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Wetting and electrowetting on corrugated substrates

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Wetting and electrowetting (EW) on corrugated substrates are studied experimentally and theoretically in this paper. On corrugated substrates, because of the anisotropy of surface morphology, the droplet shows an elliptical shape and the spreading velocities in different directions are different. Spreading of a droplet is usually controlled not only by the surface tensions but also by hemi-wicking. Our experimental results indicated that liquids along the grooves propagate much faster than those in the direction vertical to the grooves. However, spreading in both directions obeys the same scaling law of $l \sim t^{4/5}$. EW on corrugated substrates reveals some differences with that on smooth surfaces. The change of contact angles with an applied voltage follows a linear relationship in two stages instead of the smooth curve on flat surfaces. There exists a critical voltage which divides the two stages. The transition of a droplet from the Cassie state to the Wenzel state on corrugated substrates was also discussed. The extended EW equation was derived with the free energy minimization approach, and the anisotropic factor was introduced. From the extended equation, it is found that EW is affected by the anisotropic factor significantly. For the smooth surfaces, the extended EW equation will degenerate to the classical Lippmann-Young equation. Our research may help us to understand the wetting and EW of droplets on corrugated substrates and assist in their design for practical applications. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4984244>]

I. INTRODUCTION

Corrugated surfaces exist broadly in nature. When a droplet is deposited on a corrugated substrate, the droplet will be elongated along the groove and form an elliptical or ellipse-like droplet shape¹⁻⁴ and a tortuous three phase contact line.⁵ The wetting properties, e.g., the velocity of droplet spreading, the droplet shape, and the response of a droplet to the electric field, are usually not only influenced by the surface tensions but also significantly affected by the anisotropic morphology of corrugated surfaces. It is well known that spreading of a droplet can be effectively controlled by electrowetting (EW), which can date back to the electrocapillarity discovered by Lippmann in 1875.⁶ Since the 1990s, great developments have been made in EW, and nowadays these achievements can be seen in various fields such as displays,⁷⁻⁹ optics (liquid lenses,¹⁰⁻¹² various beam steering devices,¹³ reflectors), reserve batteries,^{14,15} lab-on-a-chip systems,¹⁶⁻¹⁸ and electronic papers.^{19,20} Compared to other methods of controlling the droplet, such as dielectrophoresis (DEP), EW has the advantages of easy operation, sensitive response, and electrical reversibility. Owing to the high efficiency in controlling the droplet action, EW received significant attention in recent years.

EW controls droplet spreading by applying voltages. When the applied voltage increases, the contact angle (CA) decreases. In contrast, when the applied voltage decreases, the CA increases. The schematic diagram of EW is shown in Fig.

1. The relationship between the apparent CA and the applied voltage can be described by the Lippmann-Young equation,²¹

$$\cos \theta = \cos \theta_0 + \frac{\varepsilon V^2}{2\gamma_{lv}d}, \quad (1)$$

where θ_0 , V , ε , γ_{lv} , and d represent the initial CA, the applied voltage, the dielectric constant, the liquid-vapor interface tension, and the distance between the electrodes. The main non-dimensional numbers related to EW include the Bond number $Bo = \rho g l^2 \gamma_{lv}$, the Hamaker number $Ha = A(\pi \gamma_{lv} l^2)$, and the EW number $\eta_e = \varepsilon V^2 / (2l \gamma_{lv})$, which work at the characteristic lengths of 10^{-3} m, 10^{-10} – 10^{-9} m, and 10^{-10} – 10^{-8} m, respectively,²² representing the ratios of gravity-to-surface tension, van der Waals force-to-surface tension, and electrical force-to-surface tension, respectively.

Nowadays, wetting and EW on special surfaces draw great interest. The general rough surfaces,²³⁻²⁵ curve surfaces,^{26,27} and ordered rough surfaces²⁸⁻³¹ are all paid significant attention. EW, as a prolongation of wetting, has a close relationship with wetting.³³ Similar to wetting on anisotropic surfaces,³³ the droplets also form elliptical shapes under applied voltages in EW, as sketched in Fig. 2. Droplet wettability on anisotropic surfaces was first studied in the 1990s.³² Later, Brandon and Marmur³¹ studied the final shapes of droplets on anisotropic patterned surfaces under the influence of droplet sizes. Plenty of experiments or theoretical analysis³⁴⁻³⁸ were carried out focusing on the variation of the droplet shape and the difference of the CA of droplets on anisotropic substrates. A recent review by Xia³⁹ summarized the latest evolution of the special phenomena of droplets on anisotropic surfaces. However,

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FIG. 1. EW models: (a) A droplet maintains a large CA without applied voltage. (b) The CA of a droplet decreases and the area of interface between solid and liquid increases under applied voltage.

