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Droplet Shapes on Superhydrophobic Surfaces under Electrowetting Actuation

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ABSTRACT
Droplet behavior on structured surfaces has recently generated a lot of interest due to its application to self-cleaning surfaces and in microfluidic devices. In this paper, the droplet shape and the droplet state on superhydrophobic surfaces are predicted using the Volume of Fluid (VOF) approach. Various structured surfaces are considered and the apparent contact angles are extracted from the predicted droplet shapes. Droplet dynamics under electrowetting are also modeled, including contact line friction. The model is validated against in-house experiments and experiments from the literature. The droplet state, droplet shape and apparent contact angles match well with the experimental measurements. The Cassie and Wenzel states on structured surfaces are also accurately predicted. Further, the electrowetting-induced transition from the Cassie to the Wenzel state and the reversal to the Cassie state is predicted for two different superhydrophobic surfaces. The transient wetting process, intermediate energy states and droplet shapes during electrowetting are simulated. The effective contact line friction coefficient on pillared surfaces is predicted to be 0.14 Ns/m², consistent with published values.

NOMENCLATURE

\( \hat{n} \) unit normal vector
\( r_m \) roughness number
\( t \) time
\( V \) voltage
\( d \) dielectric thickness
\( v \) velocity
\( \alpha \) volume fraction
\( \mu \) viscosity
\( \theta \) contact angle
\( \rho \) density
\( \sigma \) surface tension
\( \xi \) coefficient of contact line friction
\( \phi \) area fraction
\( \eta \) electrowetting number
\( 0 \) intrinsic value
\( c \) cassie
\( CL \) contact line
\( dyn \) dynamic
\( p \) primary phase
\( s \) secondary phase
\( w \) wenzel
\( e \) electrowetting

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INTRODUCTION

Superhydrophobic surfaces have important applications in the development of artificial self-cleaning surfaces and water-proof clothing [1]. They also find use in microfluidic-based technologies such as lab-on-chip devices, microelectromechanical systems (MEMS), and microarray biochips. Two extreme droplet states may theoretically exist on superhydrophobic surfaces: Cassie (non-wetting) and Wenzel (wetting), as shown in Figure 1a and Figure 1b respectively. The droplet rests on the top of the rough elements of the surface in the Cassie state and completely wets and penetrates the pillars in the Wenzel state. The Cassie and Wenzel states for a droplet are both possible on the same surface based on the droplet formation methodology [2].

The apparent contact angle of a sessile droplet in the Cassie ($\theta_C$) and Wenzel ($\theta_W$) states may be obtained using energy minimization [3] and is given by:

\[
\cos \theta_C = (-1 + \phi (1 + \cos \theta_0)) \\
\cos \theta_W = r_m \cos \theta_0
\]

where $\phi$ is the ratio of the area of the top surface of the pillars to the total base area of the substrate, $r_m$ is the surface roughness, defined as the ratio of the total surface area (including the sides and base) of the roughness elements to the projected surface area (not including the sides of the roughness elements). $\theta_0$ is the contact angle of the droplet on a flat surface. The equations are not valid for high roughness [2]. The state with the lower surface energy is the stable state.

![Figure 1. Schematic illustration of droplet wetting states: (a) Cassie, and b) Wenzel.](image)

Patankar [4] showed that the surface energy of a droplet and hence the preferred droplet state can be predicted exclusively based on the apparent contact angle. The wetting transition states between the Cassie and Wenzel states on structured surfaces were studied by Patankar [5,6]. The onset of the Cassie Wenzel transition is argued to occur either by a de-pinning transition, where the pressure forces overcome the surface tension forces, or by a sag transition, in which the sagging interface reaches the bottom of the pillars. These mechanisms were experimentally verified by Moulinet and Bartolo [7].

The Cassie-Wenzel transition on a surface can be controlled through various techniques like electro-wetting (EW) [8,9], and optical EW [10]. A popular method for droplet actuation on surfaces is electrowetting. The concept of EWOD (electrowetting on dielectric) is based on dielectric-liquid interfacial energy reduction by the application of a voltage between a conducting droplet and an underlying dielectric layer. Electrowetting is used in many microfluidic applications [11-13] and more recently in cooling technologies [14,15]. EW in combination with surface topology design can be used to manipulate the droplet states and contact angles [16-18] and has received significant research interest over the past decade due to advances in fabrication techniques. Krupenkin et al. [16] and Ahuja et al. [17] demonstrated EW-induced Cassie-Wenzel transition of droplets of aqueous KCl and organic solvents on superhydrophobic nano-structured surfaces. The droplet transitions from a Cassie to Wenzel state under an electrowetting force above a critical voltage [16,18]. However, no reversibility of the Cassie-Wenzel transition was observed upon removal of the voltage.

