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Near Axisymmetric Partial Wetting Using Interface-Localized Liquid Dielectrophoresis

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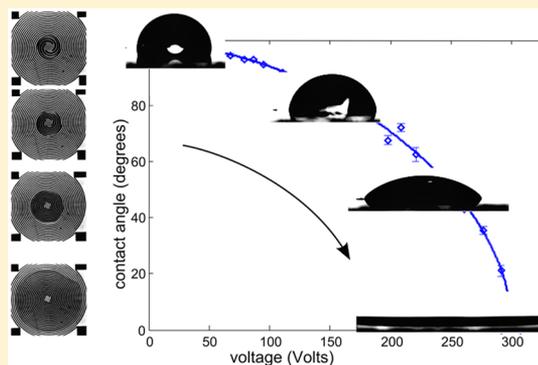
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Supporting Information

ABSTRACT: The wetting of solid surfaces can be modified by altering the surface free energy balance between the solid, liquid, and vapor phases. Liquid dielectrophoresis (L-DEP) can produce wetting on normally nonwetting surfaces, without modification of the surface topography or chemistry. L-DEP is a bulk force acting on the dipoles of a dielectric liquid and is not normally considered to be a localized effect acting at the interface between the liquid and a solid or other fluid. However, if this force is induced by a nonuniform electric field across a solid–liquid interface, it can be used to enhance and control the wetting of a dielectric liquid. Recently, it was reported theoretically and experimentally that this approach can cause a droplet of oil to spread along parallel interdigitated electrodes thus forming a stripe of liquid. Here we show that by using spiral-shaped electrodes actuated with four 90° successive phase-shifted signals, a near axisymmetric spreading of droplets can be achieved. Experimental observations show that the induced wetting can achieve film formation, an effect not possible with electrowetting. We show that the spreading is reversible thus enabling a wide range of partial wetting droplet states to be achieved in a controllable manner. Furthermore, we find that the cosine of the contact angle has a quadratic dependence on applied voltage during spreading and deduce a scaling law for the dependence of the strength of the effect on the electrode size.



1. INTRODUCTION

The wetting of solid surfaces is of interest to a wide range of disciplines and has many applications, such as creating thin films, surfaces coating, adhesion, droplet deposition, and droplet control. There are many ways to modify the wetting properties of solid surfaces, all based on altering the energy balance between the solid, liquid, and vapor phases.¹ It can be achieved either by changing the properties of the liquid^{2,3} or the solid surface,⁴ or by introducing an electric field.⁵ In recent years, uniform electric fields have proved important in manipulating⁶ and controlling droplets⁷ of conducting liquids. Using the liquid–solid contact area as one electrode, electrowetting^{8–11} reversibly increases the hydrophilicity of the solid surface and reduces the contact angle of a droplet of a conductive liquid without altering the surface chemistry or the liquid properties. Thus, a droplet can be shaped or moved leading to applications¹² such as liquid lenses,^{13–15} liquid optical elements,^{16,17} microfluidics,⁶ or droplet manipulation.^{7,18} However, there are significant limitations to the electrowetting approach including the need for any liquids of interest to be conducting and normally the need for direct electrical contact with the liquid, although there are examples of

using noncontacting co-planar electrodes.^{19,20} Also an inability to spread a droplet to a film state due to the existence of a minimum saturation contact angle is a disadvantage.²¹ Typically the minimum contact angle is $\sim 60^\circ$ for a DC voltage or 45° for an AC voltage and is due to the unexplained effect of contact angle saturation.^{22,23} All of these factors limit the range of applicability of the electrowetting approach.²⁴

Liquid dielectrophoresis (L-DEP) is the attraction of polarized dipoles into regions of relatively stronger electric fields and is a driving force for motion of bulk insulating dielectric liquids. This is because a nonuniform electric field generates unequal forces on dipoles that result in a dielectrophoretic (DEP) force causing movement of the liquid into areas of the highest gradient of the electric field.^{8,25–29} For conducting liquids, Jones has discussed the relationship between electrowetting and the electromechanical response of the liquid, for which the high frequency limit, equivalent to an insulative liquid, is liquid dielectrophoresis.⁹ For example,

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deionized water ($\sim 10^{-4}$ S/m) in air behaves as a conductive liquid for frequencies below 60 kHz and as a dielectric liquid for frequencies above 60 kHz.⁹

