Repulsion-based model for contact angle saturation in electrowetting

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We introduce a new model for contact angle saturation phenomenon in electrowetting on dielectric systems. This new model attributes contact angle saturation to repulsion between trapped charges on the cap and base surfaces of the droplet in the vicinity of the three-phase contact line, which prevents these surfaces from converging during contact angle reduction. This repulsion-based saturation is similar to repulsion between charges accumulated on the surfaces of conducting droplets which causes the well known Coulombic fission and Taylor cone formation phenomena. In our model, both the droplet and dielectric coating were treated as lossy dielectric media (i.e., having finite electrical conductivities and permittivities) contrary to the more common assumption of a perfectly conducting droplet and perfectly insulating dielectric. We used theoretical analysis and numerical simulations to find actual charge distribution on droplet surface, calculate repulsion energy, and minimize energy of the total system as a function of droplet contact angle. Resulting saturation curves were in good agreement with previously reported experimental results. We used this proposed model to predict effect of changing liquid properties, such as electrical conductivity, and system parameters, such as thickness of the dielectric layer, on the saturation angle, which also matched experimental results. © 2015 AIP Publishing LLC.

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NOMENCLATURE

a	Base radius of droplet
A	Solid-liquid contact area
$\mathbf{b}$	Boundary conditions matrix
d	Thickness of the dielectric layer
D	Electric current displacement
D_e	External electric displacement at droplet-surrounding medium interface
D_i	Internal electric displacement at droplet-surrounding medium interface
E	Electric field intensity
EC_w	Electric conductivity of water
F_R	Repulsive force between charges on the droplet surfaces
J	Electric current density
$\mathbf{k}$	Matrix of parameters
$\vec{n}$	Unity normal vector on the interface
q_{Ray}	Maximum charge can be stored by conducting droplet (Raleigh instability limit)
Q_b	Actual total charges on the base surface
$Q_{b[j]}$	Element charge on the base surface
Q_c	Total charges on the cap surface

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$Q_{c[i]}$	Element charge on the cap surface
Q_s	Electric current source
$r_{[i,j]}$	Distance between two point charges on the droplet surfaces
s	Distance on the droplet cap or base surfaces measured from the three phase contact line
S_b	Predefined distance on the base surface measured from the three phase contact line
ΔS_b	Element length on the base surface
S_c	Predefined distance on the cap surface measured from the three phase contact line
ΔS_c	Element length on the cap surface
$\mathbf{u}$	Variable matrix
V	Applied voltage
W_c	Energy stored in the dielectric layer
W_e	Work done by the external voltage source
W_R	Repulsion energy between charges on the droplet surfaces
W_s	Surface tension energy
α	Parameter indicative of the contact angle, $\alpha = 1 - (\theta/\pi)$
γ_{lv}	Liquid-vapor surface tension coefficient
δ	Lower limit for integration of surface charge density over cap and base surfaces of the droplet to avoid singularity at the three phase contact line ($\delta = 10^{-10}$ m in the current study)
ϵ	Electric permittivity
ϵ_o	Permittivity of vacuum
ϵ_d	Permittivity of insulating dielectric layer
ϵ_w	Permittivity of droplet
θ	Instantaneous contact angle
θ_o	Initial contact angle
λ_b	Correction function of the base charges
λ_c	Correction function of the cap charges
ρ_v	Volume charge density
σ	Surface charge density
σ_o	Electrostatic surface charge density on the base surface far away from TCL ($\sigma_o = \frac{\epsilon_o \epsilon_d}{d} V$)
σ_b	Surface charge density on the base surface of the droplet
σ_c	Surface charge density on the cap surface of the droplet

INTRODUCTION

Electrowetting is defined as spreading of a sessile liquid droplet sitting on an insulated electrode coated with hydrophobic layer due to applying potential difference between the electrode and the droplet itself, Figure 1(a).¹ Since the last decade, electrowetting was used as the backbone technology for many applications such as adjustable focal distance microlenses,^{2,3}

FIG. 1. (a) Electrowetting system setup, showing the initial contact angle θ_o and the instantaneous contact angle θ at an applied voltage V . (b) Contact angle ceases to decrease beyond a certain value—no matter how much the applied voltage is increased. This is contrary to Young-Lippmann equation which predicts contact angles as low as zero degrees at a certain applied voltage.

adjustable micromirrors,⁴ micropumps for drug delivery,⁵ microvalves,⁶ and electronic displays.⁷ The relationship between the droplet contact angle during electrowetting and the applied voltage can be described by Young-Lippmann equation

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

where θ is the droplet contact angle at any voltage V , θ_o is the initial contact angle, ϵ_o is the permittivity of vacuum, ϵ_d is relative permittivity of the insulating dielectric layer, d is its thickness, and γ_{lv} is the liquid-vapor surface tension coefficient.