The Cassie state is associated with very low resistance to droplet motion. To sustain the Cassie state, either reversibility of the Cassie-Wenzel transition should be achieved or the surface must be designed such that the energy barrier for a transition to the Wenzel state is extremely high. Bahadur and Garimella [19] identified contact angle retraction as a necessary condition for the reverse transition from the Wenzel state to the Cassie state. Four EW reversal mechanisms have been demonstrated to date [20-23]. Krupenkin et al. [20] achieved reversible transition by vaporizing the liquid in immediate contact with pillars by means of a heat pulse through the pillar substrate. Dhindsa et al. [21] showed that reversibility can be achieved through competitive two-liquid EW. Manukyan et al. [23] achieved reversibility by changing only a part of the interface to the Wenzel state, while other regions of the drop substrate interface remain in the Cassie state. This causes the Wenzel state without EW forces to be highly unstable and hence the interface transitions to the Cassie state. However, the method is not useful when the Wenzel transition happens all across the interface. Recently, Kumari and Garimella [22] proposed the inclusion of an additional electrode to obtain complete Cassie-Wenzel reversal of a droplet between two plates.

The other method of maintaining the Cassie state is to completely prevent the Cassie-Wenzel transition through the design of robust surfaces. Some promising robust surfaces include double roughness, non-communicating roughness, and re-entrant cavity surfaces. Analytical and experimental research has corroborated the strong effect of surface morphology on the impact behavior of a water droplet and its ability to bounce off the surface [24-29]. Jung and Bhushan [24] formulated an expression for the critical velocity of the droplet (based on the capillary pressure and the Bernoulli pressure) beyond which water droplets transition to a Wenzel state on textured surfaces. Varanasi et al. [25] developed a pressure-balance model to arrive at a condition for droplet...
infiltration into the air gap between the surface structures. Denser textured surfaces are expected to provide greater capillary pressure and superior resistance to Wenzel wetting of impacting droplets. To better understand the effect of these robust surfaces, a thorough understanding of the droplet states and the transition mechanisms under EW actuation is required.

Bahadur and Garimella [30] developed an energy minimization framework to predict the apparent contact angle of a droplet in the Cassie and Wenzel states on a structured surface under the action of EW forces. The modified sessile Cassie and Wenzel contact angles are given by:

$$\cos \theta_v^C = \left( -1 + \phi(1 + \cos \theta_0 + \eta) \right)$$

$$\cos \theta_v^w = r_m (\cos \theta_0 + \eta)$$

(3)

(4)

where \( \phi \) is the area fraction covered by the microstructures, \( r_m \) is the true area of the surface to the apparent area and the electrowetting number \( \eta \) is defined as:

$$\eta = \frac{\varepsilon V^2}{2 \sigma d}$$

Here, \( d \) is the dielectric thickness, \( \varepsilon \) is the dielectric constant, \( V \) is voltage applied and \( \sigma \) is coefficient of surface tension of the liquid.

Bahadur and Garimella later conducted experiments [19,31] to validate the energy minimization-based model, to understand different aspects of the Cassie-Wenzel transition, and to analyze the reasons for the lack of reversibility of the transition. The existence of a critical voltage and the reversibility of the Cassie-Wenzel transition were explained in terms of the presence of an energy barrier. The energy minimization methodology and its application to predicting droplet states on superhydrophobic surfaces are summarized in Bahadur and Garimella [32].

Alternative mechanisms for the electrowetting transition have been suggested. The de-pinning transition and sag transition mechanisms predicted by Patankar [5,6] under the action of mechanical forces can also apply to EW-induced transitions. Oh et al. [33] proposed that electrowetting on superhydrophobic surfaces could lead to a third transition mechanism due to Rayleigh-Taylor interfacial instability in addition to the touchdown (i.e., sag transition) or the de-pinning scenarios. This was shown to be the dominant transition mechanism for surfaces with overhangs and high contact angles.

Despite this emerging understanding, the actual transition mechanisms are difficult to visualize in experiments. Visualization can however be achieved through numerical modeling. The lattice Boltzmann method has been used to predict droplet shapes on superhydrophobic surfaces [34]. The VOF model has successfully been used to predict droplet statics [35] and dynamics [36] on smooth hydrophobic surfaces under gravitational actuation. Annapragada et al. [35] used the VOF model to predict critical angle of inclination for droplet motion on smooth inclined hydrophobic surface and the shapes of moving droplets beyond it. A dynamic contact angle model [36] was used to capture the effect of the velocity of the interface on the local contact angle. The predicted terminal velocities of the droplet were found to match experiments well.