FIG. 2. The contact line shapes of droplets under different applied voltages on smooth substrates and corrugated substrates. The droplet shows a shape of circle on the smooth substrate (a) and a shape of ellipse on the corrugated substrate (b).

the mechanism for why droplets form elliptical or ellipse-like shapes is still not elucidated clearly and EW on anisotropic surfaces has rarely been studied until now.

In this paper, we mainly focus on the properties of wetting in microscale and the difference of EW on smooth surfaces and corrugated surfaces. A dimensionless number $S_c = f_y/f_x$ was introduced to characterize the difference between smooth surfaces and corrugated surfaces, where f_x and f_y represent the characteristic ratio in the directions vertical to and along the grooves, respectively. To learn about the state of a droplet in microscale on micropattern surfaces, the micro-sight of the contact line of droplets was observed, and the spreading velocities of the liquid in the directions vertical to and along the grooves were compared. The EW process was studied with experiments and theoretical analysis. The experiments of EW were carried out to learn about the change in CAs with applied voltages on corrugated surfaces. The free energy minimization approach was employed to derive the extended EW equation on corrugated surfaces. The transition from the Cassie state to the Wenzel state of droplets and the critical voltages that occurred in the transition are also discussed. Given the broad existence of corrugated surfaces in nature, which are highly effective in leading water to spread in a microfluidic chip and other bionic products, the studies of wetting and EW on corrugated surfaces will offer important information.

II. MATERIALS AND METHODS

The corrugated substrates used in experiments were made of polydimethylsiloxane (PDMS) with resin and curing agent

(Sylgard 184, Dow Chemical, Co.) at a ratio of 10:1 by mass. The fabrication of corrugated surfaces was carried out in three steps. First, PDMS was made into several small cuboids of $0.5 \times 2 \times 5 \text{ cm}^3$ in size, and then PDMS was solidified at 80°C for 4 h. Second, the cuboids were fixed on circular tubes with different radii, and then the PDMS cuboids were put into a plasma cleaner with different irradiation times ranging from 10 min to 40 min. The wavelength and amplitude of the corrugated substrate were determined by the plasma irradiation time. Third, the cuboids were taken out and were completely relaxed. The corrugated morphology was formed on the cuboids' surface. The wavelength and amplitude of the corrugated surfaces were characterized by⁴⁰

$$L = \frac{2\pi h_f}{(1 + \varepsilon_{s(\text{pre})})(1 + \xi)^{\frac{1}{3}}} \left[\frac{Y_f (1 - \nu_s^2)}{3 Y_s (1 - \nu_f^2)} \right]^{\frac{1}{3}}, \quad (2)$$

$$A = \frac{h_f}{\sqrt{1 + \varepsilon_{s(\text{pre})}}(1 + \xi)^{\frac{1}{3}}} \sqrt{\frac{\varepsilon_{s(\text{pre})}}{\varepsilon_c} - 1}, \quad (3)$$

where $\xi = (5/32) \varepsilon_{s(\text{pre})} (1 + \varepsilon_{s(\text{pre})})$ represents the large deformation and geometrical nonlinearity in the substrate and $\varepsilon_{s(c)} = (1/4) [3Y_s (1 - \nu_s^2) / Y_f (1 - \nu_f^2)]^{2/3}$ denotes the critical buckling strain or the minimum strain needed to achieve buckling. ν is the Poisson's ratio; Y is the Young's modulus, and the subscripts s and f refer to the substrate and stiff thin film, respectively. h_f is the thickness of the stiff thin film. Note that Eqs. (2) and (3) are used for the fabrication of corrugated substrates. The schematic diagram of surface morphology and several samples is shown in Fig. 3(a). X and Y denote the directions vertical to the grooves and along the grooves, respectively, as marked in Fig. 3.