One of the challenges facing electrowetting technology is the Contact Angle Saturation (CAS) phenomenon, where contact angle ceases to decrease beyond a certain angle no matter how much the applied voltage is increased. This is contrary to Young-Lippmann equation which predicts contact angles as low as zero degrees at a certain applied voltage,⁸ Figure 1(b). CAS limits leverage of electrowetting in many applications, since the extent of deformability of the liquid meniscus determines the operating range of the intended application. For example, change of the meniscus curvature in variable focal length liquid lens depends on the extent of contact angle reduction in the droplet forming the lens.² Also, tilt-range of a micromirror supported on two identical sessile droplets is limited by how far one of the two droplets spreads relative to the other upon voltage application.⁴

Many researchers investigated CAS phenomenon using different theories and approaches. One of the first of these theories referred CAS to air ionization around the droplet Three Phase Contact Line (TCL) due to the local maximum of the applied electric field.⁹ As a result, the accumulated charges on droplet surface—upon which electrodynamic forces responsible for droplet spreading are generated—start to leak, and thus, the driving force is not able to pull the droplet wedge further. However, when the surrounding medium was changed from air to Sulfur hexafluoride (SF_6)—which is a better insulator than air, still saturation happened at the same voltage,⁹ which contradicts the proposed theory. A similar theory attributed CAS to local breakdown of the dielectric layer on top of the electrode at the TCL region when the electric field strength exceeds the breakdown strength of dielectric material. This breakdown makes the region surrounding TCL in the dielectric layer conducting, which screens the applied electric field and reduces electrodynamic forces applied on droplet surface.^{10,11} Nevertheless, this theory cannot explain experimental results by Chevalliot *et al.*,¹² where contact angle saturation was invariant with the increase in electric field strength, sharpness of the curvature at TCL, and dielectric layer thickness which all affect the electric field intensity at the TCL.

A third theory relating CAS to charge accumulation is that charge on droplet surface saturates beyond a threshold voltage and excess charges are trapped in the dielectric layer at a certain distance from the top surface which again reduces electrodynamic forces causing wetting.^{13,14} Yet, this theory concluded that saturation angle depends directly on the potential of the trapped charges in the dielectric layer which does not correlate easily with dielectric material properties.

Another early trial for explaining CAS suggested that saturation is a thermodynamic limit of the wetting phenomenon when the solid-liquid interfacial tension reaches zero value as a result of the applied voltage according to Young-Lippmann equation.¹⁵ At this limit, the saturation contact angle depends only on the solid-gas and liquid-gas surface tensions. Nevertheless, this theory was disproved when predicted values of the solid-gas surface tension using values of saturation angles obtained experimentally were found to differ significantly from the actual values of the solid-gas surface tension.¹² Similar simple explanation for CAS suggested that the normal component of the electrostatic force at the TCL, which increases significantly at small contact angles, opposes the reduction of the contact angle and causes saturation.¹⁶ However, this was only suggested as a hypothesis and was not elaborated to develop a model that can predict the contact angle at each applied voltage.

A different group of studies tried to explain CAS using the energy minimum principle to find a relationship between the applied voltage and droplet contact angle. The energy minimum

principle leads directly to Young-Lippmann equation when surface tension energy, electrical energy stored into the dielectric layer, and external work are considered. It is believed that including other possible energy consumption modes during electrowetting can lead to more accurate models of contact angle variation with the applied voltage. One of such energy consumption modes was the kinetic energy of the internal liquid flow inside the actuated droplet,¹⁷ which produced good agreement with experimental results at higher values of the contact angle but not at low ones. Another study included the energy stored in the electric double layer on the bare electrode touching the droplet;¹⁸ however, this would entail changing the saturation curve if length of the wire electrode inserted into the droplet changed—which does not agree with experimental observations. Also, this study cannot explain saturation in electrowetting setups where both high potential and ground are supplied from beneath the droplet.^{19,20}

Most previous works reported on CAS assume that the liquid drop is a perfect conductor (i.e., an equipotential domain with zero electric field inside). Shapiro *et al.*²¹ were the first to include finite liquid resistance in their model, which leads to theoretical saturation curves matching experimental data. However, this matching occurs only for selective values of the resistivity ratio, depending on the principle radius of the drop and the thickness of the dielectric layer. Any change in the dielectric thickness or initial radius of the drop leads to different value for the resistivity ratio, and thus the saturation angle, which does not match experimental data.¹²