Recently, we have shown how an interface-localized form of liquid dielectrophoresis,⁸ can be used to create spreading and superspreading of droplets of a dielectric liquid in air^{26,30,31} or a second liquid.³² This approach, described as dielectrowetting, enables the control of the oleophobicity of materials by applying a voltage. Dielectrowetting utilizes the dielectric properties of liquids, but the effect is localized to the interface³¹ and differs significantly from electrowetting.¹¹ With a suitable decaying electric field, the effect of L-DEP can be bound to the solid–liquid or liquid–vapor interface and can be used to induce spreading or superspreading of droplets of nonconducting liquids.^{30,31} Moreover, the saturation of contact angle appears lower than in the case of electrowetting,³⁰ and a significant difference is in achieving the full range of wetting from the droplet to the film state that has not been reported in the case of electrowetting.^{22–24} Full wetting has been shown to be useful for optical applications based on controlled changes to the shapes of films of liquids.^{16,17,31}

In wetting the Young's law contact angle for a partially wetting droplet can be obtained by considering the surface free energy changes as a contact line advances over a small area, ΔA . Such an advance removes solid–vapor interfacial area and replaces it with solid–liquid interfacial area thus causing a change in the surface free energy of $(\gamma_{SL} - \gamma_{SV})\Delta A$, where γ_{SL} and γ_{SV} are the solid–liquid and solid–vapor interfacial tensions, respectively. An additional surface free energy of $\cos \theta (\gamma_{LV}\Delta A)$ is also created. In equilibrium, the total change in surface free energy, $\Delta F = (\gamma_{SL} - \gamma_{SV})\Delta A + \cos \theta (\gamma_{LV}\Delta A)$ vanishes so the equilibrium contact angle is $\cos \theta_e = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV}$, which is Young's law. In the classic electrowetting (on dielectric) arrangement, the droplet is composed of a conducting liquid and rests on the top of a smooth solid dielectric of thickness d_{ins} and permittivity $\epsilon_o\epsilon_r$ which has a uniform electrical contact on its bottom surface.^{9–11} Thus, the spatial extent of the solid–liquid contact area defines an electrode and the structure provides a capacitive energy contribution, $\epsilon_o\epsilon_r V^2/2d_{\text{ins}}$ per unit area, where V is the applied voltage, to the energy balance. The cosine of the equilibrium contact angle is then modified to include a term representing the balance of capacitive energy to liquid–vapor interfacial energy,

$$\cos \theta(V) = \cos \theta(0) + \left(\frac{\epsilon_o\epsilon_r}{2\gamma_{LV}d_{\text{ins}}} \right) V^2 \quad (1)$$

In liquid dielectrophoresis, energy is stored in the liquid due to the polarization of dipoles by the nonuniform electric field. A surface fabricated interdigitated electrode structure with electrodes and gaps of size d (in our work electrode width is always equal to the gap size) and an applied sinusoidal voltage generate an electric field decaying away from the surface (assumed here to be the z -axis) in an exponential manner. The penetration depth, δ , is defined via $V(z) = V_0 e^{-2z/\delta}$ and is proportional to d according to the stripe theory of ref 26. In a manner similar to electrowetting, this results in a modification of the cosine of the equilibrium contact angle to include a term representing the balance of dielectrophoretic energy to liquid–vapor interfacial energy,³³

$$\cos \theta(V) = \cos \theta(0) + \left(\frac{\epsilon_o(\epsilon_1 - 1)}{2\gamma_{LV}\delta} \right) V^2 \quad (2)$$

where $\epsilon_o\epsilon_1$ and δ are the permittivity of the dielectric liquid and penetration depth of the electric field into the liquid. Thus, the periodicity of the surface fabricated electrodes determines a surface layer of the liquid of effective thickness, δ (Figure 1a),

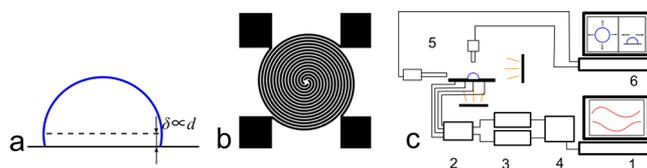


Figure 1. (a) Schematic of a droplet with the penetration depth, δ , of the electric field into the liquid, indicating its proportionality to electrode size, d . (b) Four arm spiral electrode design with electrode width and spacing between electrodes both of size d . (c) Schematic of the experimental setup: (1) software signal generating, (2) waveform generator (soundcard), (3) amplifiers, (4) ground decoupler and phase shifter, (5) imaging and light system, and (6) image capture.

which is analogous to the thickness of the solid dielectric in electrowetting and justifies the term interface-localized liquid dielectrophoresis. When the localization of the effects of liquid dielectrophoresis is used with droplets of height larger than δ and controls droplet spreading, rather than the liquid–vapor interface on the surface of a liquid film, the effect has been called dielectrowetting.³⁰