Wetting experiments were carried out on these corrugated cuboids and EW experiments were carried out on thin corrugated PDMS films. These thin films were made by reversing molds with several steps, including silanizing the surfaces of PDMS cuboids, spin-coating of PDMS liquid on these cuboids, and peeling off the thin films from cuboids after solidification at 80°C for 4 h. For these corrugated surfaces, the morphology of the surface can be described as

$$w = A \cos \frac{2\pi x}{L}, \quad (4)$$

where A and L are the amplitude and wavelength of the corrugated surfaces, respectively. For a rough surface, the characteristic ratio is defined as the ratio between the actual and projected surface areas.³¹ For the anisotropic surfaces, there are different characteristic ratios in the X and Y directions. In order to characterize the difference between the anisotropic and isotropic surfaces, we introduced a dimensionless number S_c , which is defined as

$$S_c = \frac{f_y}{f_x}, \quad (5)$$

where f_x and f_y denote the characteristic ratios in the X and Y directions of the corrugated surfaces, respectively; $f_x = A_{\text{actx}}/A_{\text{appx}} = (1/L) \int_0^L \sqrt{1 + (4\pi^2 A^2/L^2) \cos^2(2\pi x/L)} dx$ and $f_y = A_{\text{acty}}/A_{\text{app}} = 1$, where A_{actx} , A_{appx} , A_{acty} , and A_{app} denote the actual area and projected area in the X and Y

FIG. 3. The images of several samples and the experimental setups. (a) The images of partial samples and the corresponding surface wavelengths and amplitudes, scanned by atomic force microscopy (AFM). The X and Y directions were defined as the directions vertical to and along the grooves, respectively. (b) A schematic of the experimental setups used in the experiments of wetting and EW.

TABLE I. The parameters of samples used in the experiments.

Sample	1	2	3	4	5	6
L (μm)	1	2	2	2	6	8
A (μm)	2	2	1	0.5	1	1
S_c	0.239	0.434	0.683	0.877	0.939	0.964

directions, respectively. The parameters of S_c used in the experiments are listed in Table I.

In experiments, the liquid motion was captured using a high-power microscope (KH-8700) and a high-speed camera. The CAs were captured using the Contact Angle System (OCA 20, Data Physics). The schematic of the experimental setup is shown in Fig. 3(b).

III. REDEFINITION OF BASIC CONCEPTION ABOUT WETTING

In this section, we focus on the basic conceptions of wetting on corrugated surfaces. The basic conceptions of wetting and EW on smooth surfaces are well defined now. However, they are not well defined for anisotropic surfaces.

A. Redefinition of CA on anisotropic surfaces

CA is the most basic conception of wetting on a surface. It can be calculated by using the Young's equation for a droplet deposited on a smooth surface. When the droplet is deposited on a rough surface, the apparent CA is not equal to the actual CA, and it can usually be described by the Cassie or Wenzel equation. However, the Cassie and Wenzel equations do not consider the impact of morphology anisotropy on CAs. On smooth or other isotropic rough surfaces, the droplets have the same CAs in different directions. However, on anisotropic surfaces, the droplets usually have different CAs in different directions. Here, for the basic conceptions of wetting on anisotropic surfaces, we attempted to give the new definitions. Although lots of articles have been published about anisotropic wetting, the basic conceptions have never been discussed.

A droplet on corrugated substrates has different CAs in different directions. To learn about how the CA varies around

the contact line and how the CAs change in different directions with respect to the cross angle, we carried out the experiments and the results are shown in Fig. 4. From the results, we found that the CA decreases as the cross angle increases. For the surface with small S_c , the CAs maintain a big difference between the largest and smallest CAs, and the difference decreases as S_c increases. The CAs maintain a small difference when S_c is 0.963. The difference will be ignored when S_c is 1, i.e., the isotropic surfaces.