Here, we introduce a new explanation for the contact angle saturation phenomenon. We suggest that saturation is the result of repulsion between charges trapped at the cap and base surfaces of the droplet which prevents these surfaces from converging during contact angle reduction in electrowetting. Repulsion between charges trapped at surfaces of conducting droplets is a well known phenomenon and was suggested previously as a mechanism for interpretation of electrowetting of liquid droplets on solid surfaces where repulsion between accumulated charges at the TCL will cause droplet boundaries to stretch.²² Repulsion between like charges on surfaces of conducting droplets is also recognized as the cause of Coulombic fission of microdroplets^{23–27} after exceeding Rayleigh's stability limit.²⁸ Rayleigh's limit is the maximum total charge a conducting droplet can hold on its surface before the repulsion between these charges exceeds surface tension forces and results in emission of tiny droplets from the mother droplet in the coulombic fission phenomenon. There are many similarities between contact angle saturation and coulombic fission phenomena which lead us to the assumption that CAS could also be the result of repulsion between charges trapped at droplet surface. The first of these similarities is the emission of small satellite droplets from the mother droplet during electrowetting close to the saturation stage which was explicitly related to repulsion between trapped charges^{9,29} and was exploited mathematically, using variational calculus, as a potential cause for CAS in charged droplets.^{30,31} The second similarity is the common features between CAS phenomenon and the Taylor cone phenomenon,^{24,32} which is usually formed on a droplet surface before coulombic fission takes place. This second group of similarities was reported by Chevalliot *et al.*¹² as listed below:

- (1) Taylor cone angle does not change beyond a certain limit even with increasing the applied voltage which is similar to the contact angle during saturation.^{12,32}
- (2) The conical angle of Taylor cone is always the same regardless of the electrical and physical properties of the fluid used which is similar to CAS.¹²
- (3) AC fields reduce Taylor cone angle similar to the saturation angle in some reported cases.¹²

These similarities between Taylor cone formation and contact angle saturation lead us to the idea that both may be caused by the same effect which is repulsion between charges trapped at the droplet surface. Similar to the hypothesis that repulsion between like charges on the TCL may be the cause for droplet spreading,²² we believe repulsion between like charges on cap and base surfaces of the droplet will resist convergence of these two surfaces during contact angle reduction in electrowetting, which will ultimately lead to contact angle saturation. Moreover, treating the droplet, dielectric coating, and surrounding medium as lossy dielectric media, which is closer to reality, will result in the existence of an electric field inside the droplet,³³ which will induce repulsion not only between the charges on the same

surface but also between charges on adjacent surfaces (such as cap and base surfaces of the droplet at the TCL) too.

In the new work presented here, we solve for the electric field inside the droplet and charge distribution on its surface and calculate the corresponding repulsion energy. When repulsion energy is included into the energy equation of the entire system, the contact angle-voltage curve exhibits saturation and shows good agreement with previously published experimental results. Moreover, this new model allows for predicting the effect of changing properties of the droplet (e.g., its electrical conductivity) and thickness of the dielectric coating on the saturation angle, which is useful in optimizing electrowetting systems to induce largest reduction in contact angle before saturation.

THEORETICAL ANALYSIS

Young-Lippmann equation

The conventional relationship between the applied voltage and the contact angle in typical electrowetting settings was introduced by Lippmann in 1875 and is well known as the Young-Lippmann equation (1). The Young-Lippmann equation could be reproduced using minimum free energy principle where the electrowetting on dielectric (EWOD) system is dealt with as a thermodynamic system. So, the energy balance is expressed in the following equation:

$$\frac{dW_e}{dA} = \frac{dW_s}{dA} + \frac{dW_c}{dA}, \quad (2)$$

where $\frac{dW_e}{dA}$ represents the input work per unit base area of the droplet from the external power source or battery, $\frac{dW_s}{dA}$ is output work per unit base area to overcome surface tension of the liquid to increase its surface area during contact angle reduction, and $\frac{dW_c}{dA}$ is the energy stored in the system through charging the capacitor formed by the dielectric coating separating the droplet from the actuation electrode, also per unit base area of the droplet. The energy stored in the electric field throughout the dielectric layer can be approximated as the energy stored in a parallel plate capacitor (Eq. (3))

$$\frac{dW_c}{dA} = \frac{1}{2} \frac{\epsilon_o \epsilon_d}{d} V^2. \quad (3)$$

And, $\frac{dW_s}{dA}$ is the summation of the surface tension energies indicated in Eq. (4) which represents the output work done by the system due to increasing the area of the liquid-vapor interface (stretching of the system boundaries) with contact angle reduction

$$\frac{dW_s}{dA} = \gamma_{lv} (\cos \theta - \cos \theta_o). \quad (4)$$

And, $\frac{dW_e}{dA}$ is the work done by the external voltage source and is determined by the following equation:¹³

$$\frac{dW_e}{dA} = \frac{\epsilon_o \epsilon_d}{d} V^2. \quad (5)$$

After substitution of the free energies of the EWOD system from Eqs. (3)–(5) into Eq. (2), the Young-Lippmann equation can be obtained as in Eq. (1).