Thus far interface-localized L-DEP has been primarily used for spreading droplets of nonconducting liquids along parallel interdigitated electrodes (IDEs) into a non-axisymmetric stripe-shaped droplet form. Most recently, some of the present authors have shown that it is possible to use L-DEP to initiate an axisymmetric (circular) film and observe the dynamics of its dewetting back into a macroscopic equilibrium droplet that existed prior to the application of any voltage.³⁴ An outstanding challenge is to create spreading of an axisymmetric droplet with the ability to program, using a voltage, any desired axisymmetric partially wetting droplet state concluding with a film state. Achieving axisymmetric droplet shapes is essential to convert the idea of L-DEP-induced partial wetting from an interesting insight into greater practical relevance, for example in terms of liquid lenses.¹⁴ The difficulties in doing so arise from the fact that an AC voltage on parallel IDEs³⁰ create a nonuniform periodic field with maximum values located at the electrode edges.³⁵ The resulting periodic energy barriers due to the electrodes prevent the droplet spreading axisymmetrically and favor spreading along the electrodes rather than across them. Overcoming these energy barriers is the main challenge to achieving axisymmetric droplet spreading. In this work, we present a method for achieving near axisymmetric spreading of droplets, using a phase-shift signal activation that differs from previous works,^{26,30–32,36} and a spiral pattern electrode design that specifically shapes the droplet. We also show experimentally that the change in the cosine of the contact angle has a quadratic dependence on voltage in a manner similar to those of electrowetting and the stripe form of L-DEP-induced wetting. Moreover, the strength of the effect of the dielectrowetting is found to obey a scaling law related to the size of the electrodes although the exact form differs from that found for the dielectrowetting using parallel IDEs.

2. EXPERIMENTAL SECTION

Achieving axisymmetric spreading using an anisotropic liquid such as a liquid crystals has been attempted in the literature.³⁷ However, for dielectric liquids with isotropic properties, initial attempts at axisymmetric spreading using spiral and circular arc electrode designs have shown nonideal faceting of the droplets edge.³⁸ We therefore looked for inspiration to biological separation methods where spiral electrodes are used, but with a four-phase voltage actuation for traveling wave particle dielectrophoresis that creates a rotating electric field.^{35,39,40} Our hypothesis was that a rotating electric field electrode design would be less likely to have energy barriers inducing faceting. To investigate axisymmetric L-DEP-induced spreading of droplets, a prototype device was designed and fabricated based on electrode designs used for biological separations.⁴⁰

Each electrode pattern contained four spiral electrodes of width d , separated equidistantly by gaps of the same dimension, d , as the electrode width (Figure 1b) produced using a standard photolithographic etch-back technique. In biological separation experiments these four spiral electrode elements are actuated with sinusoidal signals with successive relative phase differences of 90° to generate a rotating electric field. Because the penetration depth of the electric field into the liquid is expected to be directly related to the electrode geometry, samples with electrode sizes of $d = 40, 60, 80, 100, 120,$ and $180 \mu\text{m}$ were studied. The thickness of the gold electrodes was 100 nm and the surfaces, including electrodes, were covered with a $1.7 \mu\text{m}$ capping layer of photoresist SU8-2002 (MicroChem) which can withstand $\sim 550 \text{ V}$ before electrical breakdown. This treatment provides a thin dielectric layer with a uniform smooth surface to the liquid and also ensures electrolysis and subsequent destruction of a device does not occur if the droplet becomes conductive for any reason (e.g., when using hygroscopic liquids). To achieve a high initial contact angle ($>90^\circ$), the substrate was coated with a commercial solution Novec 1700 (3M) providing an oleophobic surface.

Figure 1c shows the experimental setup. Initially, 1 kHz sinusoidal signals with phase shifts of 0° and 90° were provided by a waveform generator (SoundBlaster Omni Surround 5.1) connected to two amplifiers (TREK, PZD700A). The ground was decoupled via transformers, and amplified signals were fed into a phase shifter where each signal was split so that one part of the original signal was kept unchanged and the other one was phase shifted by 180° (inverted). Using this method, it was possible to create a four-phase approach with four signals with relative phase shifts of $0^\circ, 90^\circ, 180^\circ,$ and 270° . Each signal was then connected to one of the four spirals within the electrode pattern. Droplets of glycerol were deposited onto the electrodes (typical volume of $5 \mu\text{L}$), and both side and top view images were recorded. Since pure glycerol is a hygroscopic liquid (99.5%, Sigma-Aldrich), it was stored in a perfectly sealed container and a fresh droplet was used for every experiment. We also verified that similar results occurred at a higher frequency of 2 kHz to ensure the liquid was exhibiting a dielectric response consistent with expectations of operating above a crossover frequency of 14 Hz for dielectrophoresis to dominate, which arises from a permittivity of 42.5 and conductivity of $5.6 \times 10^{-8} \text{ S/m}$.⁹ The top view images were captured with a standard Canon camera D600 fitted with a macro-objective (Carl-Zeiss Jena, Pancolar). Side profile view images were captured using a Krüss drop shape analysis system (DSA30) that also enabled the measurement of the contact angles by fitting an ellipse to the droplet profile. Thus, all contact angles discussed in this work are macroscopic ones rather than microscopic ones, which may differ at length scales significantly smaller than the electric field penetration depth set by the electrode size. The advancing contact angle of the glycerol droplet on the surface measured by the volume addition method was 104° .

