact angle, and α is the hysteresis angle (see Figure 19.10b). This assumption stemmed from the Hoffman–Tanner law [75], which states that the advancing and receding contact angles were, respectively, larger and smaller than their Young values. The total capillary force was obtained:

$$F_{\rm x} = R_{\rm e} \gamma_{\rm lv} \left(\cos \theta - \cos \theta_0 \right) - R_{\rm e} \gamma_{\rm lv} \alpha \left(\cos \theta + \sin \theta - \cos \theta_0 + \sin \theta_0 \right), \quad (19.52)$$

where R_e is the width of the electrode. Without hysteresis ($\alpha = 0$), the droplet would move immediately even when an infinitely small voltage is applied. Taking into account the hysteresis ($\alpha \neq 0$), the minimum electric potential is given by

$$\frac{c}{2\gamma_{\rm lv}}V_{\rm min}^2 = \frac{\alpha}{1-\alpha} \Big[\sin\theta_{V_{\rm min}} + \sin\theta_0\Big],\tag{19.53}$$

where *c* is the capacitance of the dielectric film per unit area. Equation 19.53 is an implicit equation for calculating V_{\min} due to the fact that θ depends on *V*. It can be solved iteratively, considering that $\theta_{V_{\min}}$ can be obtained from the L–Y equation.

Berthier's model only considered the EW force F_{elec} and the contact angle hysteresis F_{f} . Other forces such as the viscous resistance $F_{viscous}$ and the drag force applied by the Pt electrode F_{drag} may also influence the actuation of the droplet. To include these effects, another model was proposed for the actuation force [70]:

$$F_{\rm a} = F_{\rm elec} - (F_{\rm viscous} + F_{\rm f} + F_{\rm drag}).$$
(19.54)

The horizontal component of EW force is

$$F_{\text{elec}} = 2R\gamma_{\text{lv}} \left(\cos\theta_{\text{a}} - \cos\theta_{\text{r}}\right), \qquad (19.55)$$

where *R* is the radius of the contact area of the droplet and the lotus leaf, and θ_a and θ_r are the advancing and receding angles with applied voltage, respectively. In the case of an open EWOD system [15], the viscous resistance *F*_{viscous} is described by

$$F_{\rm viscous} \approx \pi R^2 \tau_{\rm w},$$
 (19.56)

where τ_w is the shear stress which can be approximately expressed as

$$\tau_{\rm w} \approx \frac{5\eta v_{\rm open}}{2h},\tag{19.57}$$

in which *h* is the maximum height of the droplet, η is the viscosity of the liquid, and v_{open} is the actuation speed. Another resistive force is the force resulting from contact angle hysteresis F_{f} , which is given by

$$F_{\rm f} \approx 2R\gamma_{\rm lv} \left(\cos\theta_{\rm r0} - \cos\theta_{\rm a0}\right) = 4R\gamma_{\rm lv} \sin\left(\frac{\theta_{\rm r0} + \theta_{\rm a0}}{2}\right) \sin\left(\frac{\theta_{\rm a0} - \theta_{\rm r0}}{2}\right), \quad (19.58)$$

where θ_{a0} and θ_{r0} are the advancing and receding angles without applied voltage, respectively. The drag force applied by the Pt electrode can be estimated by

$$F_{\rm drag} \approx \pi D_{\rm Pt} \gamma_{\rm lv},$$
 (19.59)

where D_{Pt} is the diameter of the Pt electrode. The actuation force F_{a} should be larger than zero in order to fulfill the droplet actuation, and then the minimum voltage can be obtained. The droplet velocity can be estimated by

$$\mathbf{v}_{\text{open}} = \int_0^{t_{\tau}} \frac{F_a(t)}{m} dt, \qquad (19.60)$$

in which t_{τ} is the actuation time and *m* is the mass of the droplet.

19.3.4 MARANGONI CONVECTION

In EW, the thermal behavior and convection in droplets in both stable and unstable situations are of interest [50,76]. In this case, Marangoni convection, which results from temperature nonuniformity on the surface, concentration gradient, or even electric field, may need to be taken into consideration.

Marangoni convection is associated with surface tension gradient [76]. It occurs when the variation of the surface tension force dominates the viscous force. The Marangoni number Mg, which is dimensionless, determines the strength of the convection motion:

$$Mg = \frac{\Delta \gamma R}{\eta \zeta},\tag{19.61}$$

where *R* is the radius of the droplet spherical cap, η is the dynamic viscosity, ζ is the thermal diffusivity, and $\Delta \gamma$ is the surface tension difference between the cooler and warmer parts of the surface. The critical value of the Marangoni number is $Mg_c = 80$ [77,78]. Generally, Marangoni convection cannot be ignored if it is larger than the critical value.

Surface tension is a function of surface temperature, which means that if the temperature varies from one region to another on the surface of a sessile droplet, the surface tension will be nonuniform on the surface. As a result, the liquid will flow from the region with lower surface tension to that with higher surface tension. This kind of fluid flow is exactly the thermal Marangoni convection. According to the Guggenheim– Katayama model [15], the surface tension is related to temperature as follows:

$$\gamma = \gamma^* \left(1 - \frac{T}{T_{\rm C}} \right)^q, \tag{19.62}$$

where γ^* is a constant for a given liquid, T_C is the critical temperature in Kelvin, and q is an empirical factor. Considering that q is close to 1 and using a measured reference value γ_0 (at $T = 0^{\circ}$ C), Equation 19.62 can be rewritten as a linear approximation [15]:

$$\gamma = \gamma_0 (1 + kT), \tag{19.63}$$

where k is the thermal coefficient, for water it has a value of $-0.15/^{\circ}$ C.

For many systems, the values of ρ , η , ζ , and γ under certain temperature have been reported, and can be used to estimate the *Mg* number using Equation 19.61.

19.3.5 PRECURSOR FILM

19.3.5.1 Huh-Scriven Paradox

The movement of the contact line over a solid surface was studied by Huh and Scriven [27]. By imposing the no-slip boundary condition, they constructed a hydrodynamic model of flow near an MCL, giving viscous stress components

$$\tau_{r\theta} = \frac{2\eta}{r} (g\cos\theta - j\sin\theta)$$
(19.64)

and the pressure field

$$p - p_0 = -\frac{2\eta}{r}(g\sin\theta + j\cos\theta), \qquad (19.65)$$

where η is the fluid dynamic viscosity, p_0 is the hydrostatic datum, and g and j are undetermined coefficients. Owing to the no-slip boundary condition, r is set to zero at the contact line, making the total force exerted on the solid surface logarithmically infinite. The energy dissipation is also logarithmically diverging [79]:

$$D_{\rm visc} \approx \frac{\eta v^2}{\theta} \ln\left(\frac{r_{\rm out}}{r}\right),$$
 (19.66)

where D_{visc} is the dissipation per unit time and unit length of the contact line, v is the constant moving velocity of the bottom fluid, and r_{out} is an appropriate outer length scale. From Equation 19.66, one can infer that energy dissipation is infinite at the contact line where r equals zero. However, no matter that the total force or the energy dissipation abhors local infinities virtually, and "not even Herakles could sink a solid" is absurd, which lead to the paradox.

About the 1971 paper, Professor Chun Hum, Department of Petroleum and Geosystems Engineering, University of Texas at Austin, recalled in an email to Professor Yapu Zhao on July 6, 2011 "My Ph.D. advisor Prof. Skip Scriven (U. Minnesota, Chem. Eng.; who passed away two years ago) was a highly respected fluid mechanism expert who is also known for his early work on the interfacial fluid mechanics ('Marangoni effects'). The 'corner flow' problem was a simple exercise problem that he assigned to me; and even when I reported to him the strange solution, I did not of course recognize its meaning. Prof. Scriven however immediately realized its significance and let other people know. I was fortunate enough to piggy back along."

19.3.5.2 Possible Explanations for Huh–Scriven Paradox

Huh and Scriven pointed out that the most obvious culprit leading to stress and energy dissipation singularities at the contact line was the no-slip boundary condition [27]. Later research [59,60] shows that the Huh–Scriven paradox arises from three other ideal assumptions besides the no-slip boundary condition: incompressible Newtonian fluid, smooth solid surface, and impenetrable liquid–solid interface. A list of mechanisms that were proposed to solve the Huh–Scriven paradox is shown in Table 19.2 [79].