INTRODUCING THE REPULSION ENERGY

It is well known that in a typical electrowetting setup, electrical charge will be trapped on the cap and base surfaces of the droplet, as shown in Figure 2. However, no previous studies considered repulsion between these charges as a possible cause for CAS based on the

FIG. 2. (a) Distribution of the surface charge density on the cap and base surfaces of the droplet based on Vallet's calculations shown for a contact angle of 60° .⁹ Arrows indicate the direction of the repulsion forces between these charges on the droplet surfaces. Charge distribution on the cap surface was divided into element charges $Q_{c[i,j]}$ and that on base surface into element charges $Q_{b[i,j]}$ in order to be able to calculate the total repulsion between top and bottom charges. (b) COMSOL simulations illustrating electrostatic repulsive force distribution on droplet surfaces near the TCL, in N/m^2 . Arrow length is proportional to the magnitude of the electrostatic force and colors indicate intensity of the electric field in V/m . At such low contact angles, these forces oppose convergence of the cap and base surfaces of the droplet and prevent the droplet from achieving complete wetting.

conception that the droplet is a perfect conductor; hence, no electric field, and no repulsion, exists inside it. However, the electric field inside the droplet is not the main criterion to prove existence of repulsion between charges on its cap and base surfaces. For example, repulsion between two positive charges exists even though the electric field vanishes at the center point between the two charges. Also, the electric field inside a uniformly charged cylindrical surface is almost zero even though repulsion exists between its charges and pushes these charges outwards. Similarly, the electric field inside the droplet is vanishing due to the opposing fields resulting from the like charges on the cap and base surfaces of the droplet, which does not preclude repulsion between these charges. Repulsive forces still exist even if the field intensity within the droplet is zero and pull the cap and base surfaces of the droplet apart and oppose convergence of these two surfaces during electrowetting, Figure 2(b).

Repulsion between charges trapped at the surface of conductive droplets is also well documented and is the main cause behind Taylor cone formation³² and Coulombic fission of droplets suspended in electric fields.^{23–27} Hence, energy will be consumed to overcome these repulsive forces between droplet surfaces when they come closer as a result of voltage increase and contact angle reduction during electrowetting. This repulsion energy which we calculated was added as a new energy term in the general energy equation (2) to become in its new differential form (Eq. (6))

$$\frac{dW_e}{dA} = \frac{dW_s}{dA} + \frac{dW_c}{dA} + \frac{dW_R}{dA}, \quad (6)$$

where $\frac{dW_R}{dA}$ is the change in the repulsion energy during droplet spreading.

The surface charge density distribution was calculated by Vallet *et al.*⁹ who assumed a perfectly conducting droplet. We used the same distribution after multiplying it by a correction factor (λ) to compensate for the difference from a lossy dielectric assumption (see calculation of the correction factors λ_c and λ_b in the next section, “Calculation of the Correction Factors”). For simplicity, we assumed that surface charge density on the base surface follows a distribution similar to that of the cap surface charge density with the addition of the value of the electrostatic surface charge density $\sigma_o = \frac{\epsilon_o \epsilon_d}{d} V$, where V is the applied voltage. In this assumption, we neglected the voltage drop across the electric double layer in the liquid because its

capacitance is much higher than the capacitance of the dielectric layer.³⁴ The potential drop inside the droplet itself was also neglected based on the resistance calculations of the liquid and the dielectric layer.²¹