3. RESULTS AND DISCUSSION

We performed initial testing using voltages phase shifted by 0° and 180° applied to every other electrode to understand how spreading of glycerol might differ from actuation using the four-phase approach with successively 90° phase-shifted voltages.

We also tested spreading using an alternative approach with ground and voltage actuation rather than 0° and 180° . In these initial tests with these electrode designs using actuation voltages with 0° and 180° , with and without the 0° held at ground, film spreading was not achieved. Typically, a minimum contact angle of around 50° was observed, and higher applied voltages did not result in further spreading (Figure S1).

Figure 2 shows top view images of droplets sitting on an electrode pattern of electrode size $d = 60 \mu\text{m}$ with the voltage

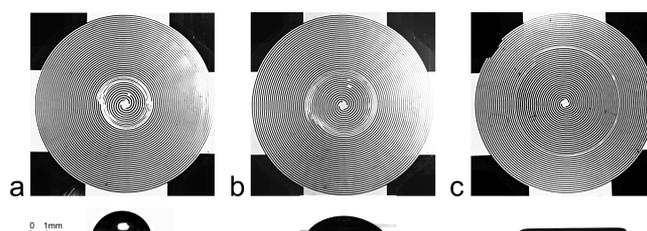


Figure 2. Different actuation of the spiral electrode array ($d = 60 \mu\text{m}$; $V_{\text{rms}} = 280 \text{ V}$): (a) voltage-ground. (b) signals of phase shifts of 0° and 180° ; (c) signals of phase shifts of $0^\circ, 90^\circ, 180^\circ,$ and 270° .

of 300 V (rms). From panels a to c of Figure 2, the pattern actuation was as follows (anticlockwise starting with the left bottom electrode pad): voltage-ground-voltage-ground (phase-shifted signals of $0^\circ-180^\circ-0^\circ-180^\circ$ and $0^\circ-90^\circ-180^\circ-270^\circ$, respectively). A small distortion from a circular axisymmetric shape was observed in all cases consistent with a spreading along the spiral structure, with the closest approximation to axisymmetry occurring for the four-phase approach (Figure 2c). Moreover, only the four-phase-shifted signal approach provided full spreading of the droplet into the film.

We now focus on experiments using only the four-phase actuation method. In these experiments, the initial side profile shape of our deposited droplets before application of a voltage is slightly deformed from a circular arc. This is consistent with expectation given the capillary length for glycerol $\kappa^{-1} = (\gamma_{\text{LV}}/\rho g)^{1/2} = 2.3 \text{ mm}$, where γ_{LV} is the surface tension, ρ the density, and g the acceleration due to gravity, and our droplets have an initial (zero applied voltage) contact radius of $r_0 \sim 1.15 \text{ mm}$ resulting in a ratio $r_0/\kappa^{-1} \sim 0.5$. Nonetheless, the contact angle at the contact line is independent of shape and, taking the droplet shown in Figure 3 on a $d = 100 \mu\text{m}$ electrode pattern as

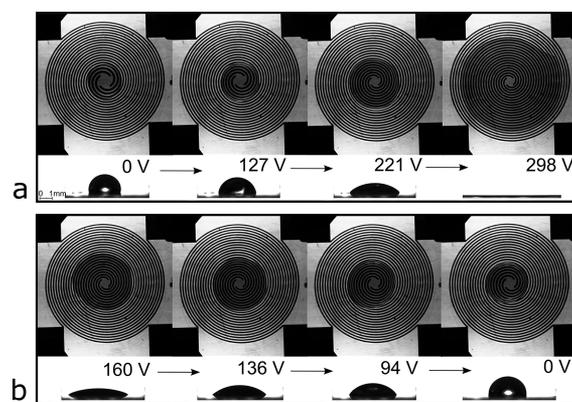


Figure 3. Top and side view images of a droplet of glycerol on spiral electrode pattern of width and gap spacing of $d = 100 \mu\text{m}$ showing the effect of (a) increasing and (b) decreasing voltage (rms).