Mohseni et al. [37] and Arzpeyma et al. [38] included EW in the VOF framework to predict the transient shape and linear motion of droplets sandwiched between two parallel electrode arrays. The model was recently improved by Keshavarz-Motamed et al. [39] and Rajabi et al. [40] to include dynamic aspects given by the simplified molecular-kinetic (MK) theory as a correction to the static EW contact angle. The dynamic model provided better predictions of droplet dynamics than the static EW model. The model was later used by Annapragada et al. [41] to study the transient response of the droplet under DC EW actuation.

The effect of EW actuation on superhydrophobic surfaces has not yet been studied. In this work we present the first full CFD numerical modeling of droplet states on superhydrophobic surfaces under EW action using the VOF methodology. The model developed by Rajabi et al. [40] is used to account for the EW and contact line friction forces. The roughness characteristics of superhydrophobic surfaces are modeled with complete geometric fidelity. The droplet shapes on superhydrophobic surfaces are predicted using the VOF model and compared against experiments from the literature. The intermediate energy states during the transient process are extracted and used to understand the EW-induced Cassie-Wenzel transition. The effective contact line friction coefficient for a superhydrophobic surface is predicted.

**NUMERICAL MODEL**

In the current work, the volume of fluid-continuum surface force (VOF-CSF) model in FLUENT [42] is used. A custom contact-angle model based on a force balance at the contact line is implemented using user-defined functions to capture the effects of surface tension, EW and dynamic contact line forces.

**VOF-CSF Method**

In the VOF method, the flow of non-interpenetrating fluids is simulated by solving a single set of Navier-Stokes equations and tracking the volume fraction of one or more secondary fluids in the domain. The volume fraction of the secondary phase \( s \) is obtained by solving the continuity equation for this phase:

$$\frac{\partial}{\partial t} \left( \alpha_s \right) + \nabla \left( \alpha_s \mathbf{v} \right) = 0$$

(6)

The volume fraction of the primary phase is calculated from:

$$\alpha_p + \sum \alpha_s = 1$$

(7)

The shape of the interface is necessary to accurately calculate the transport terms of the continuity and momentum...
equations in the finite volume formulation. For this purpose, Youngs’ Geometric Reconstruction Scheme [43], which is based on piecewise-linear reconstruction of the interface in a partially filled computational cell, is used. Further details of the implementation may be found in the FLUENT manual [42].

The momentum equation is solved for the average velocity of the mixture, and the influence of multiple phases appears through the phase fraction-dependent local properties of the material in each cell.

\[
\frac{\partial \rho \mathbf{v}}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = -\nabla p + \nabla \left[ \mu \left( \nabla \mathbf{v} + \nabla \mathbf{v}^T \right) \right] + \rho \mathbf{g} + \mathbf{F} \tag{8}
\]

Here, the gravitational acceleration is specified as \( \mathbf{g} = g \cos \beta \mathbf{\hat{n}} + g \sin \beta \mathbf{\hat{f}} \) [42]. Physical properties such as density and viscosity are volume-averaged as:

\[
\rho = \alpha \rho_p + (1 - \alpha) \rho_s \tag{9}
\]

\[
\mu = \alpha \mu_p + (1 - \alpha) \mu_s \tag{10}
\]

where subscripts \( p \) and \( s \) represent the primary and secondary phases, respectively. In the CSF formulation, when only two phases exist, the volumetric force, \( \mathbf{F} \) in (8) is given by:

\[
\mathbf{F} = \sigma \frac{\rho \kappa \nabla \alpha_s}{2(\rho_p + \rho_s)} \tag{11}
\]

where \( \kappa \) is the interface curvature for the secondary phase, given by Brackbill et al. [44] to be:

\[
\kappa = -\nabla \cdot \mathbf{n} \tag{12}
\]

In (12), \( \mathbf{n} \) is the unit vector normal to the free surface. The normal is obtained based on the volume fraction gradient given by:

\[
\mathbf{n} = \frac{\nabla \alpha_s}{|\nabla \alpha_s|} \tag{13}
\]

The interface shape at the triple line, where the two phases meet the wall, is imposed by specifying \( \mathbf{n} \) through the specification of the contact angle as:

\[
\hat{n} = \hat{n}_w \cos(\theta_w) + \hat{i}_w \sin(\theta_w) \tag{14}
\]

where \( \hat{n}_w \) and \( \hat{i}_w \) are the unit vectors normal and tangential to the wall respectively; \( \hat{n}_w \) points into the secondary fluid. In the current model, volume fraction smoothing is used to reduce the spurious velocities at the interface associated with the VOF method [45,46]. Smoothing is performed by averaging the volume fraction based on the neighboring cell volume fractions. However, over-smoothing may result in smearing of the interface to more than two cells. A smoothing relaxation value of 0.25 was found to be optimal [42].