19.3.5.3 Molecular Kinetic Theory and Properties of Precursor Film

The PF, usually a single molecular layer propagating ahead of the nominal contact line, may be one answer to the Huh–Scriven paradox [66,79,88] by introducing atomic details to eliminate the infinite dissipation. Hardy's pioneering work [89] predicted the existence of the PF when a droplet spreads. His results have been confirmed by numerous relevant theoretical [66,90] and experimental [91] studies. In order to explain the physical mechanism behind the PF phenomena, MKT [88, 92], which was proposed by Gladstone et al. [93], was adopted for instance in the EW case.

TABLE 19.2 Mechanisms Proposed to Solve the Huh–Scriven Paradox				
Ideal Assumptions	Mechanisms to Relieve the Singularity			
	Precursor film [80,81]			
No-slip boundary condition	Slip boundary condition [27,82]			
Smooth rigid solid walls	Surface roughness [83]			
Incompressible Newtonian fluid	Shear thinning [84]			
	Normal stresses [85]			
Impenetrable fluid-fluid interface	Diffuse interface [86]			
	Evaporation and condensation [87]			

19.3.5.3.1 Molecular Kinetic Theory

The behavior of the contact line is determined by the statistical dynamic behavior of molecules within its vicinity. At equilibrium (see Figure 19.11a), each molecule has the same probability for jumping left or right, and the jump frequency v^0 can be expressed as

$$\nu^{0} = \frac{k_{\rm B}T}{h_{\rm P}} \exp\left(\frac{-\Delta G_{\rm m}}{k_{\rm B}T}\right),\tag{19.67}$$

where $k_{\rm B}$ is the Boltzmann's constant, *T* is the absolute temperature, $h_{\rm P}$ is the Planck constant, and ΔG_m is the barrier energy. Once an external force (e.g., surface tension, electric field, disjoining pressure) is applied, the potential energy surface will tilt (see Figure 19.11b). The jump frequencies in forward and backward directions will be different:

$$\mathbf{v}^{+} = \frac{k_{\rm B}T}{h_{\rm P}} \exp\left(\frac{-\Delta G_{\rm m}}{k_{\rm B}T} + \frac{\lambda F_{\rm driving}}{2k_{\rm B}T}\right),\tag{19.68}$$

$$\nu^{-} = \frac{k_{\rm B}T}{h_{\rm P}} \exp\left(\frac{-\Delta G_{\rm m}}{k_{\rm B}T} - \frac{\lambda F_{\rm driving}}{2k_{\rm B}T}\right),\tag{19.69}$$



FIGURE 19.11 Schematic of the molecular kinetic theory (MKT) depiction of molecular jump to a neighboring site before (a) and after (b) application of external force. Note that application of external force results in different barriers for jump of molecule in the forward versus backward directions.

where v⁺ is the forward frequency, v⁻ is the backward frequency, $F_{driving}$ is the driving force, and λ is the distance between two neighboring surface sites. The velocity of the liquid molecules can then be written as

$$\mathbf{v} = \lambda(\mathbf{v}^+ - \mathbf{v}^-) = 2\lambda \frac{k_{\rm B}T}{h_{\rm P}} \exp\left(\frac{-\Delta G_{\rm m}}{k_{\rm B}T}\right) \sinh\left(\frac{\lambda F}{2k_{\rm B}T}\right).$$
(19.70)

If $\lambda F_{\text{driving}} \ll 2k_{\text{B}}T$, which is true in most cases, then Equation 19.70 simplifies to

$$v \approx \frac{F_{\text{driving}}}{\lambda v},$$
 (19.71)

where $\upsilon = (h_P / \lambda^3) / [\exp(\Delta G_m / k_B T)]$ denotes the friction coefficient per unit length of the contact line. υ has the same dimension as dynamic viscosity with unit of Pa·s. Equation 19.71 predicts that to a first approximation, velocity is directly proportional to the driving force, which is similar to a macroscopic friction.

Without considering the PF, Blake and Haynes [94] took $w = \gamma_{Iv} (\cos \theta_0 - \cos \theta)$ for a spreading droplet, that is, wetting process. Here, $w = F_{driving}/\lambda$ is the work per unit area performed by the driving force, θ_0 and θ represent static and dynamic contact angles, respectively. When the droplet is small, w becomes complicated. By considering the PF, the driving work on the spreading droplet can be written as $w = w_V + w_P + w_S$ [95], where w_V is the work per unit area arising from vdW interactions, w_P is from the polar interactions between water molecules, and w_S is from the different structures of the PF from the bulk liquid. In the case of EW, an additional average electric energy $w_E \sim \sum_i \left[-|E||\mu_i|L(|E||\mu_i|/k_BT) \right]$ contributes, where μ is the dipole moment vector. Then, the governing equation for EW can be expressed as

$$v = 2v_0\lambda \sinh\left(\frac{w_v + w_p + w_s + w_E}{2nk_BT}\right).$$
(19.72)

For $w_V + w_P + w_S + w_E \ll nk_BT$, $v \sim (w_V + w_P + w_S + w_E)/\zeta_0$, where ζ_0 represents a friction coefficient per unit length, having the same dimension as dynamic viscosity.

19.3.5.3.2 Properties of Precursor Film

Previous studies considered that the PF advanced adiabatically much faster than the liquid above it, and hence, concluded that the PF behaved diffusively. However, a recent study [88] showed that the PF itself is not diffusive, but no-slip and solid-like and has the lowest mobility in a droplet. By using MD simulations, the propagation of the PF in wetting was obtained. The results showed that the molecules which finally formed the PF came almost from the surface in the initial state of the droplet. That is to say, the continuous and fast diffusion of surface water molecules to the front of the PF allows for fast propagation of the PF. Figure 19.12 shows the



FIGURE 19.12 MD simulations of the movement of water molecules belonging to different regions of the droplet. (With permission from Q. Yuan and Y.P. Zhao, Precursor film in dynamic wetting, electrowetting, and electro-elasto-capillarity, *Phys. Rev. Lett.*, 104, 246101. Copyright 2010 by the American Physical Society.)

movement track of each water molecule during spreading. It can be seen that some water molecules move very fast at the surface, but once diffused to the region of the PF, they will be pinned by the surface and damped quickly, and then act as PF molecules with the lowest mobility. Besides, MD simulation of the EW process showed that the PF propagates even faster in EW compared with that in wetting.

Equation 19.72 derived from MKT is too complicated to have an analytical solution. Therefore, the power law $R \sim t^{n(E)}$ [88,96] was used to fit the relationship between *R* (spreading radius) and *t* (spreading time). The fit gave n = 0.1554 in wetting (E = 0 V/nm) and n = 0.1819 in EW (E = 0.245 V/nm), see Figure 19.13. The data of *R* versus *t* fits the power law very well. A critical electric field E_c (about 0.175 V/nm) and a saturated field E_s (about 0.625 V/nm) were obtained, which was in accordance with the experimental observation [4] in Figure 19.13c.

19.3.6 Spontaneous Electrowetting

Spontaneous EW is one of the variants of the classical EW configuration [97]. Unlike classical EWOD configuration, where the conducting droplet is placed on a dielectric film-coated planar electrode, spontaneous EW adopts a parallel line electrode configuration and the droplet is of high permittivity. Both configurations are shown in Figure 19.14 for comparison [40]. While in classical EW, a change in contact angle arises and the droplet will be stabilized at a certain apparent contact angle by applying a voltage, in spontaneous EW, a macroscopic finger of liquid film is pulled out ahead of the droplet and this front-running EW film maintains a constant contact angle. In this section, a theoretical analysis of the spontaneous EW will be presented first. Then, a detailed comparison between spontaneous EW and classical EW will be given.

A detailed theoretical analysis of spontaneous EW that combines electrodynamics with hydrodynamics was proposed by Yeo and Chang [40,98,99]. The electrode



FIGURE 19.13 Propagation of the radius *R* of the precursor film (PF) as a function of time *t*, that is, $R \sim t^{n(E)}$ (*n* is a parameter relevant to *E*). (a) The spreading of the droplet (the external electric field E = 0). (b) Electrowetting (EW) of the droplet when E = 0.245 V/nm. (c) The change in *n* with respect to *E*. The horizontal line is n = 0.1554 when the droplet spread (E = 0). The left and right dashed lines represent the critical electric field E_c and the saturated field E_s in EW, respectively. (With permission from Q. Yuan and Y.P. Zhao, Precursor film in dynamic wetting, electrowetting, and electro-elasto-capillarity, *Phys. Rev. Lett.*, 104, 246101. Copyright 2010 by the American Physical Society.)

configuration in which the electric field is predominantly tangential to the TCL is shown in Figure 19.15. Given the absence of free space charge, the electrostatic potential Φ satisfies the Laplace equation

$$\nabla^2 \Phi_i = 0, \tag{19.73}$$

where i = v, l represents vapor and liquid, respectively. The boundary conditions are stipulated by continuity of the normal and tangential fields across the liquid–vapor interface Γ as



FIGURE 19.14 Schematics of classical versus spontaneous electrowetting (EW). (a) Classical configuration of EW, where a conducting droplet is deposited above an electrode coated with a dielectric film. (b) Spontaneous EW configuration, where a high permittivity polar dielectric droplet is placed on a parallel line electrode.