To calculate the repulsion energy, the surface charge distribution on the droplet cap and base surfaces was divided into N and M small charge elements, respectively, and the repulsive force between each two point charges on these two surfaces, Figure 2(a), was calculated from Eq. (7) according to Coulomb's law. The number of elements N and M was increased gradually until its increase did not produce any changes in the final saturation curve of contact angle vs voltage

$$F_{R[i,j]} = \frac{1}{4\pi\epsilon_o\epsilon_w} \frac{Q_{c[i]}Q_{b[j]}}{r_{[i,j]}^2}, \quad (7)$$

where $Q_{c[i]}$ and $Q_{b[j]}$ are the i -th and j -th charge elements on the cap and base surfaces of the droplet, respectively, as calculated by Eqs. (8) and (9) and $r_{[i,j]}$ is the distance between these two charge elements on the cap and base surfaces of the droplet

$$Q_{c[i]} = 2\pi\lambda_c\sigma_o \left(a - \frac{(2i-1)\Delta S_c}{2} \cos\theta \right) \int_{(i-1)\Delta S_c}^{i\Delta S_c} \frac{1}{(\alpha+1)^\alpha} \left(\frac{d}{\pi|s|} \right)^{\frac{\alpha}{\alpha+1}} ds, \quad (8)$$

$$Q_{b[j]} = 2\pi\lambda_b\sigma_o \left(a - \frac{(2j-1)\Delta S_b}{2} \right) \int_{(j-1)\Delta S_b}^{j\Delta S_b} \left(\frac{1}{(\alpha+1)^\alpha} \left(\frac{d}{\pi|s|} \right)^{\frac{\alpha}{\alpha+1}} + 1 \right) ds, \quad (9)$$

where α is a function of the droplet contact angle, $\alpha = 1 - \theta/\pi$,⁹ and λ_c and λ_b are the correction functions to compensate for the perfect conductor assumption in these equations which is not true. λ_c and λ_b are the ratios between actual charge distribution on droplet cap and base surfaces, respectively, to the theoretical charge distribution calculated by Vallet *et al.*, based on a perfect conductor assumption. Both λ_c and λ_b are functions of the contact angle, see next section, "Calculation of the Correction Factors," and Figure S1 in the supplementary material³⁸ for more details.

The differential repulsion work was calculated from Eq. (10), and the derivative of the repulsion work was calculated in terms of the quantities of charges and their separation distances in Eq. (11)

$$dW_{R[i,j]} = F_{R[i,j]} dr_{[i,j]} + r_{[i,j]} dF_{R[i,j]}, \quad (10)$$

$$\frac{dW_{R[i,j]}}{dA} = \frac{1}{4\pi\epsilon_o\epsilon_w} \left(\frac{Q_{b[j]}Q_{c[i]}}{r_{[i,j]}^2} \frac{dr_{[i,j]}}{dA} + \frac{1}{r_{[i,j]}^2} \left(Q_{b[j]} \frac{dQ_{c[i]}}{dA} + Q_{c[i]} \frac{dQ_{b[j]}}{dA} \right) - 2Q_{b[j]}Q_{c[i]} \left(\frac{dr_{[i,j]}}{dA} \right) \right). \quad (11)$$

Then the total repulsion energy between all charge elements on cap and base surfaces was calculated by summing the energy resulting from repulsion between each two element charges across all the cap and base surfaces. A code was written on MapleTM symbolic calculations software to calculate the total repulsion energy as a function of droplet contact angle. This new term of repulsion energy was substituted into Eq. (6) to produce the modified Young-Lippmann equation

$$V = \left(\frac{\cos\theta - \cos\theta_o}{\epsilon_o\epsilon_d - \frac{1}{2\gamma_{lv}d} \frac{d\overline{W}_R}{dA}} \right)^{\frac{1}{2}}, \quad (12)$$

$$\text{where } \frac{d\overline{W}_R}{dA} = \frac{1}{V^2} \sum_{i=1}^N \sum_{j=1}^M \frac{dW_{R[i,j]}}{dA}.$$

CALCULATION OF THE CORRECTION FACTORS λ_c AND λ_b

The correction factors used to compensate for the difference between the actual (based on the lossy dielectric assumption) and theoretical (based on a perfect conductor assumption) charge distribution on cap and base surfaces of the droplet were calculated according to the definitions $\lambda_c = \frac{Q_{c,actual}}{Q_{c,th}}$ and $\lambda_b = \frac{Q_{b,actual}}{Q_{b,th}}$, where $Q_{c,th}$, $Q_{b,th}$, $Q_{c,actual}$, and $Q_{b,actual}$ are the total theoretical and actual charges on the cap and base surfaces, respectively. $Q_{c,th}$ and $Q_{b,th}$ were calculated by integrating the theoretical surface charge density distribution, according to Vallet *et al.*,⁹ over lengths of $S_c = 100d$ on droplet cap surface and $S_b = a$ on droplet base, where d is the dielectric layer thickness and a is the base radius of droplet, Eqs. (13) and (14). $Q_{c,actual}$ and $Q_{b,actual}$ were calculated numerically by COMSOL 4.3 software package based on lossy dielectric consideration for electrowetting system (see “Numerical Analysis” section).