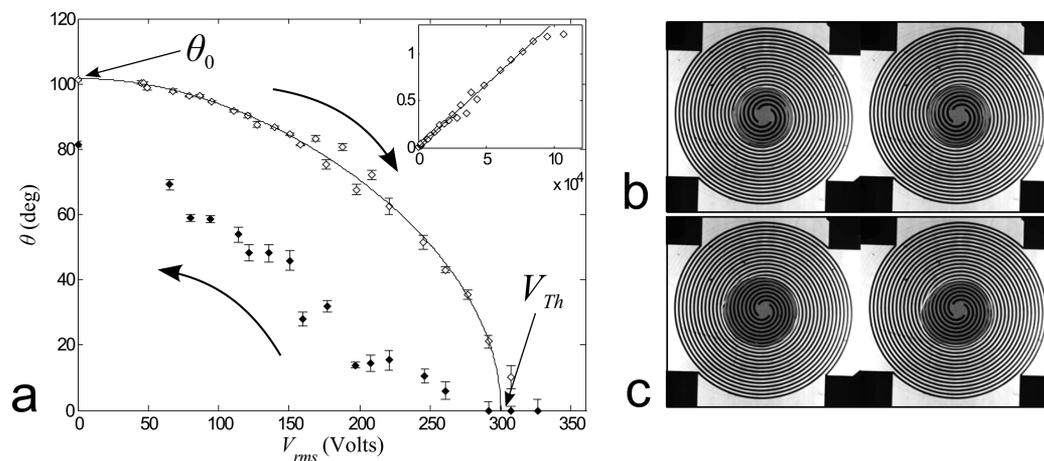


Figure 4. (a) Contact angle–voltage relationship. Open and filled circles represent the increasing and decreasing voltage half-cycles, respectively. The height of the droplet goes from 1.52 to 0.08 mm with the increasing voltage half-cycle (Figure S2). Inset: data plotted as $\Delta \cos \theta = \cos \theta(V_{\text{rms}}) - \cos \theta(0)$ versus V_{rms}^2 . The solid line is the fit using data with contact angles above 20° . (b) Two consecutive top view images of a droplet during the increasing voltage half-cycle showing the smooth change in shape. (c) Two consecutive top view images of a droplet during decreasing voltage half-cycle showing discontinuous jumps as the droplet retracts.

a typical example, it was found to be $\theta(V=0) = 102.0 \pm 0.7^\circ$. Viewed from above, at zero voltage the droplet shows a circular outline indicating a good initial axisymmetry. When the voltage is increased, the liquid is driven along the spiral electrodes resulting in an increased contact radius. The initial movement looks like a slight adjustment of the side view profile of the droplet with the contact angle falling from 102° to 90° . From the top view, the contact line motion along the spiral is visible and this gives a distortion of the axisymmetry related to the spatial resolution of the electrode pattern defined by the size of the electrode width and gap. With increasing voltage, the droplet continues a spreading motion along the spiral toward the edges of the electrode pattern. This spreading increases the contact diameter while reducing the vertical height of the droplet. When observed from the side profile, the contact angle of the droplet decreases. Eventually the voltage causes the droplet to fully spread into a film that appears to retain an almost circular shape when viewed from above. This reduction in observed contact angle continues to angles well below the saturated contact angle usually observed in electrowetting. However, as the contact angle reduces to less than $\sim 15^\circ$ – 20° , the thin spreading film of liquid appears to retain a finite contact angle localized at the edge of the film.^{31,32} This general spreading behavior with applied voltage was observed in all experiments on all electrode patterns irrespective of the precise value of the spiral width and gap d .

Figure 4 shows both an increasing voltage half-cycle and a decreasing voltage half-cycle for a droplet on a $d = 100 \mu\text{m}$ electrode pattern plotted using the root-mean-square voltage, V_{rms} ; dielectrowetting can achieve contact angles well below the electrowetting saturation minimum as evident in these data. The top view droplet shape changes are smooth for the increasing voltage half-cycle, but involve jumps during the decreasing voltage half-cycle as the droplet retracts (Figure 4b,c). The solid curve is a fit to a quadratic voltage dependence of $\cos \theta$ during the increasing voltage half-cycle for contact angles above 20° ; this is shown by the inset in Figure 4a. The initial data point before the voltage was applied lies above the trend of the decreasing contact angle with the increasing voltage. This is likely to be due to the deposition method of the droplet and the initial contact angle being defined by contact

angle hysteresis.⁴¹ A similar effect is visible when the voltage is changed from increasing to decreasing and the contact angle changed from a receding contact angle to an advancing contact angle. Eventually as the voltage is removed entirely, the droplet regains a circular shape when viewed from above and achieves a contact angle of $\sim 80^\circ$. An example of droplet spreading for repeated voltage cycles is shown in the Supporting Information (Figure S3). In the remainder of this section, we focus on the changes in contact angle as the voltage increases during the first applied half-cycle, which were always observed to be smooth changes in droplet shape.