FIGURE 19.15 Schematic of the spreading droplet on a horizontal substrate for the case of spontaneous electrowetting. The inset is an enlarged view of the region near the three-phase contact line. The upper right depicts a y-z cross-section of the electric field in the droplet within the contact line region.

$$\left[\varepsilon_{0}\varepsilon_{i}\frac{\partial\Phi_{i}}{\partial\boldsymbol{n}}\right]_{v}^{l} = \left[\frac{\partial\Phi_{i}}{\partial\boldsymbol{t}}\right]_{v}^{l} = 0 \quad \text{on } \Gamma,$$
(19.74)

in which the square brackets $[\cdot]_v^l$ indicate a jump in the inner quantity across the interface. The normal continuity of the electric field can be expressed as

$$\varepsilon_1 E_{\rm nl} = \varepsilon_{\rm v} E_{\rm nv} \quad \text{on } \Gamma.$$
 (19.75)

As was mentioned above, the droplet is of high permittivity, thus the permittivity of the droplet is much large than that of the ambient vapor phase, that is, $\varepsilon_1 \gg \varepsilon_v$. Since E_{nv} is of finite value, the value of E_{nl} is small and can be neglected, and $E_1 \approx E_{tl}$. In this special case, the electric field in y-z plane will be dominant due to the polarity of the electrodes, and the Laplace equation for the electrostatic potential in the liquid phase can be rewritten as

$$\frac{\partial^2 \Phi}{\partial y^2} + \frac{\partial^2 \Phi}{\partial z^2} = 0.$$
(19.76)

The boundary condition at the solid–liquid interface is given by the potential of the electrodes

$$\Phi = \pm V \quad \text{at } y = \mp R_e/2, \tag{19.77}$$

where R_e is the electrode separation distance, and the boundary condition at the liquid-vapor interface in the limit $\varepsilon_1 \gg \varepsilon_v$ is given by

$$E_{\rm nl} = \frac{\partial \Phi}{\partial z} = 0. \tag{19.78}$$

By using the method of images (or mirror images, which is a mathematical tool used in electrostatics to simply calculate the distribution of the electric field), the solution to Equation 19.76 with the boundary conditions in Equation 19.77 and 19.78 was given [40] as

$$E_{\rm tl} = \frac{4V}{\pi R_{\rm e}} \left(1 - \frac{8h^2}{R_{\rm e}^2} \right).$$
(19.79)

The tangential field is maximum at the three-phase contact line where h = 0, and decays linearly along the interface away from the contact line. Unlike classical EW, in spontaneous EW, the field is not singular at the contact line. The fluid pressure can then be obtained:

$$p = \gamma_{\rm lv} \frac{\partial^2 h}{\partial x^2} - p_{\rm M} = \gamma_{\rm lv} \frac{\partial^2 h}{\partial x^2} - \frac{8\varepsilon_0 \varepsilon_{\rm l} V^2}{\pi^2 R_{\rm e}^2} \left[1 - \frac{16\tan^2 \theta_{\rm f}}{R_{\rm e}^2} (x_{\rm f} - x)^2 \right], \quad (19.80)$$

where $p_{\rm M}$ is the interfacial Maxwell pressure:

$$p_{\rm M} = \frac{\varepsilon_0 \varepsilon_{\rm l}}{2} \left(E_{\rm n}^2 - E_{\rm t}^2 \right), \tag{19.81}$$

and x_f is the position of the three-phase contact line, θ_f is the contact angle or slope of the capillary ridge (see Figure 19.16). The Maxwell stress is not singular and is responsible for negative capillary pressure in the contact line region, thus pushing out a thin spontaneous EW film ahead of the macroscopic spreading drop. This spontaneous EW film was first observed by Jones et al. [100] and Ahmed et al. [101]. It advances much faster than the macroscopic spreading drop and behaves in a selfsimilar manner. In particular, it should not be confused with the molecular PF, for it is macroscopic with thickness of several μ m while the molecular PF is microscopic with only a few Å in thickness.

The governing equations for the two cases of EW (classical and spontaneous EW) are the same, while the boundary conditions are different, thus leading to different phenomena and properties. Comparisons between the two cases are given in Table 19.3 [40].

At the end of this section, we try to establish a more systematic framework of the EW problem. The method based on the phase-field model can be a broader way to solve EW. It can be used not only for obtaining the static contact angle, but also for exploring the dynamic details. In the phase-field model, which is



FIGURE 19.16 Spontaneous electrowetting film generated between the parallel planar line electrodes. The inset indicates the enlargement of the capillary ridge region. θ_{f} is the apparent static contact angle.

TABLE 19.3 Comparisons between Classical and Spontaneous Electrowetting

	Classical (Static) EW	Spontaneous EW
Configuration	Plate electrodes coated with dielectric film	Planar parallel line electrodes
Electric field	Normal to the vapor phase	Tangent to the liquid phase
	Singular and confined to small region ~ <i>d</i> (<i>d</i> is the thickness of the dielectric film)	Nonsingular and vanish when $h \sim R_e$ (h is the local thickness of the droplet, R_e is the width of the two electrodes)
Maxwell pressure	Point force at contact line	Body force within contact line region
gradient	Can be balanced by surface forces	Net force and cannot be balanced by surface forces
Spontaneous EW film	Have no spontaneous EW film	Have self-similar spontaneous EW film
Phenomenon	Static change in apparent contact angle	Dynamic spreading with spontaneous film

based on the basic principles of thermodynamics, the free energy function is defined as [102]

$$F(\phi, \nabla \phi) = \int_{V} \left(\Psi(\phi) + \frac{1}{2} \kappa |\nabla \phi|^{2} \right) dV + \int_{S} \phi(\phi) dS,$$
(19.82)

where ϕ is an order parameter used to distinguish different fluids, that is, $\phi = 1$ for one fluid (water droplet in the EW case) and $\phi = -1$ for the other fluid (air in the EW

case). In Equation 19.82, the first term $\Psi(\phi)$ is the bulk free energy density and takes the form

$$\Psi(\phi) = a(\phi^2 - 1)^2, \tag{19.83}$$

where *a* is a constant. The second term is the interfacial energy density with κ being another constant. The last term in the surface integral is the surface energy density, which can be taken as

$$\varphi(\phi) = -\gamma_{\rm lv} \cos \theta \frac{\phi(3-\phi^2)}{4} + \frac{1}{2}(\gamma_{\rm sl} + \gamma_{\rm sv}), \qquad (19.84)$$

where $\cos \theta$ is obtained by the L–Y equation. The order parameter ϕ is governed by the Cahn–Hilliard equation:

$$\frac{\partial \phi}{\partial t} + (\mathbf{u} \cdot \nabla)\phi = \nabla \cdot (M\nabla\mu), \qquad (19.85)$$

where μ is the chemical potential defined as the variation of free energy with respect to the order parameter:

$$\mu = \frac{\delta F}{\delta \phi} = \frac{d\Psi(\phi)}{d\phi} - \kappa \nabla^2 \phi = 4a\phi(\phi^2 - 1) - \kappa \nabla^2 \phi.$$
(19.86)

In phase-field models, interfaces between different phases are "diffuse" interfaces with a small, but finite, thickness. The EW problem can be solved by combining Equations 19.82 and 19.85 with specific boundary conditions. It is hard to have an analytical solution, and numerical simulations are often used [102,103]. However, since using a phase-field model for EW is still in its initial step, further studies are needed.

19.4 EXPERIMENTS AND MOLECULAR DYNAMICS SIMULATIONS

In this section, we will give a brief overview of EW-related experiments and MD simulations. While some of them were conducted to verify the existing theories, a number of experiments and MD simulations were also aimed at exploring new phenomena and mechanisms.