$$Q_{c,th} = 2\pi\sigma_o \left(a - \frac{S_c}{2}\cos\theta\right) \int_{\delta}^{S_c} \frac{1}{(\alpha+1)^\alpha} \left(\frac{d}{\pi|s|}\right)^{\frac{\alpha}{\alpha+1}} ds, \quad (13)$$

$$Q_{b,th} = 2\pi\sigma_o \left(a - \frac{S_b}{2}\right) \int_{\delta}^{S_b} \left(\frac{1}{(\alpha+1)^\alpha} \left(\frac{d}{\pi|s|}\right)^{\frac{\alpha}{\alpha+1}} + 1 \right) ds. \quad (14)$$

The lower integration limit in Eqs. (13) and (14) was set as δ instead of zero in order to avoid the singularity in the charge distribution at the TCL. Then, δ was assigned a value of $10^{-10}d$ in the final calculations to find the total charge on both cap and base surfaces of the droplet. Same procedure was followed when calculating the repulsion energy between the two first charge elements closest to the TCL on cap and base surfaces. The singularity at the TCL is a common challenge for modeling electrowetting systems and one of the recent methods to overcome this challenge in the analysis of precursor films. The precursor film is a one-molecule thick layer of the liquid that precedes the TCL. When included in the analysis, the precursor film introduces a new length scale that eliminates singularity of the charge density at the TCL.³⁵

NUMERICAL ANALYSIS

We built a finite element model to calculate the actual surface charge distribution on the cap and base surfaces of the droplet based on the assumption of a lossy dielectric droplet, lossy dielectric layer, and lossy surrounding medium, Figure 3. We used COMSOL Multiphysics 4.3 to build our model. For each modeled case, we solved for the electric field inside the droplet and its surrounding medium and calculated the surface charge density $Q_{c,actual}$ and $Q_{b,actual}$ at each applied voltage and its corresponding contact angle based on Young-Lippmann equation.

FIG. 3. (a) Geometry of the axisymmetric case solved by COMSOL and its boundary conditions, (b) Mesh used to model CAS; inset shows mesh refinement in the dielectric layer and on droplet cap surface at the TCL where average element size is $0.125\ \mu\text{m}$.

Then, we found the correction factors $\lambda_c = \frac{Q_{c,actual}}{Q_{c,th}}$ and $\lambda_b = \frac{Q_{b,actual}}{Q_{b,th}}$ as a function of contact angle of the droplet, supplementary Figure S1.³⁸

MODEL DETAILS

The Electric Currents module and electrostatic module were used for solving the current continuity equations for lossy media, Eqs. (15) and (16). These equations were reduced to Laplace equation when using DC applied voltage at electrostatic steady state condition where the solution of Laplace equation depends only on the electrical conductivity.³³

$$\nabla \cdot J = Q_s, \quad (15)$$

$$\nabla \cdot D = \rho_v, \quad (16)$$

where J is the electric current density, Q_s is the electric current source, D is the electric current displacement, and ρ_v is the volume charge density.

The electrical charge on droplet cap and base surfaces were calculated by integrating the surface charge density equation (17) over corresponding droplet surface.

$$\sigma = \vec{n} \cdot (\vec{D}_e - \vec{D}_i), \quad (17)$$

where σ is the surface charge density, $\vec{n}$ is the unity vector normal to the interface, and D_e and D_i are the external and internal electrical displacements on droplet surface, respectively.

Boundary conditions used in our model are shown in Figure 3(a). We built several meshes to determine the optimum mesh size to be used for different zones across the droplet boundaries. The final mesh used had smallest element size of $0.125 \mu\text{m}$ in the vicinity of the TCL, Figure 3(b). The model involved a parametric study to solve for the electric field in the whole geometry sweeping through different contact angles. Average time for solving the parametric study with the current mesh was 6 h using a core i5 desktop with 4 GB of RAM.

NUMERICAL METHODS

Equations of current and charge conservation were solved on the modeled geometry, using COMSOL 4.3 finite element package. The electric current and electrostatic modules were used simultaneously to model the axisymmetric CAS geometry. We used free triangular elements and MUMPS direct solver³⁶ to solve the system of equation in the form $\mathbf{u} = \mathbf{K}^{-1}\mathbf{b}$, where $\mathbf{u}$ represents the variables (unknowns) matrix, $\mathbf{K}$ represents matrix of parameters, and $\mathbf{b}$ represents boundary conditions matrix. The relative tolerance used as a convergence criterion was 10^{-3} .