**Contact Angle Model Based On Contact Line Force Balance**

The VOF-CSF model requires contact angles to be specified as a boundary condition, and therefore an accurate specification of the apparent contact angle at the contact line is important. The apparent contact angle is obtained based on a force balance at the triple contact line. The forces acting on the contact line are surface tension, EW, and contact line friction forces. The combined effect of the former two forces gives the EW contact angle \( \theta_{\text{ew}} \) through the Young-Lippmann equation:

\[
\cos \theta_{\text{ew}} = \cos \theta_0 + \frac{1}{\sigma} \left( \frac{\mathbf{V}^2}{d} \right) \tag{15}
\]

The dynamics of the contact line motion can be understood based on the molecular-kinetic (MK) theory. The MK theory predicts that the contact line friction force \( F_{\text{CL}} \) per unit length acting at the triple contact line is given by:

\[
F_{\text{CL}} = \xi \mathbf{v}(t) \tag{16}
\]

where \( \xi \) is the coefficient of friction and \( \mathbf{v}(t) \) is the instantaneous velocity of the contact line. The value of \( \xi \) during EW has been shown to be independent of voltage by Decamps and Coninck [47]. The apparent angles with \( \theta_{\text{ew}} \) and without EW \( \theta_{\text{ew}} \) are given respectively by:

\[
\cos \theta_{\text{ew}} = \cos \theta_0 + \frac{1}{\sigma} \left( \frac{\mathbf{V}^2}{d} - \xi \mathbf{v}(t) \right) \tag{17}
\]

\[
\cos \theta_{\text{ew}} = \cos \theta_0 - \frac{1}{\sigma} \xi \mathbf{v}(t) \tag{18}
\]

The main inputs required for this contact angle model are the intrinsic contact angle \( \theta_0 \) and the coefficient of contact line friction \( \xi \). The implementation of the contact line friction is similar to that in Arzpeyma et al. [39].

**Simulation Setup**

Three sets of 3D VOF simulations are run in succession to mimic the various processes of EW on superhydrophobic surfaces, viz: (i) droplet placement (Cassie state), (ii) electrowetting (Wenzel state), and (iii) EW retraction (Cassie/Wenzel). Droplet placement is simulated by releasing a known droplet volume from a point just above the surface. The contact angle on all surfaces is specified as the intrinsic contact angle \( \theta_0 \) and the contact line friction \( \xi \). A 3D tetrahedral mesh is generated in the fluid region. The \( yz \) plane cross-section of the computational domain, mesh (light gray) and boundary conditions are shown in Figure 2 along with the initial droplet shape (dark gray). Exploiting droplet symmetry along the \( xz \) and \( yz \) planes, only one-quarter of the domain is modeled, with symmetry boundary conditions along \( xz \) and \( yz \) planes and the results are mirrored for presentation. A quarter sphere of the required droplet size and material is initialized in the domain. A no-slip boundary condition is specified at the bottom wall. The remaining domain boundaries are specified-pressure boundaries, set at a gauge pressure of zero [42]. The droplet is allowed to settle on the surface under the action of gravity and the simulation
is said to have converged when the droplet reaches a steady shape.

The second simulation is used to mimic the EW process when a voltage is applied across the droplet as shown in Figure 3. The contact angle model based on a contact line force balance discussed above is implemented as a contact angle boundary condition on the contact line. It is implemented in the VOF-CSF model through user-defined functions (UDFs) in FLUENT. The electrode needle on the top is neglected. Similar to the droplet placement simulation, the electrowetting simulation is said to have converged when the droplet reaches a steady shape.

The third set of simulations is then performed to simulate the EW retraction process. The applied voltage is removed, and the droplet allowed to retract to a new steady state. A contact angle boundary condition accounting just for the frictional forces is applied on all surfaces in this simulation.

RESULTS AND DISCUSSION

The methodology described above is first used to predict the droplet states on superhydrophobic surfaces. The results are compared and validate against in-house experiments and experiments from the literature [48]. The state and shape of water droplets on two fluoroalkylsilane coated surfaces with different pillar heights from Yoshimitsu et al. [48] exhibiting different droplet states (Cassie and Wenzel) are considered. The roughness factors for the surfaces are tabulated in Table 1. For a surface morphology described by square pillars of width $a$ and pitch $b$ and with pillar height $h$, the roughness parameters $r_m$ and $\phi$ are defined as:

$$ r_m = 1 + \frac{4ab}{h} $$  \hspace{1cm} (19)

$$ \phi = \frac{a^2}{b^2} $$  \hspace{1cm} (20)

The corresponding surface morphologies are shown in Figure 4. The surface geometry is modeled with fidelity and the droplet steady-state shape is simulated using the VOF methodology. The contact angle on all structured surfaces is specified as the intrinsic contact angle ($\theta_0 = 114^\circ$). The tops of the pillars for the $r_m = 1.1$ surface were reported to have rough corners by Yoshimitsu et al. causing pinning at the edges [48]. To account for the rough edges the contact angle near the edges was increased to $180^\circ$ to mimic contact-line pinning.