19.4.1 Electrowetting Experiments on Surfaces with Various Configurations

Conventional EW experiments are focused on ideal planar surfaces, which means that the surfaces are planar and smooth. However, ideal planar surfaces are relatively simple to model, while surfaces with different geometries and rough properties are more common. Wetting can be seen as a specific state of EW, that is, EW at V = 0. The study of wetting on structured surfaces has been conducted for tens of years, both theoretically and experimentally. In contrast, the theoretical and experimental research in EW is not that flourishing. In this section, typical experiments of EW on surfaces with various configurations, including planar, rough and curved surfaces, are presented.

19.4.1.1 Electrowetting on Planar Surfaces

The L–Y equation is the basis of EW or EWOD, which has been verified by many experiments [5,6,38,52,54]. Poly(dimethylsiloxane) (PDMS) is widely used as a base material for bio-MEMS/NEMS devices [104,105] because of its excellent properties of being optically transparent, chemically inert, and flexible. However, since the surface of PDMS is inherently hydrophobic, it is difficult to transfer and spread aqueous solutions [106]. EW is an effective way to hydrophilize the PDMS surface. Therefore, the study of PDMS as the dielectric film in EWOD is of great significance.

Dai and Zhao [54] conducted a series of EWOD experiments using PDMS as the dielectric film. Figure 19.17 shows the images of a droplet on the PDMS film of 9.1 μ m thickness. During the experiment, the voltage was increased from 0 to 360 V and back to 0. As shown in the three images in Figure 19.17, the contact angles changed from 110.1° to 46.9° and back to 104.6°, respectively. The surface converted from hydrophobic to hydrophilic and the decrease in the contact angle was 63.2°, so the effect of EW on a thin PDMS film was remarkable. They also studied the effect of PDMS film thickness on contact angle variation. Their results showed that the change in the contact angle increased with the thinning of the PDMS films, which was in good accord with the L–Y prediction.

Nanoscale EW effects were studied using atomic force microscopy by Guan et al. [107]. In their study, poly(methyl methacrylates) (PMMA) was used as the bare material. Adhesive interaction between the atomic force microscope (AFM) tip and the dielectric surface reflected the change of surface tension under the influence of applied voltage, thus leading to the EW effect. The results were in good accord with the Y–L prediction under a low electric field between the tip and the dielectric surface. Their study of nanoscale EW behavior provided complementary insights into macroscopic contact angle studies.

19.4.1.2 Electrowetting on Rough Surfaces

Surface roughness can increase the hydrophobicity of solid surfaces. EW can make the surface more hydrophilic. Both roughness and EW can physically modify the effective apparent contact angle by affecting the surface tension balance without altering the chemical properties of the surface or fluid. A combination of these two mechanisms will result in a large change in contact angle, or even change the surface from superhydrophobic to completely wetting.

EW on nanostructured superhydrophobic surfaces was investigated by Krupenkin et al. [46]. The surfaces were constructed by etching a microscopic array of cylindrical nanoposts into the surface of a silicon wafer. Each post had a diameter of about 350 nm and a height of about 7 μ m, and the distance between posts varied from



FIGURE 19.17 Images of water droplet on PDMS film with thickness of 9.1 μ m. The three images are under the voltage of 0 V, 360 V, and (back to) 0 V, respectively.

1 to 4 μ m. Several types of liquids were investigated, including water, alkanes, alcohols, ionic liquids, and various mixtures of these. In their experiment, the transition between a rolling ball droplet state and an immobile droplet state with the application of voltage was observed. In the rolling ball state, the droplet did not penetrate the nanoposts, which corresponded to the Cassie–Baxter model; in the immobile droplet state, the droplet completely wet the grooves, which corresponded to the Wenzel model. A transition from the rolling ball to the immobile droplet state was observed at a critical voltage of 22 V.

EW on superhydrophobic SU-8 (an epoxy-based negative photo-resist) patterned surface was investigated by Herbertson et al. [47]. The scanning electron microscopic

image of the completed structure consisting of cylindrical pillars is shown in Figure 19.18a. The SU-8 pillars provided necessary surface roughness. The electrolyte solution was deionized water with 0.01 M KCl. In this experiment, voltages were applied from 0 to 130 V and back to zero. The change in the cosine of the contact angle as a function of voltage is shown in Figure 19.18b. A high hysteresis in the contact angle was observed. EW on an ideal planar surface can be described by the L–Y equation and a reversible change in the contact angle is expected. However, in their experiment, reversibility was not observed, as the starting contact angle was 152° but the ending was 114°. This phenomenon can be explained as discussed in Section 19.3.2.1, by change of wetting behavior from the Cassie–Baxter to the Wenzel regime due to applied voltage, which is an irreversible process. It is also observed that there is a



FIGURE 19.18 (a) Left: The scanning electron microscope (SEM) image of a superhydrophobic patterned surface (SU-8) consisting of cylindrical pillars. Right: The schematic of the microstructures. (b) Cosine of contact angle of electrolyte fluid on (SU-8) as a function of the square of applied voltage (from 0 to 130 V and back to 0 V). (From *Sens. Actuators A: Phys.*, 130, D.L. Herbertson et al., Electrowetting on superhydrophobic SU-8 patterned surfaces, 189. Copyright 2006, with permission from Elsevier.)

critical voltage, where there is a change in the slope of the data line in the EW process. From Figure 19.18b, the critical voltage is near 45 V, before which the contact angle changes little whereas after which the contact angle changes appreciably. It can also be explained by the transition from the Cassie–Baxter to the Wenzel regime, at the critical voltage. The Wenzel model was used to fit the experimental data for the voltage range from 45 to 130 V, giving a roughness factor of 1.92 ± 0.1 . For voltage below 45 V, the liquid was considered unable to wick into the grooves and the Cassie–Baxter model was employed to explain the observation [43]. Both theoretical explanations were in good accord with the experimental data.

19.4.1.3 Electrowetting on Curved Surfaces

Kim and Steckl [26] studied the feasibility of using paper as a cheap and flexible substrate for e-paper, electronic display, and other EW devices. In their experiments, the paper was completely rolled into a cylinder, which was covered with a ground electrode, a dielectric film, and a fluoropolymer top layer, as depicted schematically in Figure 19.19b. Several categories of paper were investigated. The contact angle variations on these substrates as a function of voltage 0–60 V are shown in Figure 19.20.



FIGURE 19.19 (a) Photographs of electrowetting on rolled-paper substrate. Insets show the contact angle with (right) and without (left) applied voltage. (b) Schematic of the EW structure. (From D.Y. Kim and A.J. Steckl, Electrowetting on paper for electronic paper display, *ACS Appl. Mater. Interfaces*, 2, 3318. Copyright 2010, American Chemical Society.)



FIGURE 19.20 Contact angle (θ) versus applied voltage (*V*) on rolled substrate with different materials. All substrates were covered with a 1.0-µm-thick parylene-C dielectric film. The dashed line is the theoretical prediction using the Lippmann–Young (L–Y) Equation 19.6. The black line is the experimental data on a glass substrate. Three different materials of paper are tested, that is, SAPPI (HP), Kromekote, and Glassine. (From D.Y. Kim and A.J. Steckl, Electrowetting on paper for electronic paper display, *ACS Appl. Mater. Interfaces*, 2, 3318. Copyright 2010, American Chemical Society.)

The dotted line is the predicted CA value using the L–Y equation on planar surface $(\cos \theta = \cos \theta_{\rm Y} + (\epsilon V^2/2d\gamma_{\rm lv}))$. It can be seen that the experimental values deviate from the theoretical prediction, and the deviations are different for different categories of paper. It may arise from different properties of the paper. Possible variations of paper properties could be surface coating, roughness, thickness, and water uptake. Variations in surface curvature may also contribute to the variation of measured contact angles.

Fan and coworkers [22] studied "droplet-on-a-wristband" based on the study of EWOD in curved devices. They conducted a series of experiments on wrist-band-like curved surfaces whose curvatures (reciprocal of radius) were 0, 0.02, 0.04, and 0.06 mm⁻¹, and found that the curvature had no noticeable influence on the required driving voltages at the center point.

In Section 19.3.2.2, the theory of EW on curved surfaces has been presented. It predicts that at the present experimental condition (ξ or the ratio of *d* to *R* is small), the variation of the contact angle on curved surfaces is close to that on planar surfaces, and the surface curvature effect is not obvious. The experiments above accord well with the theoretical prediction. However, according to the theory, when *R* becomes very small or EWOD is on and below microscale, such as EWOD in CNTs or on graphene substrate, the influence of the surface curvature cannot be neglected.