RESULTS AND DISCUSSION

To include the effect of repulsion between electrical charges trapped at cap and base surfaces of the droplet in modeling contact angle saturation, actual surface charge density on both surfaces were evaluated numerically, Figure 4, and used to calculate repulsion energy. Initially, when the contact angle is large, applied voltages are low, which results in low charge density on cap and base surfaces of the droplet ($\sigma = \epsilon E$). Also, the cap and base surfaces of the droplet are far from each other due to the large contact angle. This results in low energy requirement to overcome repulsion between trapped charges. Hence, most of the applied electrical energy is consumed to charge the capacitor beneath the droplet (the dielectric layer) and to overcome surface tension to increase droplet surface, which are the two other energy terms in Young-Lippmann equation. This is why the contact angle-voltage curve follows the Young-Lippmann equation without deviation at large contact angles. When droplet spreads at higher voltages, a lower contact angle results in narrow spacing between cap and base surfaces of the droplet, which increases energy consumption to overcome repulsion between these charges. Moreover, since voltage is already higher at low contact angles, the electrical charge density is higher on cap and base surfaces, which contributes to increase in energy consumption (Figure 4, Multimedia view). Theoretically, the contact angle would never reach zero since this would require overcoming infinite repulsion force as indicated by Eq. (7) when r tends to zero. This behavior is clearly shown when the ratio between repulsion

FIG. 4. Numerical simulation results showing (a) Electric potential distribution in the modeled geometry. (b) Distribution of the accumulated charges on the cap surface of the droplet where the charge density is high at the TCL and decreases gradually further away from TCL (distribution plotted at contact angle = 60° , applied potential = 44 V, dielectric thickness = $0.5 \mu m$, relative permittivity of dielectric material = 3.8). (Multimedia view) [URL: <http://dx.doi.org/10.1063/1.4907977.1>] (c) and (d) Charge distributions in the vicinity of the TCL on droplet base and cap surfaces, respectively, obtained from COMSOL simulations at contact angle = 60° , applied voltage = 36 V according to experimental parameters of Chevalliot *et al.*¹² (parameters mentioned in Table I.)

energy and the energy stored in the dielectric layer is plotted against the contact angle, Figure 5. At low contact angles, repulsion energy is much larger than energy stored in the dielectric layer, which consumes most of the input work by the external power source leaving little energy to overcome surface tension and reduce contact angle.

FIG. 5. Ratio between repulsion energy and energy stored in the dielectric layer vs droplet contact angle according to experimental parameters of Drygiannakis *et al.*¹⁰ (parameters listed in Table I). Repulsion energy increases significantly with reduction of contact angle. Repulsion energy and the stored energy in the capacitor are equal at $\theta \approx 57^\circ$.

TABLE I. Parameters used in COMSOL simulations for Drygiannakis *et al.*¹⁰ and Chevalliot *et al.*¹² Electrowetting setups.

Parameter	Drygiannakis <i>et al.</i> ¹⁰	Chevalliot <i>et al.</i> ¹²
Volume of droplet (m ³)	5×10^{-9}	1×10^{-9}
Initial contact angle (deg)	114	157
Thickness of dielectric layer (m)	0.5×10^{-6}	1.3×10^{-6}
Relative permittivity of surrounding medium	1	2.5 (approximately)
Relative permittivity of dielectric layer	3.8	3.15
Relative permittivity of water	80	73
Electrical conductivity of liquid drop	5.5×10^{-6} S/m	4.14×10^{-2} S/m
Electrical conductivity of surrounding medium	5×10^{-15} S/m	1×10^{-14} S/m
Electrical conductivity of dielectric layer	1×10^{-14} S/m	1×10^{-14} S/m
Surface tension between the liquid drop and the surrounding medium	0.072 N/m	0.01 N/m

We compared the results of our model with two previously published experimental studies on contact angle saturation. The first one is by Drygiannakis *et al.*,¹⁰ and the second one is by Chevalliot *et al.*¹² (parameters used for both cases are listed in Table I). Correction factors, λ_c and λ_b were evaluated numerically for the physical and geometrical parameters used in both experiments and were obtained as functions of contact angle, supplementary Figure S1.³⁸ The values of both correction factors λ_b and λ_c were mostly less than unity corresponding to the actual surface charge density (assuming water is a lossy dielectric) being less than the theoretical surface charge density when water is treated as a perfect conductor with zero electric field within the droplet. This is attributed to existence of electric field inside the droplet in the actual case, thus reducing the discontinuity of the electric field at the droplet cap and base surfaces which contributes directly to reduce the surface charge density.³⁷ Moreover, λ_c was much less than λ_b because the electric field on the air-side of the droplet is much less than that on the dielectric-side; thus, the effect of reducing the discontinuity of the electric field on cap surface is more significant compared to reducing the discontinuity on the base surface of the droplet.