The equilibrium droplet shapes (the $\alpha_s = 0.5$ contour) from the simulation are compared with the corresponding experimental images in Figure 5. Colored contour lines of volume fraction ($\alpha_s$) are superimposed on the experimental droplet images for easier comparison. The apparent contact angles were calculated based on the $\alpha_s = 0.5$ contour from the simulations and are tabulated in Table 1 along with the predicted droplet states. The corresponding experimental
measurements are shown in parentheses and are clearly well-predicted by the simulation. Further, the experimentally observed droplet state is also replicated well by the simulations.

The methodology was further validated against deionized water droplet placement experiments on Teflon-coated SU-8 pillars grown on a silicon substrate. The fabrication was conducted in the Birck Nanotechnology Center at Purdue University. The pillared surface is made up of SU-8 pillars of square cross section which are 13μm wide and 32μm tall with a pitch of 25μm. The droplet shape on the SU-8 structure is predicted using the droplet placement methodology. The intrinsic contact angle ($\theta_0$) is specified to be 117.3°, based on measurements of contact angles of droplets on a smooth horizontal Teflon surface. The surface features and the profile view of the droplet on the surface are shown in Figure 6. The predicted droplet shape ($\alpha_s = 0.5$) is shown in blue. The colored contour lines of volume fraction are overlapped on the grayscale experimental droplet image for better comparison. The apparent contact angle is predicted to be 148° which compares well with the experimental measurements (147.9°±1°), validating the efficacy of the methodology used here. In the experiments, deionized water droplets were dispensed on to the surface and the contact angle was recorded using a goniometer. The droplet state on pillared surfaces was determined by direct visual observation of the space in between the structural pillar elements.

<table>
<thead>
<tr>
<th>$r_m$</th>
<th>$\theta_a$</th>
<th>Droplet State</th>
</tr>
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<tr>
<td>1.1</td>
<td>155° (154°±1°)</td>
<td>Wenzel (Wenzel)</td>
</tr>
<tr>
<td>1.3</td>
<td>138° (138±0.5°)</td>
<td>Cassie (Cassie)</td>
</tr>
</tbody>
</table>

Figure 6. The SU-8 surface roughness structure and comparison of predicted droplet shape on the surface. The volume fraction colored contour lines are superposed to facilitate visual comparison. Grayscale image: experimental droplet shape; blue contour: $\alpha_s = 0.5$.

**EW on Superhydrophobic Surfaces**

In this section we present simulations of transient motion of a water droplet on a microstructured surface coated with Teflon. Realistic pillared and cratered structures are chosen based on the work of Bahadur and Garimella (Surface 5 from [19] and Surface 8 from [31]). Both surfaces are chosen so that the Cassie state is the initial stable state. This facilitates capturing the Cassie-Wenzel transition. Table 2 shows the surface parameters ($r_m$, $\phi$) and the pillar height ($h$) of the two surfaces considered in this work. The ($r_m$, $\phi$) values for a pillared surfaces are given by Eqns. (19) and (20), respectively. For a surface morphology described by square craters of width $a$, crater-wall thickness $2t$, and crater depth $h$, the roughness parameters $r_m$ and $\phi$ can be expressed as:

\[
r_m = 1 + \frac{4ah}{(a+2t)^2}
\]

\[
\phi = 1 + \frac{a^2}{(a+2t)^2}
\]

The isometric views of the roughness structures are shown in Figure 7. The EW simulation mimics the experimental setup shown in Figure 3.
Table 2. Apparent contact angle predictions of stable droplet states from droplet placement, EW and retraction simulations on microstructure surfaces along with the surface specification.

| Surface | \( r_m \) | \( \phi \) | \( h \) | \( \eta_{\text{critical}} \) | Placement State | \( \theta_{\text{w}} \) | EW State | \( \theta_{\text{w},\text{EW}} \) | Retraction State | \( \theta_{\text{w},R} \) | \( \Delta\theta_{\text{R}} \) (%)
<table>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pillars</td>
<td>2.87</td>
<td>0.23</td>
<td>43.1</td>
<td>0.5 ± 0.25 (0.3)</td>
<td>Cassie</td>
<td>154°</td>
<td>Wenzel</td>
<td>118°</td>
<td>Wenzel</td>
<td>121°</td>
<td>7.2% (6.6%)</td>
</tr>
</tbody>
</table>
| Craters | 2.64       | 0.15   | 85.5   | 1.47 (1.45)     | Cassie          | 148°      | Mixed       | 118° (109°)    | Mixed          | 120° (109°)   | 6.5% (0%)