Chen [108] studied EW in carbon nanotubes by means of MD simulations. The studies looked into the influence of surface curvature and adopted Lippmann's model of EW for a cylindrical capacitor. The results showed that the MD simulations were in good accord with the theoretical predictions.

Compared with the flourishing development of EW experiments on a macroscopic level, experiments or MD simulations of EW on and below microscale are rare in the published work. More studies are needed in future work.

19.4.2 BREAKDOWN OF THE DIELECTRIC FILM

Electrical breakdown of the dielectric film is a common failure form in EW, so how to reduce the critical breakdown voltage is of great importance. In typical EW experiments, the wire electrode is inserted into the droplet and maintains direct contact with it throughout the whole EW process. This method may lead to droplet contamination by the electrode, and the critical breakdown voltage is low. Feng and Zhao [51] put forward a new EW contact mode, aimed at effectively protecting the dielectric film from electrical breakdown. A PDMS membrane (thickness: 7.6 μ m) was used to demonstrate the instability process in their experiment. The distance between the wire electrode and the PDMS membrane had influence on the EW behavior of the PDMS membrane. The EW process in contact mode can be divided into three steps (see Figure 19.21):

- *Step 1.* The DC voltage is increased to a certain value (350 V in the experiment). In this step, the wire electrode does not contact the droplet.
- *Step 2*. The electrode-membrane distance is reduced until the conductive droplet is in contact with the wire electrode. In this step, the contact angle will decrease and reach equilibrium, after which the wire electrode is separated from the droplet.
- *Step 3.* The moving stage is adjusted to make the droplet contact the wire electrode again. As a result the contact angle will continue to decrease until it reaches a new equilibrium.

Step 2 and step 3 are unstable processes whose characteristic times are on the order 10 ms. The droplet will oscillate at its natural frequency of about 100 Hz. It was observed that the unstable process in fact started when the wire electrode was still a short distance above the droplet. When the voltage was increased to a high value, electrical breakdown of the dielectric film occurred. The whole process was recorded with a high-speed camera at 200 Hz (see Figure 19.22, voltage: 800 V, PDMS thickness: 4.8 μ m). A spark can be seen in Figure 19.22b and this was taken as the start of an electrical breakdown. The whole process of EW from instability to electrical breakdown, which means that the dielectric film has been destroyed (see Figure 19.23d).

In their contact mode EW, the contact time between wire electrode and droplet was less than 5 ms, which dramatically lowered the chance of breakdown. In their experiment, voltage even higher than 800 V did not induce breakdown in the PDMS



FIGURE 19.21 Droplet instability process of first contact with an electrode in EW contact mode. (a) The wire electrode does not contact the droplet. The DC voltage is increased to a certain value (350 V in the experiment). (b) The electrode–dielectric film distance is reduced until the conductive droplet is in contact with the wire electrode. (c) The contact angle decreases. (d) The contact angle reaches equilibrium and the wire electrode is separated from the droplet. (e) The moving stage is adjusted to make the droplet contact the wire electrode again. (f)–(i) The contact angle continues to decrease until it reaches a new equilibrium. (From J.T. Feng and Y.P. Zhao, Experimental observation of electrical instability of droplets on dielectric layer, *J. Phys. D: Appl. Phys.*, 41, 052004, 2008. With permission.)



FIGURE 19.22 Breakdown process in electrowetting (EW) contact mode. The whole process was recorded with a high speed camera at 200 Hz (voltage: 800 V, PDMS thickness: $4.8 \mu m$). The whole process is about 30 ms and the interval between each picture is 5 ms. (a) Initial state. (b) A sparkle can be seen. This is taken as the start of an electrical breakdown. (c) Electrical breakdown. (d)–(f) Electric energy is turned to dynamic energy of conductive liquids and a sputtered spray can be seen. (From J.T. Feng and Y.P. Zhao, Experimental observation of electrical instability of droplets on dielectric layer, *J. Phys. D: Appl. Phys.*, 41, 052004, 2008. With permission.)



FIGURE 19.23 Images depicting the complete process in electrowetting (EW) contact mode (from instability to electrical breakdown, voltage 800 V, thickness of the PDMS film 4.8 μ m). (a) Initial state. (b) First contact. The contact angle changes from 112.8° to 85.9°. (c) Second contact. The contact angle changes from 86.2° to 74.2°. (d) Bubbles can still be observed after breakdown. The contact angle is 76.7°. (From J.T. Feng and Y.P. Zhao, Experimental observation of electrical instability of droplets on dielectric layer, *J. Phys. D: Appl. Phys.*, 41, 052004, 2008. With permission.)

membrane (thickness: $4.8 \,\mu$ m) during the first two steps, while in normal mode the average critical voltage is 228 V.

19.4.3 VOLTAGE-INDUCED DROPLET ACTUATION

EW is an important technique for carrying out elementary operations on droplets, such as generating, transporting, splitting, and merging [4,21,109,110]. It can directly change the wettability and local contact angle of droplets on the solid surface by changing voltage applied to the microelectrode array under the dielectric film. This results in the asymmetric deformation of droplets and allows the actuation and control of droplets.

19.4.3.1 Droplet Transportation

Enclosed configuration is more common in digital microfluidics devices [69,111,112]. Figure 19.24 [69] shows the schematic of an EW microactuator. A droplet is sand-wiched between two sets of planar electrodes whose two surfaces are coated with a thin dielectric film. The upper plate consists of a single continuous ground electrode, whereas the bottom one has an array of independently addressable control electrodes. The droplet volume is controlled such that it contacts the upper ground electrode and its footprint overlaps with at least two adjacent control electrodes. The



FIGURE 19.24 Schematic cross-section of an electrowetting microactuator. (With permission from M.G. Pollack, R.B. Fair and A.D. Shenderov, Electrowetting-based actuation of liquid droplets for microfluidic applications, *Appl. Phys. Lett.*, 77, 1725. Copyright 2000, American Institute of Physics.)

surrounding medium can be either air or a fluid that is immiscible to prevent evaporation of the droplet. All electrodes are initially grounded, so that the initial contact angle is the equilibrium contact angle described by the Young equation. Then, the potential on the adjacent electrodes is increased until motion is observed. This threshold potential, which is caused by the contact angle hysteresis, is dependent on the system. A prototype device consisting of a single linear array of seven interdigitated control electrodes at a pitch of 1.5 mm was fabricated and tested by Pollack et al. [69]. In their experiments, 30–40 V was required to initiate movement of the droplet. Sustained droplet transport over thousands of cycles at switching rates of up to 20 Hz was demonstrated. This rate corresponded to an average droplet velocity of 3.0 cm/s, which cannot be achieved with thermocapillary systems because it will require temperature difference between the ends of the drop in excess of 100°C [113]. Their results demonstrated the feasibility of EW as an actuation mechanism for droplet-based microfluidic systems. Several other possible microactuator electrode arrangements are illustrated in Figure 19.25.



FIGURE 19.25 Several possible microactuator electrode arrangements investigated for moving droplets between electrodes.

19.4.3.2 Voltage-Induced Droplet Actuation on a Lotus Leaf

The general operations of a droplet using EW techniques can often be limited by an irreversible behavior. When the applied voltage is larger than a certain value, the hydrophobic property of the sample surface could not recover completely because of contact angle hysteresis. This irreversible behavior can be decreased with the use of super-hydrophobic surfaces such as dielectric films. A superhydrophobic surface [114,115] with a contact angle higher than 150° has aroused considerable attention. It is of great interest to study droplet actuation on the superhydrophobic surface owing to its two outstanding characteristics: a large contact angle and a low contact angle hysteresis.