B. Redefinition of hydrophobic and hydrophilic surfaces

The hydrophobic surface is defined as $\theta > 90^\circ$, where θ is the CA of a droplet on the surface, and the hydrophilic surface is defined as $\theta < 90^\circ$. For the general surfaces, the apparent CAs are equal with each other in different directions. The hydrophilic surface can be defined with apparent CA being less than 90° . However, for the anisotropic surfaces, the apparent CAs around the droplet are not equal with each other. The problem happens when the apparent CA in the direction along the grooves is larger than 90° and that in the direction vertical to the grooves is less than 90° . The hydrophilicity cannot be determined with one CA. Here, considering the variety of CAs on different corrugated surfaces, we define

FIG. 4. The change of CA with respect to the cross angle on the corrugated substrate. Inset: snapshots of a droplet from the side view with $S_c = 0.434$.

the hydrophilicity as

$$\theta_z = \frac{1}{2} \frac{\theta_{\max} + \theta_{\min}}{S_c} < 90^\circ, \quad (6)$$

where $\theta_{\max}$ and $\theta_{\min}$ represent the maximum and minimum CAs on anisotropic surfaces, respectively. S_c represents the ratio of characteristics between the directions vertical to the grooves and along the grooves on anisotropic surfaces. For the isotropic surfaces, $\theta_{\max}$ equals to $\theta_{\min}$ and S_c equals to 1. Then $\theta_z = \theta < 90^\circ$ is the degradation form of the redefinition.

IV. EXPERIMENTAL RESULTS AND DISCUSSIONS

In this section, we present the experimental results and discussions of wetting and EW on corrugated substrates.

A. Wetting of liquid on corrugated substrates

The micro images of droplet spreading on corrugated surfaces are shown in Fig. 5. Liquid spreading is usually controlled by the competition between the driving forces and energy dissipation. The driving force originates from the imbalance of surface tensions, expressed as $F_d = \gamma_{lv} (\cos \theta - \cos \theta_0)$, and energy dissipation is caused by a viscous resistance at mesoscale and molecular friction at microscale of moving contact lines.^{41–43} The derived scaling law is $l \sim t^n$ and corroborated by experiments and simulations, where $1/10 \leq n \leq 1/7$ is the scaling exponent. However, the evidence proved that the spreading velocity is not often so slow. Yuan and Zhao⁴⁴ proved that the spreading velocity will be much faster when the surface morphology is taken into account, and the spreading velocity on micropillar array surfaces obeys the scaling law of $l \sim t^{2/3}$ due to the acceleration effect enacted by the pillars. In our experiments, when a droplet spreads on corrugated surfaces, because of the action of hemi-wicking,⁴⁵ not only the surface tension but also the Laplace pressure contributes to the driving forces. As a result, the scaling law of spreading has a larger scaling exponent as $l \sim t^{4/5}$ [Fig. 5(a)]. On corrugated substrates, the structures may guide the liquid in the grooves, in a manner similar

to wicking. The phenomenon that occurs here is not classical wicking but hemi-wicking: As the film progresses in the microstructures, it develops an interface with air, leaving a few dry islands behind it.⁴⁵

In experiments, we got the velocities of liquid spreading in the X and Y directions. The experimental results indicated that the spreading of the droplet in the X and Y directions obeys the same scaling law. The difference between them is that one is faster with a larger intercept in logarithmic coordinates, and the other is slower. However, the spreading of liquid in the Y direction is continuous, and in the X direction, it is intermittent [Fig. 5(a)]. This phenomenon is also seen in Fig. 5(b), in the snapshots of liquid spreading in different times. From 52 ms to 64 ms, the liquid continuously spreads forward along the Y direction; however, the liquid spreading in the X direction is temporarily stopped by the periodic structure. From 64 ms to 76 ms, the liquid along the Y direction is still spreading forward, and the liquid in the X direction spreads forward for a certain distance [Fig. 5(b)]. Viscosity also has an influence on the velocities of droplet spreading. With a bigger viscosity, the velocity decreases. On the contrary, the velocity becomes relatively large with the viscosity of silicone oil being 50 mPa s compared to 100 mPa s [Fig. 5(a)].

The droplet spreading in two directions obeys the same scaling law, which indicates the same principle that drives the liquid to spread in the X and Y directions. In the wetting process, the liquid always spreads along the groove first. When the liquid spreads along the groove for a certain distance, because of inertia and extrusion of liquid in grooves, the liquid will quickly enter the next groove, leading to the spreading of the droplet in the X direction. This process is controlled by the surface tensions. At the initial stage, liquids stop at the front of the ridge under the balance of surface tensions, and the CA at microscale is equilibrium CA [Fig. 6(a)]. As the droplet spreads and due to the extrusion of liquid in grooves, the CA becomes large but the contact line keeps still owing to the CA hysteresis at the intermediate stage [Fig. 6(b)]. As the liquid spreading continues, the CA becomes large enough and the liquid quickly crosses the ridge into the next groove [Fig. 6(c)].