In the experiments [19, 31], 3 μl deionized water droplets were dispensed on the surface and the contact angle was recorded using a goniometer. A 125 μm-diameter chrome wire was then inserted in the droplet to supply the EW voltage. The voltage was ramped up in steps of 5 V until the occurrence of complete transition was observed. The contact angle measurements were made based on the images after transition. The droplet states in the case of pillared surfaces were based on visual observations of the space in between the pillars. This is not possible in the case of cratered surfaces, and hence droplet states were determined in this case by mechanically dragging the droplet on the surface. Further details can be found in Bahadur and Garimella [31]. The droplet in the Cassie state offered much lower resistance to dragging than a droplet in the Wenzel state; in the Wenzel state, the droplet was almost impossible to drag. Another test to distinguish the Cassie and Wenzel states consisted of measuring the tilt angle at which the droplet rolls off the surface. A droplet in the Cassie state rolls off the surface at tilt angles of less than 10°; a droplet in the Wenzel state does not move even if the surface is inverted (held upside down). This drastic difference in the tilt angles of the Cassie and Wenzel states was used in conjunction with the drag tests to ascertain the existence of the Cassie and Wenzel states for cratered surfaces.

In both the simulations and the experiments, the droplet size is chosen so that it occupies 15 structural elements. The water/air surface tension is taken to be 0.072 N/m. As the contact line friction is a local phenomenon, the contact line friction coefficient for a smooth surface is used. The value of \( \zeta \) is set at 0.4 Ns/m² based on experimental data for the water/ smooth Teflon surface combination from Wang and Jones [49]. Annapragada et al. [41] verified the accuracy of the friction model for transient EW of droplets on smooth surfaces using VOF simulations and a simplified mathematical model. The transient droplet shape as well as the contact radius was well predicted by the model.

Droplet Shape and Transition Mechanism

An important feature of the simulations is that three-dimensional droplet shapes can be obtained so that the wetting characteristics may be understood. The \( xz \)-plane cross-section of the static droplet shapes after the three simulation steps are shown in Figure 8 for pillars and cratered surfaces. The voltage is varied until EW induced Cassie-Wenzel transition is observed. The electrowetting number is increased in steps of 0.25. Figure 8a-c shows droplet images on a pillared surface. The stable state without any electrical actuation is the Cassie state (Figure 8a). As the voltage is increased, the droplet is seen to wet all the pillars uniformly (Figure 8b) at \( \eta = 0.5 \). The droplet spreads on the surface forming contacts with additional pillars. Upon removal of the voltage (Figure 8c) the droplet remains pinned, which is consistent with experimental observations. It can be seen that this surface shows very little contact angle retraction upon the removal of the EW voltage.

Figure 8d-f shows the droplet cross-sections for the cratered surface. The droplet is seen to wet the craters only at the periphery (Figure 8e) at \( \eta = 1.47 \). The droplet is seen in the simulations to wet at \( \eta = 1.25 \) (not shown) but does not spread much. To remain consistent with the experiments, the voltage is increased to \( \eta = 1.47 \), where a significant change in droplet shape is observed. The contact angle retraction is small and the droplet remains pinned to the craters even after the EW force is removed. The droplet wetting behavior is consistent with the experimental observations [31].

For a more quantitative comparison, the apparent contact angle (\( \theta_a \)) for each droplet state and the critical voltage required for the Cassie-Wenzel transition are tabulated in Table 2 along with the corresponding experimental observations shown in parentheses. The critical transition voltage is defined as the voltage above which the droplet
reaches the bottom surface with a noticeable contact angle and shape change. The definition is based on the work of Bahadur and Garimella [31]. The predicted apparent contact angles as well as the transition electrowetting numbers match well with the experiments. The electrowetting numbers in the present work are increased in steps of 0.25 and hence the transition is captured only at \( \eta = 0.5 \). In the case of cratered surfaces, the electrowetting number of \( \eta = 1.5 \) corresponds to an electrowetting contact angle of \( \theta_e = 0^\circ \) and hence a smaller value (1.47) was used. The retraction of the droplet to its original state is reported in Table 2 in terms of the contact angle retraction \( (\Delta \theta_e) \) given by:

\[
\Delta \theta_e = \left( \frac{\theta_e,0 - \theta_e,EW}{\theta_e,R - \theta_e,EW} \right)
\]  

(23)

Here, \( \theta_e,0, \theta_e,EW \) and \( \theta_e,R \) are the apparent contact angles of the droplet after placement, electrowetting and retraction, respectively; these are also reported in the table. The contact angle decreases as the droplet is electrowetted; this is accurately predicted by the model. When the voltage is removed, the contact angle does not revert to \( \theta_e,0 \) but remains in the same state as before electrowetting retraction, i.e., in the Wenzel state for pillared surfaces (Figure 8c) and a mixed state for cratered surfaces (Figure 8f). The retraction of the apparent contact angle is greater for pillared surfaces. The lower contact angle retraction of droplets on cratered surfaces is due to contact line pinning near the edges of microstructural features. The predicted contact angle retraction values match well with the experiments.