EW on lotus leaf (EWOL) was studied [70] because it is superhydrophobic (contact angle of greater than 150°) and a weak conductor. The scanning electron microscopy (SEM) images of a fresh lotus leaf (on both sides) are shown in Figure 19.26. There



FIGURE 19.26 Images of lotus leaf under various magnifications. (a) An image of water droplet deposited on a lotus leaf. (b)–(e) Scanning electronic microscopy (SEM) images of the lotus leaf: (b) top side of lotus leaf, (c) papilla, (d) backside of the lotus leaf, and (e) the vein. The lotus surface has many papillae with radius of about 4 μ m. (With permission from J.T. Feng, F.C. Wang and Y.P. Zhao, Electrowetting on a lotus leaf, *Biomicrofluidics*, 3, 022406. Copyright 2009, American Institute of Physics.)

are many papillae with radius of about 4 µm on the lotus surface. The contact angles of water on lotus and dorsal leaves are 159° and 141°, respectively. Experiments with applied voltage of 150 V were conducted to demonstrate the process of droplet motion induced by applied voltage. It was found that the droplet climbed up the vein (a height of 1.3 mm) of the leaf. This is because the lotus leaf is not an equipotential plate. There is a gradient of the electrical potential between two sides of the droplet, resulting in an asymmetric deformation of droplets, which allows actuation and control of droplets. The voltage-induced droplet motion induced in the top side is different from that in the bottom side of the lotus leaf. In these experiments, applied voltage on the top side of the leaf caused the advancing contact angle of the droplet to jump from 154° to 114°, and then recover from 114° to 124° when the droplet totally settled down. When the voltage was applied to the bottom side of the leaf, however, the advancing contact angle jumped from 141° to 79° , and recovered from 79° to 96° when the droplet stopped moving. The recovery of the contact angle may be a result of residual charges in the droplet moving to the leaf gradually. Moreover, the experiments showed that when the applied voltage was more than 300 V, a lot of heat would be generated and the lotus leaf would be dehydrated by the heat. High voltage also caused the appearance of the lotus leaf to change significantly (see Figure 19.27).

In this experiment, the actuation potentials were greater than 100 V, the actuation speed of droplet motion was on the order of 10 mm/s, and the actuation time was on the order of 10 ms. Figure 19.28 shows the variation of the contact angles when 150 V was applied on the top side of the lotus leaf. It can be seen that the change of the advancing contact angle is different from that of the receding contact angle. Toward the end of the motion, the advancing contact angle still increased while the receding contact angle was approximately constant. This is because the droplet separated from the Pt electrode toward the end of the motion, which opened the electrical circuit, and with release of the residual charges in the droplet the advancing angle increased. The capacitance of the lotus leaf can be estimated from the actuation criterion [67]:



FIGURE 19.27 The lotus leaf before (left) and after (right) application of 400 V. (With permission from J.T. Feng, F.C. Wang and Y.P. Zhao, Electrowetting on a lotus leaf, *Biomicrofluidics*, 3, 022406. Copyright 2009, American Institute of Physics.)



FIGURE 19.28 Advancing and receding contact angles as a function of time after contact of the droplet and the electrode (the applied voltage is 150 V). (With permission from J.T. Feng, F.C. Wang and Y.P. Zhao, Electrowetting on a lotus leaf, *Biomicrofluidics*, 3, 022406. Copyright 2009, American Institute of Physics.)

$$\frac{c}{2\gamma_{\rm lv}}V_{\rm min}^2 = \frac{\alpha}{1-\alpha} \Big(\sin\theta_{V_{\rm min}} + \sin\theta_0\Big),\tag{19.87}$$

where *c* is the capacitance of the lotus leaf per unit area and V_{\min} is the minimum electric potential for actuation. In this case, $\theta_{V_{\min}} \approx \theta_0$ and the contact angle hysteresis α is sufficiently small; Equation 19.87 can be simplified as

$$C \approx \frac{4\gamma_{\rm lv}\alpha\sin\theta_0}{V_{\rm min}^2}.$$
 (19.88)

Equation 19.88 was used to estimate the capacitance of the lotus leaf per unit area to be about 0.63 μ F/m² [70].

19.4.3.3 All-Terrain Droplet Actuation

Conventional study of digital microfluidics was mainly concentrated on droplet actuation on a single plane. As digital devices develop fast nowadays, conventional planar devices are not sufficient, and flexible and portable devices are in strong demand. Abdelgawad et al. [116] studied all-terrain droplet actuation (ATDA), showing that ATDA can be used to manipulate droplets across a wide range of geometries, including inclined, declined, vertical, twisted, and upside-down configurations. In their study, an open digital microfluidic device configuration was used to take full advantage of its flexibility. ATDA devices were formed by patterning arrays of copper electrodes and coating them with PDMS and Teflon-AF. Droplets were actuated by applying potentials to sequential pairs of electrodes. This enabled droplet movement on surfaces with different configurations. In all the geometries investigated, droplet movement was found to be facile and fast, with no significant differences relative to conventional planar microfluidics.

Since droplets have never before been manipulated on all-terrain surfaces, the researchers developed a model for predicting droplet motion. Unlike conventional planar situation, where the actuation force $F_{\rm EWOD}$ and the resistive friction force $F_{\rm f}$ work together to determine droplet motion, gravity effect was also considered in the ATDA situation and an additional force F_g was introduced. For example, for droplet movement up an inclined plane, F_{g} was calculated simply as the projection of droplet weight down the inclined plane. The researchers gave the maximum device inclination angle at which the actuation force (for a given droplet volume) was predicted to be larger than or equal to the resistive force, that is, $F_{\text{EWOD}} \ge F_{\text{f}} + F_{\text{g}}$. The experimental results showed good agreement with the theoretical prediction using $F_{\text{EWOD}} \approx \frac{1}{2}\pi R \gamma_{\text{Iv}} (\cos \theta_{\text{a}} - \cos \theta_{\text{r}}) \text{ and } F_{\text{f}} = e^{(0.4084 \ln V + 0.4153)} [116].$ The curve predicted that a droplet with volume less than ~7.3 µL can be driven up a 90° incline, whereas droplets with larger volumes can only be driven up inclinations with reduced angle. Moreover, it was observed that for an inclination angle far below the maximum, lower actuation force (and lower applied potential) was required to drive the droplet up the inclined plane.

19.4.4 IN SITU OBSERVATION OF THERMAL MARANGONI CONVECTION

An experiment on *in situ* observation of thermal Marangoni convection in sessile droplets was conducted by Wang and Zhao [117]. Infrared (IR) thermal imaging was applied to visualize transient temperature distribution on the surface of the droplet, while microparticle image velocimetry (micro-PIV) was used to illustrate the fluid field inside.

In the experiment, a droplet of aqueous KCl solution was trapped between a PDMS hydrophobic layer and an indium tin oxide (ITO) conductive glass hydrophilic layer (see Figure 19.29). When a platinum electrode with a diameter of 100 μ m touched the apex of the droplet (60 V DC voltage applied), current passed through



FIGURE 19.29 Schematic of surface flow in a droplet of aqueous KCl. The isotherms at different times are marked to show the development of the temperature field on the surface. The arrows indicate the direction of surface flow.

and heated the droplet. With the occurrence of the temperature gradient, the surface tension of the droplet between the bottom and the apex became uneven. The warmer region at the apex had smaller surface tension than the cooler region at the bottom. Consequently, the liquid on the surface flows downward when the liquid inside the drop flows upward. The heated surface region developed isotherms as shown by the dashed line profile in Figure 19.29. Since the cross-section was small at the apex, the current density was high and most of the heat was generated there (see Figure 19.30a). In the picture, the maximum surface temperature achieved was 100°C at the top region of the droplet. In this experiment, the *Mg* number of the droplet was calculated using Equation 19.61 to be 4.24×10^4 (R = 1 mm, $a = 0.14 \times 10^{-6} \text{ m}^2/\text{s}$, $v = 8.94 \times 10^{-7} \text{ m}^2/\text{s}$, and $\Delta T = 20^\circ\text{C}$). This value is of the same order as that reported by Evren-Selamet et al. [118]. The thermal evolution was recorded in Figure 19.30a–d. The four thermal images were taken in series with a constant time interval of 0.5 s. The results agreed well with the theory of Marangoni convection.

The interior flow field, which was detected by the micro-PIV method, is shown in Figure 19.31. Two symmetrical vortices appeared as soon as the electrode touched the droplet. In the center of the droplet, the particles in the solution moved swiftly from the bottom ITO glass electrode to the top Pt electrode. The flow velocity in the center reached the maximum of about 17.5 mm/s; in the center of the vortex near the surface, the particles did not move and the velocity dropped to zero. Note that, in this experiment, gravity-driven flow was negligible because of the small variation in density. Also, the influence of liquid evaporation was ignored since the duration of the observation was short, and the flow was entirely due to Marangoni convection.

In ideal EWOD devices, the Mg number is less than the critical value ($Mg_c = 80$), so Marangoni convection can be neglected. However, if the dielectric film under the drop-let developed a hole, just like the case in this experiment, the Mg number would be much larger than the critical value, and Marangoni convection must be taken into account.



FIGURE 19.30 Infrared thermal image of a droplet of KCl solution trapped between PDMS and indium tin oxide (ITO) conductive glass. Left image is the temperature distribution on the droplet surface when the Pt electrode contacts the droplet. The temperature is highest at the top region and lowest at the bottom region. Right images (a)–(d) show the evolution process of temperature distribution. The time interval between every two neighboring pictures is 0.5 s.