The experimentally observed quadratic dependence on voltage, V_{rms} , of $\Delta \cos \theta(V_{\text{rms}}) = \cos \theta(V_{\text{rms}}) - \cos \theta(0)$ in the inset in Figure 4, is consistent with theoretical expectations both from electrowetting and for dielectrowetting of stripe droplets.^{30,31,36} Such a straight line relationship can be characterized by two parameters, which are usually the slope and intercept. The slope represents the strength of the effect from the electric field and for electrowetting, according to eq 1, and is determined by the ratio of the permittivity to the thickness of solid dielectric multiplied by the liquid–vapor interfacial tension, $\epsilon_o \epsilon_r / 2\gamma_{\text{LV}} d_{\text{ins}}$. In the dielectrowetting case, according to eq 2, the strength is determined by the ratio of the permittivity of the liquid minus that of air to the penetration depth of the electric field multiplied by the solid–vapor interfacial tension, $\epsilon_o(\epsilon_l - 1)/2\gamma_{\text{LV}}\delta$. Thus, the slope represents the change of stored capacitive energy (electrowetting) or dielectrophoretic energy (dielectrowetting) to the solid–liquid interfacial energy.

For the case of straight planar parallel interdigitated electrodes the penetration depth scales with the periodicity of the electrodes, for equal width electrodes to gaps both of size d , and so gives $\epsilon_o(\epsilon_l - 1)/2\gamma_{\text{LV}}\delta \propto \epsilon_o(\epsilon_l - 1)/2\gamma_{\text{LV}}d$.³⁰ Thus, in both cases, the strength of the voltage-induced effect has an inverse dependence on the size either of the insulator thickness, d_{ins} , or the electrode gap, d . In both cases, the intercept for the straight line plot for $\cos \theta(V_{\text{rms}})$ is given by the cosine of the initial contact angle, $\cos \theta(0)$, prior to application of a voltage. However, when analyzing plots of the type of Figure 4, it is convenient to use a parameter, V_{Th} , representing the threshold voltage at which the contact angle would vanish, i.e., $\cos \theta(V_{\text{Th}})$

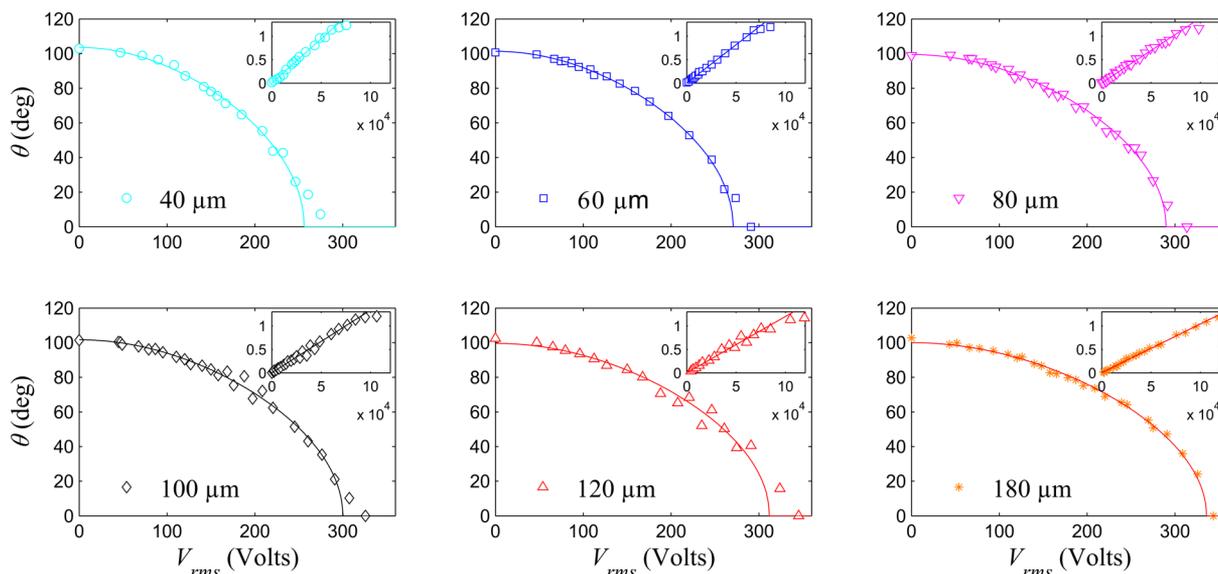


Figure 5. Contact angle–voltage relationship for the increasing voltage half-cycles for all electrode sizes ($d = 40, 60, 80, 100, 120,$ and $180 \mu\text{m}$). Inset: data plotted as $\Delta \cos \theta = \cos \theta(V_{\text{rms}}) - \cos \theta(0)$ versus V_{rms}^2 . The solid lines are fits using data with contact angles above 20° .