FIG. 5. (a) The spreading velocities of silicone oil on corrugated substrates, with silicone oil viscosities being 50 mPa s and 100 mPa s, respectively. The droplet spreading in the X and Y directions follows the scaling law of $l \sim t^{4/5}$. The velocity in the X direction is smaller than that in the Y direction. (b) The liquid spreading in the X and Y directions. The spreading is continuous in the Y direction and intermittent in the X direction.

FIG. 6. The schematic diagram of droplet propagation in the X direction. (a) Liquid stops at the front of the ridge; (b) contact line stays still while the CA increases due to the CA hysteresis; (c) liquid crosses the ridge into the next groove.

The spreading along the X direction is a result of the spreading and extrusion of the liquid in the Y direction.

B. EW on corrugated substrates

The morphology of surface has an important influence on the EW of droplets. The experimental results of the CA changing with the applied voltage are shown in Fig. 7. The CA changing process along the X and Y directions and the changing process on the smooth surface are all measured, respectively. In Fig. 7, we found that CAs in the X and Y directions maintain a fixed difference under applied voltages, and the changing of the CA with the applied voltage shows an obvious linear relationship. From the experimental results, we have learnt that the CA on the smooth surfaces decreases slower than that on the corrugated surfaces under a small applied voltage. As a result, the CA on the smooth plane is close to the CA in the X direction. When the applied voltage is beyond a critical value, the decrease in the CA with the applied voltage accelerates. As a result, the CA on the smooth plane is close to the CA in the Y direction on corrugated surfaces (Fig. 7).

The process of CA changing with the applied voltage can thus be divided into two distinct processes, which correspond to the Cassie state and the Wenzel state, respectively.

FIG. 7. The curves of EW on corrugated and smooth substrates, respectively. Squares and triangles represent CAs in the X and Y directions on corrugated substrates and circles represent CAs on smooth surfaces. The changing process of CA with applied voltage can be divided into two stages, and in both stages the CA changes with applied voltage linearly. Inset: the image of the droplet from the side view under the applied voltage 200 V.

When a droplet is deposited on a rough surface under voltage, at the initial stage, the droplet stays in the Cassie state. In the Cassie state, the spreading of droplets is controlled by the surface tensions and the electric field forces under applied voltage. The CA is determined by the equilibrium of these forces, and this can be described by the Lippmann-Young equation. Considering the characteristic ratio of the surface, the contact areas between the solid and liquid on corrugated surfaces are less than that on smooth surfaces. By adopting the free energy minimization approach and considering the actual contact areas κdA (κ is the ratio of contact areas to the projected areas, dA is the projected areas change), $dF = (\gamma_{sl} - \gamma_{sv} + \gamma_{lv} \cos \theta) r dA + dU - dW = 0$, we can get the Lippmann-Young equation of $\cos \theta = \cos \theta_0 + \frac{1}{\kappa} \cdot \frac{\epsilon V^2}{2\gamma_{lv}d}$, where $\kappa < 1$. Thus, the CA decreases more rapidly in the Cassie state. This leads to the approach of θ_s with θ_x and the repulsion of θ_s off θ_y . As the applied voltage increases, the state of droplets transports from the Cassie state to the Wenzel state. When a

FIG. 8. The critical voltages in which the transition from the Cassie state to the Wenzel state happens. The X axis is the dimensionless number S_c and Y axis is the critical voltage. The critical voltage decreases with S_c and shows nearly a linear relationship.

FIG. 9. The transition from the Cassie state to the Wenzel state: (a) The schematic diagram of the droplet on the corrugated substrate; (b) The forces lead to the transition under applied voltage in the interface between solid and liquid. As the applied voltage increases, the electric field force increases. The contact of liquid and solid surfaces happens when the applied voltage exceeds the critical voltage; (c) The droplet stays in the Cassie state while the voltage is below the critical voltage; (d) The droplet stays in the Wenzel state while the voltage is beyond the critical voltage.

droplet stays in the Wenzel state, θ_x and θ_y decrease slower than θ_s due to $\kappa > 1$. This makes θ_s close to θ_y and far away from θ_x . The detailed EW equations in the Cassie state and Wenzel state were derived and discussed in Sec. V.