To shed more light on the wetting characteristics of the surfaces, Figure 9 shows a three-dimensional view of the droplet in the electrowetted state on pillared and cratered surfaces. The droplet free surface is show in light blue and the wetted surface is shown in dark blue. The droplet is seen to wet the pillars uniformly whereas the cratered surface has air pockets in the middle. As reported by Bahadur and Garimella [31], the droplet does not wet the craters when it is resting on them in the initial Cassie state. The craters surrounding these are shown to be filled with water.

The three-dimensional view also shows that the droplet cross-section is different at various angular cross-sections and he apparent contact angles differ when measured along different orientations of the microstructured surface. The difference is significant for smaller droplets and between measurements in the \( xz \) plane or at an angle of \( 45^\circ \) to this plane. All reported values in this work are an average of 8 readings taken at 22.5° intervals along the z-axis. The standard deviation was found to be 3°.

Figure 8. Droplet states during electrowetting: (a-c) droplet on pillared surface and (d-f) droplet on cratered surface.

**Droplet Transient Motion Analysis**

To understand the transient behavior of the droplet, the system surface energy and the contact line length are plotted as a function of time (Figure 10 and Figure 11, respectively) for the pillared surface. Such transient details cannot be obtained from typical energy minimization approaches, such as that of Bahadur and Garimella [30]. It was also assumed by Bahadur and Garimella [30] that the droplet interface moves parallel to the horizontal which is shown not to be the case later in this section. The transient surface energy \( (E_t) \) of the droplet over a structured surface is calculated as:

\[
E_t = (A_d (\cos \theta_0 + \eta) + A_{sl}) \sigma
\]

(24)

where, \( \sigma \) is the surface tension of the liquid (water), \( A_d \) is the solid/liquid contact area, \( A_{sl} \) is the liquid/air interface area. The droplet surface energy is normalized based on the surface energy of a spherical droplet of the same size given by \( (\alpha A_{sl})_{\text{spherical}} \). The droplet contact line length is normalized based on the contact line length for a droplet resting on a smooth surface with \( \theta = \theta_e \). For the present case, \( \eta = 0.5 \) and \( \theta_e = 120^\circ \) and \( (\eta + \cos \theta_0) = 0 \) which implies that the total energy is mainly dependent on \( A_{sl} \). \( A_{sl} \) is shown in Figure 10 (black dotted line) to complete the understanding of the transition. The contact area is seen to increase during the electrowetting phase. The droplet contact line length is extracted by calculating the length of the \( \omega_s = 0.5 \) line on the microstructured surface. In Figure 10 and Figure 11, the energy path and the contact line length during electrowetting are shown as red solid lines where as the retraction path is shown as a red dashed line. Snapshots (A-D) of the droplet cross-section on the \( yz \)-plane at different time intervals are shown below the plot in Figure 10 to highlight key events during the transient motion. Bahadur and Garimella [30] showed that when \( (\eta + \cos \theta_0) \) is positive, the Wenzel state is more stable than the Cassie state. When a voltage \( (\eta = 0.50) \) is applied at time \( t = 0 \) ms, the value of \( (\eta + \cos \theta_0) = 0.08 \) and the droplet starts to move from an initial stable Cassie state to a more stable Wenzel state. The liquid/air interface touches the bottom surface at \( t = 0.2 \) ms (A). The contact line length increases until touchdown.

The interface first de-pins from the pillar top and starts to slide down the pillar side walls. Hence, the electrowetting...
transition in the present work is seen to be the de-pinning transition proposed by Patankar [6] at the pillars. De-pinning occurs when the Laplace pressure inside the bulk of the droplet is greater than the capillary pressure due to the interface near the pillars. For the sag transition to occur, the interface has to sag and reach the bottom surface while pinned to the top of the pillars. This is depicted in Figure 12. The interface between two pillars before (dashed blue line) and after electrowetting (red solid line) are shown along with the maximum height (black solid horizontal line) for occurrence of the sag transition. As the electrowetted contact angle ($\theta_e$) is lower than the intrinsic contact angle ($\theta_0$), the interface will wet the bottom surface even for $\theta = \theta_0$. This implies that the initial state before electrowetting will also be in the Wenzel state. Hence the sag transition is not a plausible electrowetting transition.