FIGURE 19.31 PIV images of the droplet heated by an electrode. (a) Vortices formed with an upward stream in the center. (b) Visualized flow field.

19.4.5 Electro-Elastocapillarity: Electrowetting on Flexible Substance

Ever since self-assembled three-dimensional microstructures have been realized using elastocapillarity (EC) [119], studies on EC phenomenon have attracted considerable attention because of its realized and potential applications in NEMS/MEMS [120]. Since wrapping of droplet with flexible substrate in EC is spontaneous, it is irreversible, which restricts its application. The PF may be the key to solving this problem due to its unique transport properties. Besides, voltage is applied in order to produce reversible wrapping and unwrapping, and this phenomenon is called electro-elastocapillarity (EEC) [88]. In the case of EW, a typical electric energy $E \cdot \mu$ (*E* is the electric field vector and μ the dipole moment vector) in the PF cannot be neglected relative to thermal energy k_BT (k_B is the Boltzmann's constant and *T* the absolute temperature). Polarization is strongest in the PF and dipolar water molecules may therefore be attracted to the PF [88]. Hence, the PF plays a critical role in EW.

An EEC process was simulated, using graphene to wrap the droplet [88]. The graphene automatically wraps the droplet when the radius of the droplet is larger than the EC length $L_{\rm EC} = (B/\gamma)^{1/2}$ [121], where *B* is the flexural stiffness (for graphene its value is about 0.2 nN · nm [122]). Then, the wrapped droplet is unwrapped on a gold substrate under E = 0.544 V/nm along the -y direction (see Figure 19.32). To avoid interfering with the process, the vdW force between the graphene and the substrate is reduced to 0.1% under the electric field. As the propagation of the PF is faster than the liquid above it and the PF actually acts solid-like, the PF pushes the graphene and unwraps it with a force on the order of 1 nN/nm. Thus, reversible wrapping and



FIGURE 19.32 The dynamic electroelastocapillary (EEC) process of a droplet on gold substrate. The wrapped droplet in (a) progressively unwraps (b–g) on the gold substrate under E = 0.544 V/nm along the –y direction. The line under the droplet represents the graphene. (From Q. Yuan and Y.P. Zhao, Precursor film in dynamic wetting, electrowetting, and electro-elasto-capillarity, *Phys. Rev. Lett.*, 104, 246101. Copyright 2010 by the American Physical Society.)

unwrapping of the droplet with graphene is realized. The dynamic process of EEC is a promising candidate for drug delivery application at a micro- or nanoscale.

19.4.6 Electrowetting in a Hydrophilic Interior Corner

Liquid transport in an interior corner is a crucial requirement for a variety of applications, such as aerospace, micro/nanofluidics, biology, fuel cell, and so on. It is of great interest to improve the transport velocity in these applications. The topological structure of the interior corner leads to significant changes in the dynamics of wetting. A droplet will spread until its dynamic contact angle reaches an equilibrium value θ_0 (Young's equation) when placed on a hydrophilic surface. The question is, what will happen when the two contact lines of the droplet on wedge surfaces encounter at a hydrophilic interior corner with an interior angle of 2α ?

Dynamic wetting in a hydrophilic interior corner was simulated by Yuan and Zhao [123]. The atomic details of a water droplet in a hydrophilic gold interior corner with different interior angles in dynamic wetting were explored. The droplet was pulled along the bisector of the interior angle toward the interior corner by an attractive vdW force *F*. Then, the droplet spread on the substrate driven by the disjoining pressure. According to the MD results, the wetting transition is controlled by the interior angle. When $2\alpha < 135^\circ$, an apparent PC advances along the interior corner, while the PF advances on the wedge surface, as shown in Figure 19.33c and d for $2\alpha = 45^\circ$. The PC propagated much faster than the PF and completely wetted the interior corner. When $2\alpha \ge 135^\circ$, only the PF was observed and partially wetted the interior corner, while



FIGURE 19.33 Formation mechanism and propagation characteristics of precursor chain (PC): (a) Initial (t = 0) oblique view. (b) Initial (t = 0) cross-section of the simulation domain. (c) Final (t = 50 ns) oblique view. (d) Final (t = 50 ns) cross-section of the simulation result. The interior corner consists of gold atoms. (e) The propagation length of the PC as a function of time (points are molecular dynamics simulations; lines are fits to power law). PC: red (26.6°), green (45.0°), blue (63.4°), cyan (90°), and purple (116.6°). PF: black. (From Q. Yuan and Y.P. Zhao, Topology-dominated dynamic wetting of the precursor chain in a hydrophilic interior corner, *Proc. R. Soc.* A, 468, 310, 2012. By permission of The Royal Society of Chemistry.)

no apparent PC could be found. The propagation lengths of the PC as a function of time for different interior angles are shown in Figure 19.33e. The data were fitted using a power law function similar to the treatment of the PF [88]. The velocity of PC v_{PC} , which is the slope of the length-time curve, is about 10⁻¹ m/s. This is one order of magnitude higher than v_{PF} (~10⁻² m/s). When 2 α was small (2 α = 26.6°, 45.0°), the

propagation length initially remained zero for a characteristic time of about 10 ns, during which the droplet was pulled to the interior corner. The existence of the PC brings atomic details to eliminate stress singularity in the interior corner.

The advance velocity of the PC was one order of magnitude faster than the PF. MKT was used to investigate the transport properties of the PC. The results showed that (1) the PC was driven by the disjoining pressure, whose energy could be obtained from theoretical derivations and MD results (2) because water molecules were confined in the interior corner, the potential surface near the interior corner was lower and smoother than that on the bare surface, and quickly decayed over a distance of about the size of one water molecule. Hence, the PC could generate, exist stably, and propagate fast. In the PC, a one-dimensional (1D) hydrogen-bond (H-bond) chain generated the pressure to drive the PC to slip like ice. With an increase of 2α , the potential surface near the interior corner became high and rough, and the transport properties of the PC gradually changed and became the same as those of the PF.

EW in a hydrophilic interior corner was also explored. Models of EW in hydrophilic interior corners with $2\alpha = 26.6^{\circ}$ and 90.0° are shown in Figure 19.34 [124]. Figure 19.35a and b shows the propagation of the PC in wetting and under EW in the interior corner with interior angles of 26.6° and 90.0° , respectively [124]. Owing to the effect of



FIGURE 19.34 Configurations of EW in interior corners; surface gold atoms are charged (q = 0.02e): (a) opening angle, 26.6°, (b) opening angle, 90°. (Adapted from Q. Yuan. The electro-mechanical coupling property of topological wetting interface dynamics at nanoscale: [D]. Beijing: Graduate University of Chinese Academy of Sciences, 2011.)



FIGURE 19.35 Comparison of precursor chain (PC) propagation in wetting versus electrowetting (EW) in an interior corner: (a) opening angle of 26.6°, (b) opening angle of 90°. (Adapted from Q. Yuan. The electro-mechanical coupling property of topological wetting interface dynamics at nanoscale: [D]. Beijing: Graduate University of Chinese Academy of Sciences, 2011.)

the electric driving work in EW, the advance speed of PC was one order of magnitude (i.e., 10⁻¹ m/s) faster than that in the wetting process. As the interior angle becomes smaller, the charge density within its vicinity becomes larger so that the propagation velocity further increases (compared with that in the wetting process) more obviously.

19.4.7 ELECTROWETTING AS A TOOL FOR SUPPRESSING THE COFFEE STAIN

Ring-like solid residues along the contact line remain, after evaporating drops of colloidal suspensions or solutions of nonvolatile species. This is known as the coffee stain effect, which is undesired in applications such as coating and printing. Eral et al. [125] proposed a method to solve this problem by applying EW with an alternating (AC) voltage to an evaporating droplet. Coffee stains are formed because of the

combination of contact line pinning and the resulting flux (Marangoni flows and electroosmotic flows) of solvent and solute toward the contact line. EW can be a particularly effective tool to counteract the coffee stain effect because of its ability to address both aspects of the problem simultaneously. It can not only set pinned contact lines in motion and weaken the contact angle hysteresis, but can also generate internal flow fields within the drops.