C. Critical voltage from the Cassie state to the Wenzel state

From the experimental results, there exists a critical voltage V_a , where the transition from the Cassie state to the Wenzel state happens. From the results above, we know that for a fixed size of surface pattern, V_a remains still. When the size of the surface structure changes, V_a changes. To get a clear idea about the effects of the structure size on V_a , we carried out the experiments of testing the critical voltages on the samples with different S_c . The relation between S_c and V_a is presented in Fig. 8. The experimental results indicated that the critical voltage decreases as S_c increases. This shows that the transition from the Cassie state to the Wenzel state is more likely to occur with a small anisotropic characteristic ratio.

From the experimental results above, a droplet spreads in the Cassie state when $V < V_a$ [Fig. 9(c)], and the Cassie state to Wenzel state transition happens when V reaches V_a . When V is beyond V_a , the droplet spreads in the Wenzel state [Fig. 9(d)]. We analyzed the forces existing in the interface of liquid to solid. The forces determining the transition includes van der Waals forces, Laplace pressure, air pressure, hydrostatic pressure, and Maxwell stress as shown in Fig. 9(b). Maxwell stress is expressed as $\mathbf{T} = -(1/2)\epsilon E^2 \mathbf{I} + \epsilon \mathbf{E} \otimes \mathbf{E}$, where $\mathbf{I}$ is a second order unit tensor and $\otimes$ is the dyadic product of tensor.⁴⁶ The component expression of Maxwell stress is $T_{ij} = \epsilon [E_i E_j - (1/2)\delta_{ij} E^2]$, where δ_{ij} is Kronecker delta. For the transition from the Cassie state to the Wenzel state, it was mainly controlled by the Laplace pressure and Maxwell stress.

V. THEORETICAL DEDUCTION FOR THE EW EQUATION

Three methods are usually used to deduce the EW equation, including the thermodynamic approach,⁴⁷ the free energy minimization approach,⁴⁸ and the electromechanical

approach.⁴⁹ In these three methods, the free energy minimization approach regards the droplet, the conductive substrate, the insulation layer, and the electric power as one thermodynamics system and employs a differential with $dF/dA = 0$, where dF and dA represent the changes of free energy and interface areas, respectively. Here, this approach was employed to derive the extended EW equation. The change of free energy can be expressed as

$$dF = \gamma_{sl}dA - \gamma_{sv}dA + \gamma_{lv}dA \cos \theta + dU - dW, \quad (7)$$

where γ_{sl} , γ_{sv} , and γ_{lv} represent the solid-liquid, solid-vapor, and liquid-vapor interface tensions, respectively. dU and dW represent the changes of electric field energy in the insulating layer and the work done by the electric power, respectively. For a droplet deposited on the corrugated substrate, assuming that the CA is sufficiently small and the droplet, regarded as a part of the ellipsoid, has two same semi-major axes. The expression of surface free energy in the integral form can be described as

$$F = \pi ab \gamma_{lv} \left[k + \frac{1}{\sqrt{k^2 - 1}} \ln \left(k + \sqrt{k^2 - 1} \right) \right] - \pi ab (S_i - \epsilon E^2 d) - W, \quad (8)$$

where a and b are the semi-major and semi-minor axes of the droplet elliptic undersurface, respectively; $k = b/a$; and $S_i = \gamma_{sv} - (\gamma_{sl} + \gamma_{lv})$. For the corrugated substrates, assuming the ratio of the increased solid-liquid interface to the total increased interface is α and the ratio of the increased actual area to the increased apparent area is β , as depicted in Fig. 10, then, Eq. (7) can be expressed as

$$dF = \gamma_{sl}\alpha\beta dA - \gamma_{sv}\alpha\beta dA + \gamma_{lv}(1 - \alpha)\beta dA + \gamma_{lv}dA \cos \theta + dU - dW. \quad (9)$$