Table 1. Controlling Experimental Parameters (θ_0 and V_{Th}) and Parameters ($\cos \theta_0$ and $(1 - \cos \theta_0)/V_{\text{Th}}^2$) Deduced from Data in Figure 5

d (μm)	θ_0 (deg)	V_{Th} (V)	$\cos \theta_0$	$(1 - \cos \theta_0)/V_{\text{Th}}^2$
40	103.6 ± 2.2	256.0 ± 1.9	-0.235 ± 0.037	$(1.88 \pm 0.06) \times 10^{-5}$
60	101.3 ± 1.2	270.7 ± 1.8	-0.196 ± 0.021	$(1.63 \pm 0.04) \times 10^{-5}$
80	99.4 ± 1.7	289.8 ± 0.9	-0.163 ± 0.029	$(1.39 \pm 0.04) \times 10^{-5}$
100	101.7 ± 1.7	300.1 ± 1.0	-0.203 ± 0.029	$(1.34 \pm 0.03) \times 10^{-5}$
120	99.6 ± 1.5	312 ± 1.2	-0.167 ± 0.026	$(1.20 \pm 0.02) \times 10^{-5}$
180	100.0 ± 1.1	336 ± 1.5	-0.174 ± 0.019	$(1.04 \pm 0.02) \times 10^{-5}$

= 1, rather than the slope, together with the cosine of the initial contact angle, $\cos \theta(0)$.³¹ In this notation the slope is defined as $(1 - \cos \theta_0)/V_{\text{Th}}^2$, where θ_0 is defined by $\cos \theta_0 = \cos \theta(V_{\text{rms}}=0)$. The similarity between eqs 1 and 2 can then be seen as experimental results for both electrowetting and dielectrowetting and can be analyzed using an equation with similar format,³¹ the derivation of eq 3 is provided in the Supporting Information.

$$\cos \theta(V_{\text{rms}}) = \cos \theta_0 + (1 - \cos \theta_0) \left(\frac{V_{\text{rms}}}{V_{\text{Th}}} \right)^2 \quad (3)$$

This allows an experimental test of the quadratic dependence on V_{rms} of $\cos \theta(V_{\text{rms}})$ and a determination of the strength of the voltage-induced effect, $(1 - \cos \theta_0)/V_{\text{Th}}^2$ via its dependence on two controlling parameters θ_0 and V_{Th} .

To test the validity of eq 3 for the four-phase activation of our spiral electrode pattern designs, Figure 5 plots the full set of results for all spiral electrode pattern sizes $d = 40\text{--}180 \mu\text{m}$. In each case, the inset plots $\Delta \cos \theta = \cos \theta(V_{\text{rms}}) - \cos \theta_0$ as a function of V_{rms}^2 , and therefore tests its linearity. In each case, the linear fit has been taken over all data points above $\theta = 20^\circ$ and these fits are then displayed as the solid curves in the main figure in each panel.

The controlling experimental parameters for these experiments on the spiral electrode pattern design and the parameters deduced from the experiments are summarized in Table 1.

Figure 6 shows that the dependence (log base 10) of the slopes in the insets in Figure 5, i.e., $\log((1 - \cos \theta_0)/V_{\text{Th}}^2)$, on

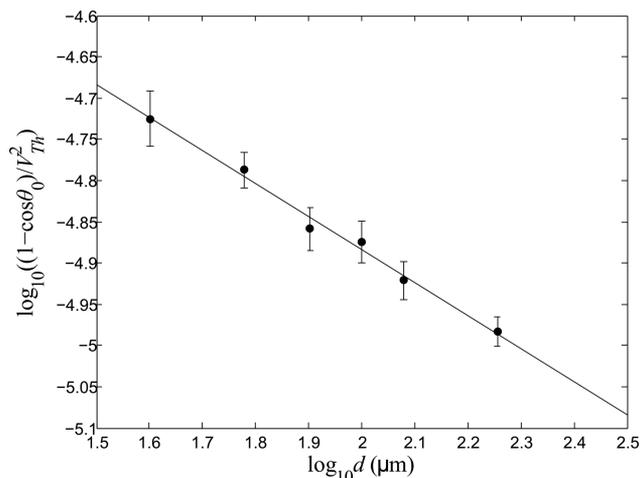


Figure 6. Experimentally determined dependence of $\log((1 - \cos \theta_0)/V_{\text{Th}}^2)$ on $\log d$.