In the experiments, a transparent ITO glass, which was covered with a 5- μ m-thick layer of SU8, was used as the electrode. Voltage with a fixed root-mean-square amplitude of $U_{\rm rms} = 200$ V was applied throughout at frequencies varying from 6 Hz to 100 kHz. Different aqueous solutions were prepared and tested, including the colloidal suspensions of fluorescently labeled carboxyl-terminated polystyrene particles, ranging from 0.1 to 5 μ m in diameter, as well as DNA solutions. The experimental suppression of the coffee stain effect using EW was given in Ref. [125]. The behavior referred to three different frequency regimes:

- 1. The quasistatic regime, at frequencies below the lowest eigenfrequency of the drop, that is, typically up to about 10 Hz for millimeter drops.
- 2. The hydrodynamic regime, in the range of the eigenfrequencies of the drop from several tens of Hz to a few kHz.
- 3. The electrothermal regime, at frequencies allowing for penetration of the electric field into the liquid bulk. It can be seen that smallest residue spots were achieved in the hydrodynamic regime or by a combination of high frequencies with low-frequency amplitude modulation.

19.5 SUMMARY AND CONCLUSIONS

This chapter briefly reviews the EW and EWOD as an MCL problem, in which the "Huh–Scriven paradox" is of main scientific concern. Systematic research is needed to focus on the elimination of the singularities for electrical and mechanical fields at the TCL, and a unified framework needs to be constructed. PF and PC are proven to be two effective physical mechanisms for the nano-EW of droplet spreading on a flat substrate [79] and in an interior corner [112]. Are slip boundary, diffuse liquid–vapor interface, or other mechanisms still applicable in the EW and EWOD cases as those in the classical MCL problem? This is still an open question.

EWOD has been widely used as a tool to manipulate microdroplets. Unlike macrosystems, surface tension effect will be significant due to the increase in surface-tovolume ratio in such microsystems. Therefore, a good understanding of the relevant characteristic time and length scales will assist the study of surface effects and help with the design of new micro- and nanosystems. In Section 19.2, some characteristic time and length scales are discussed. Capillary characteristic time and Lord Rayleigh's period are used to measure the strength of the droplet mass compared with surface tension, whereas viscous characteristic time is the ratio of the liquid viscosity to surface tension. These characteristic timescales may have a direct or indirect effect on the actuation of droplets. Then, the EW number is defined and used to measure the strength of the electrostatic energy relative to surface tension. Considering size effects, other two characteristic length scales are also given, representing the line tension and Debye screening length, respectively.

The L-Y equation is the fundamental of EWOD. It can be derived using different approaches, three of which are given as examples: the thermodynamic approach, the energy minimization approach, and the electromechanical approach. Since it is derived under ideal assumptions that cannot be always satisfactory in reality, it needs to be modified in various situations. Two different models, that is, the Cassie-Baxter model and the Wenzel model, are used to modify and extend the L-Y equation for use on rough surfaces. It was found that rough surfaces can attain better hydrophobicity than smooth surfaces. Then, considering the surface curvature effect, an extended L-Y equation on curved surfaces is obtained and a curvature-modified EW number is introduced. The surface curvature effect will become even more significant with decreasing system size, so it cannot be neglected on and below microscale. Besides, it is found that concave surfaces can enhance wettability better than convex surfaces when applying the same voltage. Next, EWOD under high voltage is discussed. The experiments showed that the L-Y equation was only applicable under a low voltage. Contact angle saturation and dielectric film breakdown may happen under high voltage and the phenomenon cannot be explained by the L-Y equation. The mechanism is still not clear and possible explanations are proposed. EWOD at micro- and nanoscales are then discussed. The line tension works at or under microlevel, in which case the L-Y equation should be modified by adding this effect. As was presented in Section 19.2, the droplet is conductive at nanoscale because its characteristic length is less than the Debye screening length. An expression for EWOD is given for such situations. The L-Y equation or its extensions discussed above are focused on static cases. However, for many practical applications, however, dynamic properties are of great interest. Actuation of the droplet is one of the most common forms of dynamic movement. Here, the problem is concerned with minimum actuation voltage, which is relevant to contact angle hysteresis. A mechanical analysis is presented and an expression for minimum actuation voltage is proposed. Next, the Marangoni convection, which is related to uneven heat distribution on the droplet, is taken into consideration. The value of the Marangoni number can be a criterion for deciding whether the Marangoni convection should or should not be considered. Finally, the molecular PF, which may be one of the answers to the Huh-Scriven paradox, is discussed. At the end of Section 19.3, compared with the conventional EWOD, another form that is known as spontaneous EW is discussed.

In Section 19.4, relevant experiments and molecular dynamics simulations corresponding to the theories in Section 19.3 are presented, including the conventional EWOD experiments, breakdown of dielectric film under high voltage, voltage-induced droplet actuation, *in situ* observation of thermal Marangoni convection, wetting and EW in a hydrophilic interior corner, and the EEC phenomenon. The voltage-induced droplet actuation experiments are particularly discussed in relation to its application in devices and other potential uses. An experiment on droplet with actuation time on the order of 10 ms is presented. An all-terrain droplet actuation is shown, demonstrating the feasibility of future flexible devices. The feasibility is further verified by the electro-elastocapillarity phenomenon (both in experiments and simulations), which is a good candidate for drug delivery at the micro- or nanoscale. At the end of Section 19.4, EW as an efficient tool for suppressing the coffee stain effect is presented. While considerable studies have been conducted and great progress has been made in recent decades, there are still many unknowns about the EW phenomenon, and more researches are needed. Since EW at micro- and nanolevels performs differently from that at macroscopic level due to scale effect, the study of EW at small scales is of great interest and significance. Several applications based on EW have already entered the market while lots of potential applications are under study. We hope that this review will stimulate further studies and progress in EW.

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SYMBOLS

Α	droplet base area (m ²)
С	capacitance per unit area (F/m ²)
Ca	capillary number (dimensionless number)
d	thickness of the dielectric film (µm)
$d_{\rm E}$	thickness of the electrical double layer (m)
D	droplet diameter (m)
$D_{\rm visc}$	energy dissipation per unit time and unit length of the contact line
	$(\mathbf{J} \cdot \mathbf{m}^{-1} \cdot \mathbf{s}^{-1})$
е	charge of an electron (C)
Ε	electric field intensity (V/m)
Ew	EW number (dimensionless number)
f_1, f_2, R_1	surface roughness factor
F	free energy (J)
$F_{\rm d}$	electrostatic force (N)
$F_{\rm drag}$	drag force applied by the Pt electrode (N)
Fe	net electrostatic force acting on the liquid-vapor surface (N)
$F_{\rm elec}$	electrowetting (EW) force (N)
$F_{\rm f}$	contact angle hysteresis force (N)
F _{viscous}	viscous resistance (N)
$\Delta G_{\rm m}$	barrier energy (J)
Н	local thickness of the droplet (m)
h	maximum height of the droplet (m)
$h_{ m P}$	Planck constant (J·s)
k	thermal coefficient (/°C)
k _B	Boltzmann's constant (J/K)
l	characteristic length (m)
т	droplet mass (kg)
Mg	Marangoni number (dimensionless number)
$M_{ m i}$	molar concentration (mol/m ³)

p	pressure (Pa)
R	radius of the contact line (m)
R _e	width of the electrode (m)
R _s	radius of the substrate (m)
t	characteristic time (s)
Т	absolute temperature (K)
Τ	Maxwell stress tensor
$T_{\rm LR}$	Lord Rayleigh's period (s)
$T_{\rm c}$	capillary characteristic time (s)
$T_{\rm vis}$	viscous characteristic time (s)
U	electric energy (J)
v	velocity (m/s)
V	voltage (V)
$W_{\rm B}$	work that the voltage source performs (J)
Z_i	valency
α	contact angle hysteresis (°)
$\gamma_{\rm lv}$	liquid-vapor surface tension (N/m)
$\gamma_{\rm sl}$	solid-liquid interfacial tension (N/m)
$\gamma_{\rm sv}$	solid-vapor interfacial tension (N/m)
δ	average distance between the liquid and the solid molecules (m)
\boxtimes	dielectric constant (F/m)
ζ	thermal diffusivity (m ² /s)
η	droplet dynamic viscosity (Pa · s)
θ	contact angle (°)
$\lambda_{\rm D}$	Debye length (m)
μ	chemical potential (J/mol)
μ	free dipole (C/mol)
ν	molecule jump frequency (Hz)
ξ	order parameter representing for d/R_s
ρ	droplet mass density (kg/m ³)
σ	surface charge density (C/m ²)
τ	line tension (N)
$\tau_{\rm w}$	shear stress (N/m ²)
Φ	electrostatic potential (V)
χ	geodesic curvature at the contact point (m ⁻¹)
φ	an order parameter used to distinguish different fluids

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