A droplet keeps stable on a surface when its free energy reaches a minimum, namely, $dF = 0$. Dividing dF by dA and making it equal to 0, then Eq. (9) is

$$\gamma_{sl}\alpha\beta - \gamma_{sv}\alpha\beta + \gamma_{lv}(1 - \alpha)\beta + \gamma_{lv} \cos \theta + \frac{dU}{dA} - \frac{dW}{dA} = 0. \quad (10)$$

FIG. 10. The schematic diagram of the increased solid-liquid interface, increased liquid-vapor interface, increased actual area, and increased apparent area. Here, we define that α is the ratio of the increased solid-liquid interface to total increased interface, and β is the ratio of increased actual area to increased apparent area.

According to the electromagnetics, $dU = \epsilon E^2 dv$, where E is the electric field intensity and v is the volume saturated with an electric field, $v = \int_0^d A(h)dh$, where h is the thickness of the insulating layer. The increased electric field energy can be calculated as the situation of a droplet on the smooth substrate approximately, and then the electric field energy can be written as

$$\frac{dU}{dA} = \frac{1}{2} \epsilon_p \int_0^d E^2 dh = \frac{1}{2} \epsilon_p \int_0^d \frac{V^2}{d^2} dh = \frac{1}{2} \frac{\epsilon_p V^2}{d}. \quad (11)$$

The work done by electric power per unit area can be calculated as

$$\frac{dW}{dA} = V \epsilon_p E(d) = \frac{\epsilon_p V^2}{d}. \quad (12)$$

Considering that the spreading velocities in the X and Y directions are different, the equation of minimizing energy method should include the increased areas in the two directions. If the increased area in the X direction is dA , the increased area in the Y direction is λdA (λ is the velocities ratio between the Y and X directions). Here we substituted θ_x and θ_y into Eq. (9) to derive the EW equation, and the experimental results indicate that the CAs in the X and Y directions keep a fixed ratio. Then the equilibrium equation should be changed as

$$\gamma_{sl}(1+\lambda)\alpha\beta - \gamma_{sv}(1+\lambda)\alpha\beta + \gamma_{lv}(1+\lambda)(1-\alpha)\beta + \gamma_{lv}(\cos\theta_x + \lambda\cos\theta_y) + \frac{dU}{dA} - \frac{dW}{dA} = 0. \quad (13)$$

When a droplet stays in the Cassie state, namely, $\beta = 1$, the equation can be written as

$$\gamma_{sl}(1+\lambda)\alpha - \gamma_{sv}(1+\lambda)\alpha + \gamma_{lv}(1+\lambda)(1-\alpha) + \gamma_{lv}(\cos\theta_x + \lambda\cos\theta_y) + \frac{dU}{dA} - \frac{dW}{dA} = 0. \quad (14)$$

We then simplify the equation and introduce the expression of electric field energy and the work produced by electric power, from which we get the following equation:

$$\gamma_{sl}\alpha - \gamma_{sv}\alpha + \gamma_{lv}(1-\alpha) + \frac{\gamma_{lv}}{1+\lambda}(\cos\theta_x + \lambda\cos\theta_y) - \frac{1}{2} \frac{\epsilon V^2}{d} = 0. \quad (15)$$

Then the classical form is given as

$$\frac{1}{1+\lambda}(\cos\theta_x + \lambda\cos\theta_y) = \alpha \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} - \frac{1}{2} \frac{\epsilon V^2}{d\gamma_{lv}} - (1-\alpha), \quad (16)$$

or

$$\frac{1}{1+\lambda}(\cos\theta_x + \lambda\cos\theta_y) = \alpha \cos\theta_0 - \frac{1}{2} \frac{\epsilon V^2}{d\gamma_{lv}} - (1-\alpha). \quad (17)$$

If the surface is isotropic, then $\lambda = 1$. The equation mentioned above can get the degeneration form as (now $\theta_x = \theta_y$)²⁵

$$\cos\theta = \alpha \cos\theta_0 + \frac{1}{2} \frac{\epsilon V^2}{d\gamma_{lv}} - (1-\alpha). \quad (18)$$

The equations in the X and Y directions on the anisotropic surface can be expressed as

$$\frac{1}{1+\lambda} \cos(\varphi_x \theta_x + \psi_x) = \alpha \cos\theta_0 + \frac{1}{2} \frac{\epsilon V^2}{d\gamma_{lv}} - (1-\alpha), \quad (\text{X direction}) \quad (19)$$

$$\frac{1}{1+\lambda} \cos(\varphi_y \theta_y + \psi_y) = \alpha \cos\theta_0 + \frac{1}{2} \frac{\epsilon V^2}{d\gamma_{lv}} - (1-\alpha), \quad (\text{Y direction}) \quad (20)$$

where φ and ψ represent the combination of $\cos\theta_x$ and $\cos\theta_y$.