When the repulsion energy was added to the energy equation (2), the modified Young-Lippmann equation exhibits the saturation phenomenon and produces results in good agreement with previously reported experimental results, Figure 6.

EFFECT OF DROPLET ELECTRICAL PROPERTIES

To further test the validity of our model, we investigated the effect of droplet electrical conductivity on CAS phenomenon and compared our model results with previous

FIG. 6. Comparison between Young-Lippmann model (blue dashed line), our model results (red line), and experimental results (diamonds) for (a) Drygiannakis *et al.*¹⁰ and (b) Chevalliot *et al.*¹² The mild deviation of the theoretical saturation curve in Chevalliot's case was due to uncertainty in determining the permittivity of the surrounding medium which was a blend of silicon oils with different permittivities. In our model and corresponding simulations, we used the permittivity of silicon oil which has the biggest percentage in the blend (80%).

FIG. 7. (a) Liquid conductivity had little effect on saturation curves which agrees with previous experimental results by Chevalliot *et al.*¹² Relative permittivity was kept constant ($\epsilon_w = 73$) in all theoretical curves. (b) Total charge on cap and base surfaces of the droplet did not change with the increase in electrical conductivity within the range examined in (a).

experimental results. Droplet conductivity was varied between 5.5×10^{-6} S/m (DI water conductivity) to 5.7×10^{-2} S/m (sea water conductivity), and the saturation curve was plotted in each case. We found that conductivity had little effect on the saturation curve and final saturation angle which agrees well with previous results,¹² Figure 7. This could be attributed to the fact that surface charge density on cap and base surfaces of the droplet did not change within the conductivity range studied here, Figure 7(b). Only a slight decrease in saturation angle occurred when conductivity increased from 5.5×10^{-6} S/m to 57×10^{-3} S/m, beyond which no changes happened in the saturation angle. This slight reduction in saturation angle could be attributed to a decrease in the electric field intensity within the droplet at higher conductivities which reduces repulsion energy. This is similar to previous reports that increasing droplet conductivity, by addition of salt, was found to decrease the emission of satellite droplets in electrowetting systems.^{9,29} The latter phenomenon is also similar to the Coulombic fission where increasing droplet conductivity leads to emission of finer droplets rather than larger ones,²⁴ which again confirms that contact angle saturation is likely the result of repulsion between charges on droplet surface.

EFFECT OF DIELECTRIC THICKNESS

The thickness of the dielectric coating was found to have an effect on the voltage at which saturation takes place but not on the saturation angle itself, Figure 8. For thicker dielectric coatings, the intensity of the electric field inside the dielectric layer decreased considerably at the

FIG. 8. (a) Effect of the thickness of the dielectric coating on CAS. The final saturation angle was found not to change at different dielectric thicknesses; however, the voltage at which saturation takes place was found to increase significantly with the increase in dielectric thickness. (b) Surface charge density on base surface of the droplet decreases considerably with the increase in the thickness of the dielectric coating (curves at contact angle of 60°). Surface charge distribution on cap surface did not change when thickness of the dielectric coating was increased from $1.3 \mu\text{m}$ to $5.5 \mu\text{m}$.

same voltage. Lower intensity of the electric field resulted in lower surface charge density on the base surface (Figure 8(b)) of the droplet since $\sigma = \epsilon E$, where σ is the surface charge density on the base surface, ϵ is the permittivity of the dielectric coating, and E is the electric field intensity inside the dielectric layer. This means that a higher voltage is required to induce the necessary amount of surface charge on the cap and base surfaces of the droplet that is able to generate high enough repulsion to cause saturation.

CONCLUSION

We introduced a new model for interpretation of contact angle saturation phenomenon based on repulsion between the charges accumulated on the cap and base surfaces of the droplet, which is a well known phenomenon in conducting droplets undergoing coulombic fission. This repulsion energy increases significantly at lower contact angles resulting in consuming most of the applied external work in overcoming repulsion rather than overcoming surface tension to reduce the contact angle. Effect of changing droplet electrical conductivity on the saturation angle was also investigated. Saturation angle was found to slightly decrease with the increase in liquid conductivity. Increasing the thickness of the dielectric coating was found to increase the voltage at which saturation happens without affecting the saturation angle itself. This is attributed to reduction in the density of the charge trapped at the base surface of the droplet for thicker dielectric coatings. Our results are in good agreement with previously reported experimental results both in terms of voltage dependence of the contact angle and effect of electrical properties and dielectric thickness.

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