the electrode size (log base 10), i.e., $\log d$, is linear. The best fit equation is $\log((1 - \cos \theta_0)/V_{\text{Th}}^2) = -0.400 \log d - 4.080$; the slope is obtained exactly as $-0.400 \pm 0.020 \text{ V}^{-2}$. Similarly, we observed a linear log–log behavior of the threshold voltage with a best fit relationship, $\log V_{\text{Th}} = 0.185 \log d + 2.110$. Thus, all our data, shown in Figure 5, can be scaled using a dependence on $V_{\text{rms}}^2/d^{0.400}$ as shown in Figure 7. Plots of the contact angle–voltage relationship and $\Delta \cos \theta = \cos \theta(V_{\text{rms}}) -$

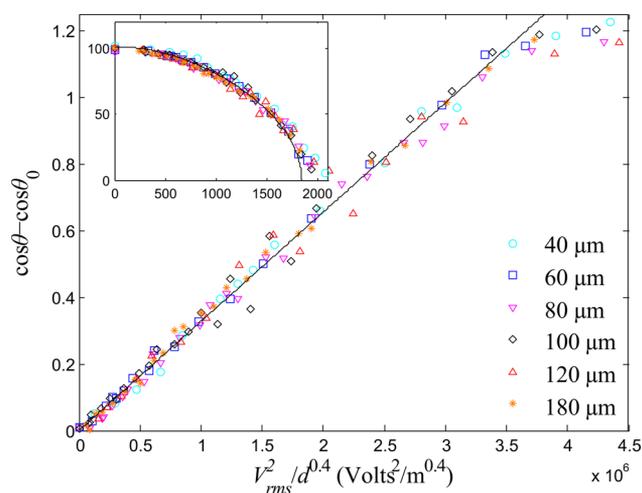


Figure 7. Data plotted as $\Delta \cos \theta = \cos \theta(V_{\text{rms}}) - \cos \theta(0)$ versus $V_{\text{rms}}^2/d^{0.4}$, scaled on the master curve. Inset: Scaled contact angle–voltage dependence.

$\cos \theta(0)$ versus V_{rms}^2 together with the scaled data are provided in the [Supporting Information](#) (Figure S4a,b, respectively).

In these experiments, the scaling of the strength of the dielectrowetting with electrode size is $\sim 1/d^{0.4}$. Thus, the strength of the dielectrowetting effect on droplets using the four-phase activated spiral electrode pattern size differs from the $1/d$ scaling of stripe droplets previously observed using the straight interdigitated electrodes.^{30,31} In dimensional terms, eqs 2 and 3 suggest there must be additional physical dependence which would scale as $1/d^{0.6}$ influencing the strength of the dielectrowetting. In these spiral electrode pattern designs, the most obvious physical parameter would be related to the length of the spiral contacted by the liquid. This lays the experimental basis for future theoretical calculations to clarify the relationship between electrode pattern design and actuation, and the resulting electric field distribution and its influence on the total energy of a droplet including interfacial energies. We believe that our demonstration of the possibility of removing the stripe limitation in dielectrowetting may inspire other types of electrode designs and alternative approaches to achieve axisymmetric droplet spreading using dielectrowetting to be developed in the future. More generally, it is interesting that dielectrowetting, which manipulates the dipoles of a dielectric liquid, can achieve low contact angles and film states, but electrowetting, which manipulates the electrical charges of a conducting liquid, cannot. This may help in understanding the origin of such saturation effects in electrowetting.^{11,23}

4. CONCLUSION

Our experiments show that it is possible to spread a droplet of an isotropic dielectric liquid in a near axisymmetric manner by using spiral electrodes and four-phase electric signals with successive 90° phase shifts. The results also show how liquid dielectrophoresis can be used to reduce the contact angle of a droplet in a voltage-controlled manner without needing to contact the droplet directly. The results also show that it is possible to obtain a sequence of partial wetting states concluding with a film state, which it has not been possible to observe in literature studies on electrowetting. The ability to control the contact angle by dielectrowetting has significance for processes such as droplet-based microfluidics,⁴² lab-on-a-chip systems,⁸ liquid-based optics,^{16,17,36} coating, and other

processes where enhanced or controlled spreading are desired. It is also relevant for any process involving control of films, such as in inking and painting where controlled spreading of droplets may be beneficial, or in high speed coating involving forced wetting⁴³ where increasing the wetting delays the beginning of bubble entrainment.^{44,45} Finally, it is possible that dielectrowetting could be combined with superoleophobicity to control nonaqueous droplets in air across the full contact angle range, keeping the near axisymmetric circular shape of the droplet when viewed from above that is essential for developing dielectric liquid lenses.^{26,36}

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the [ACS Publications website](#) at DOI: [10.1021/acs.langmuir.6b03010](https://doi.org/10.1021/acs.langmuir.6b03010).

Details about the actuation of the electrode array, maximum droplet thickness, repeated cycles, contact angle–voltage behavior, and threshold voltage format electrowetting/dielectrowetting equation (PDF)

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Notes

The authors declare no competing financial interest.

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