When a droplet stays in the Wenzel state, namely, $\alpha = 1$, then equations can be written as

$$\frac{1}{1+\lambda} \cos(\varphi_x \theta_x + \psi_x) = \beta \cos\theta_0 + \frac{1}{2} \frac{\epsilon V^2}{d\gamma_{lv}} - (1-\beta), \quad (\text{X direction}) \quad (21)$$

$$\frac{1}{1+\lambda} \cos(\varphi_y \theta_y + \psi_y) = \beta \cos\theta_0 + \frac{1}{2} \frac{\epsilon V^2}{d\gamma_{lv}} - (1-\beta). \quad (\text{Y direction}) \quad (22)$$

For the droplets with relatively little CA, the second order approximation can be employed to analyze the EW equation. The Taylor series of $\cos\theta$ is expressed as

$$\cos\theta = 1 - \frac{\theta^2}{2} + \frac{\theta^4}{4!} + o(\theta^4). \quad (23)$$

If the Taylor series is truncated to second order, and substituted into the EW equation, the EW equation can be expressed as

$$1 - \frac{\theta^2}{2} = \cos\theta_0 + \frac{1}{2} \frac{\epsilon V^2}{d\gamma_{lv}}. \quad (24)$$

By comparing the two functions of $y = \cos\theta$ and $y = 1 - \theta^2/2$, we can see that when $\pi\theta/180$ is small, the two functions approximate each other. As the value of $\pi\theta/180$ becomes larger, the two functions separate. When $\pi\theta/180$ is small enough, the difference between $\cos\theta$ and $1 - \theta^2/2$ will be negligible. At this point, we introduced the parameter S_c to reconcile the difference. The EW equation can then be expressed as

$$\cos(S_c \theta) = f_1 \left(\cos\theta_0 + \frac{1}{2} \frac{\epsilon V^2}{d\gamma_{lv}} \right) - f_2, \quad (25)$$

where $f_1 = \alpha\beta(1 + \lambda)$ and $f_2 = 1 - \alpha\beta$. When a droplet is on an isotropic surface with $S_c = 1$, the EW equation can degenerate into the form

$$\cos \theta = f_1 \left(\cos \theta_0 + \frac{1}{2} \frac{\varepsilon V^2}{d\gamma_{lv}} \right) - f_2. \quad (26)$$

When $\beta = 1$, the EW equation can degenerate to the form deduced by Dai and Zhao.²⁵ For a droplet on smooth surfaces, namely, $\alpha = 1$ and $\beta = 1$, we can obtain $f_1 = 1$ and $f_2 = 0$. Then, the extended EW equation degenerates to the classical form.

VI. CONCLUSIONS

In this paper, wetting and EW on corrugated substrates were studied experimentally and theoretically. To characterize the differences between isotropic surfaces and anisotropic surfaces, an anisotropic factor $S_c = f_y/f_x$ was defined. On corrugated substrates, droplets exhibit elliptical shapes instead of spherical shapes and the spreading velocities in different directions are different. The droplet spreading follows the same scaling law of $l \sim t^{4/5}$ in both X and Y directions due to the acceleration by the grooves. In the process of EW, the relation between applied voltages and CAs is obviously linear both in the Cassie state and the Wenzel state. There exists a critical voltage where the transition from the Cassie state to the Wenzel state happens. The critical voltage varies with the size of the surface structure. The extended EW equation on the corrugated surfaces was derived with the free energy minimization approach. From the extended equation, it is found that EW is significantly affected by the anisotropic factor. For the smooth surfaces, the extended EW equation will degenerate to the classical Lippmann-Young equation. Our study may offer help in both the understanding of wetting and EW on anisotropic surfaces and in future designs for practical applications.

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