The rest of the lower droplet interface continues to collapse on to the bottom surface, wetting a greater area of the pillars as the transition proceeds as seen from Figure 10. The contact length during this phase (A–B, Figure 10) decreases as greater numbers of pillars are wetted and no interface exists on the pillars. This downward motion of the interface causes the bulk of the droplet to move down and at $t = 0.6$ ms (B), the top liquid/air interface starts to move down lowering the surface area and hence the total energy. Oscillations in contact line length are seen between (B) and (C). The contact length increases as more pillars are involved in the wetting process and decreases when the interface reaches the bottom of these pillars. The droplet progressively wets more pillars (C) and reduces the water/air interface area until it reaches a stable Wenzel state (D).

The removal of voltage results in the normalized energy level increasing to a value of 0.75. The energy level does not change much from this value as the transient proceeds, and settles down to a steady state value of 0.742. Thus, there is an 8% energy retraction due to the pinning of the droplet interface seen in Figure 10. This is consistent with the experimental observations [30] of apparent contact angle retraction which directly reflects the energy retraction [4] and the contact angle retraction comparison is shown in the last column of Table 2.

The droplet reaches equilibrium during the electrowetting process in 2.6 ms which is an order of magnitude smaller than the transition time for water droplets spreading on a smooth surface of 20 ms [41]. The droplet spreading model developed by Annapragada et al. [41] is used to calculate the effective horizontal friction coefficient of the microstructured surface. The contact line friction coefficient is varied to match the droplet stabilization time (2.6 ms), which is taken as the time to reach 99% of the stable radius. The effective friction coefficient friction is predicted to be 0.14 Ns/m². The value is in the range measured by Jung and Bhushan [1] for water sliding on circular pillar patterned surfaces.

Figure 9. Three-dimensional view of the droplet in the electrowetted (Wenzel) state on (a) pillared surface and (b) cratered surface.

Figure 10. Surface energy of a droplet during transition. The electrowetting path is shown in solid lines and the retraction path after the voltage is removed is shown in dashed lines. The retraction path in the absence of contact line friction (CLF) is shown in dash dot lines. The normalized transient wetting area ($A_{sl}$) is shown in dotted lines with the axis shown on the right. Key features during the transient process are marked (A – interface touchdown at bottom, B – top of the droplet starts to move down, C – interface crosses additional row of pillars, D – maximum wetting reached).
Figure 11. Contact line length of a droplet during transition. The electrowetting path is shown in solid lines and the retraction path after the voltage is removed is shown in dashed lines. The retraction path in the absence of contact line friction (CLF) is shown in dash dot lines.

Figure 12. Illustration of sag transition. The interface between two pillars before (blue dashed line) and after electrowetting (red solid line) are shown along with the maximum height (solid black horizontal line) for occurrence of sag transition.

Effect of Contact Line Friction Model
The retraction simulations were performed with and without the contact line friction model. The droplet states predicted by the two models are shown before (Figure 13a) and after retraction (with contact line friction: Figure 13b and without CLF: Figure 13c). The droplet retracts more in the case of no contact line friction. The retraction in energy from the retracted Wenzel state is 46%, as seen from Figure 10. Including the contact line friction model is crucial to capturing the true physics of the droplet motion. The simulations show that reducing contact line friction can increase the contact angle retraction. However, reversal to the Cassie state is not observed, and a complete Cassie-Wenzel reversal [30] does not occur.

CONCLUSIONS
A generalized numerical model to predict the transient behavior of the droplet shape under electrowetting actuation on microstructured surfaces is presented. A VOF simulation approach is used. The droplet placement model is validated against in-house experiments and experiments from the literature. The model is used to predict droplet states during the placement, electrowetting, and retraction steps. The model accurately predicts the droplet states and shapes of water droplets on superhydrophobic surfaces under the action of electrowetting forces. The critical voltage required for an EW-induced Cassie-Wenzel transition is also accurately predicted. The droplet motion during the transition is shown to originate at the contact line. The transient surface energy and the contact line length are mapped out. Using the mathematical model proposed by Annapragada et al. [41] the effective contact line friction is predicted; the value of 0.14 Ns/m² obtained is in the same range as that reported in the literature for pillared surfaces. The de-pinning transition is shown to be the prevalent EW transition mechanism for the microstructure surfaces and the sag transition is shown to be physically not possible during electrowetting. Contact line frictional forces are shown to affect the final stable droplet state. The use of the present model in developing robust surfaces and to prevent the Cassie-Wenzel transition is ongoing.

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REFERENCES


