Electrowetting with Electrolytes

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A theory of electrowetting is developed for systems containing an interface between two immiscible electrolytic solutions. Laws for the dependence of contact angle on electrode potential are presented. Ionic impermeability of the liquid-liquid interface and nonlinear double-layer responses rationalize observed phenomena such as contact-angle saturation and droplet contraction or detachment. The theoretical results can be applied to design new, precisely controllable microfluidic devices.

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The effect of electric fields on the wetting of solids, called electrowetting, has been studied since the earliest investigations of electrocapillarity [1]. Today this area has rejuvenated: it pertains to developing technologies such as variable-focus lenses, microfluidic devices, and electronic paper [2–4]. Promising applications of electrowetting inspire current experiment and theory [5–10].

Typically, the dependence of contact angle on potential is approximated by quadratic laws,

\[ \cos \alpha_c = \cos \alpha^0_c + \frac{1}{2} B \Phi_0^2, \]  

which follow from the Gibbs adsorption isotherm [1]. Here \( \alpha_c \) is the (internal) contact angle of the droplet with the electrode, \( \alpha^0_c \) is the angle at zero voltage, \( B \) is an effective specific capacitance per unit surface tension, and \( \Phi_0 \) is the potential relative to a reference electrode in the medium surrounding the droplet. There are expressions for \( B \) when the droplet and surroundings are insulators, when the droplet is perfectly conductive, and in both of these situations with an insulating substrate [6]. The laws hold at small potential, but do not capture the saturation to a limiting angle observed at large potential [10–13].

Recently a new configuration, in which the droplet and its surrounding medium contain mutually immiscible electrolytes [16,17], has gathered attention [14,15]. Interfaces between two immiscible electrolytic solutions (ITIES) are used for biomimetics, catalysis, surface cleaning, and assembly of nanoparticle arrays [16,17]. ITIES are well suited for electrowetting: interfacial capacitances can be tuned independently by adjusting electrolyte concentrations; potentials can be varied widely and electrochemically controlled. This allows detailed characterization of droplet contraction or detachment (dewetting), effects also observed in similar systems [18,19].

Electrowetting with ITIES was described at small potentials in Ref. [20], which gives an expression for \( B \). Here we establish the contact-angle law for a broader potential range. The augmented theory describes contact-angle saturation and dewetting, setting a framework for experimental study of this novel configuration.

This Letter considers a single liquid droplet (phase \( d \)), which rests on a planar, conductive electrode (phase \( e \)), and is surrounded by an immiscible liquid (phase \( s \)), as shown in Fig. 1. Binary salts are dissolved in each liquid. The salts share no ions and each is immiscible in the adjacent phase, making the boundary between \( d \) and \( s \) an ITIES. The volume of phase \( s \) and the electrode separations are assumed large compared to the droplet; buoyancy is neglected. We seek the dependence of the contact angle, \( \alpha_c \), on the potential read by the voltmeter, \( \Phi_0 \).

Free-energy functional.—The equilibrium properties of this system can be derived from its Gibbs free energy,

\[ G = \sum_{j=d,s} \int \left[ F \sum_{i=+,\cdot} \frac{Z_{ji}}{2} \left( \frac{\Phi - \Phi^0_j}{F} - \frac{\epsilon_0 \sigma_j}{2} |E|^2 \right) + \frac{RT}{2} \sum_{i=+,\cdot} \left( c_{ji} \ln \frac{c_{ji}}{c_{ji}^{\text{ref}}} - c_{ji} + c_{ji}^{\text{ref}} \right) \right] dV + \sum_{j=d,s} p_j^{\text{ref}} V_j + A_{de} \gamma_{de} + A_{se} \gamma_{se} + A_{ds} \gamma_{ds}. \]  

where \( F \) is Faraday’s constant, \( \epsilon_0 \) the permittivity of free space, \( R \) the gas constant, and \( T \) the absolute temperature.

FIG. 1. (Left) Experimental setup. Phases \( d \) and \( s \) are immiscible electrolytic solutions. The potential drop between the working electrode (\( e \)) and the counterelectrode is controlled by a potentiostat. A voltmeter measures the potential drop from \( e \) to a reference electrode in the bulk of \( s \), which is in electrochemical equilibrium with one of the ions dissolved there. A dotted arc shows the contact angle, \( \alpha_c \). (Right) Sketch of shape change and charge accumulation with potential.
Subscripts d, s, and e denote phases, and + and − denote cations and anions, respectively. Integrals over the phase volumes $V_j$ account for electrostatic and mixing free energy. The integrand contains the potential $\Phi$ and corresponding electric field magnitude $|E|$, the dielectric constant of phase $j$, $\varepsilon_j$, and the equivalent charge $z_{ji}$ and concentration $c_{ji}$ of ion $i$ in phase $j$. Mechanical work, $p_j^\text{ref} V_j$, is included separately. Remaining terms give the capillary contribution to $G$, dependent on the areas $A_{jk}$ and surface tensions $\gamma_{jk}$ of the interfaces between phases $j$ and $k$. Lagrange multipliers constrain $G$ in each phase: $\Phi_j^\text{ref}$ and $c_{ji}^\text{ref}$, respectively, determine conservation of charge and ions; $p_j^\text{ref}$ sets pressure or volume.

Ions cannot cross the droplet boundaries. Thus the droplet interior has zero net charge and its net ion contents are fixed. The charge constraint sets $\Phi_d^\text{ref}$ and those on ion content determine $c_d^\text{ref}$ and $c_e^\text{ref}$. Electrode separation is large, allowing the surroundings to be considered semi-infinite ($\Phi_d^\text{ref} = 0$). ITIES typically involve symmetric electrolytes with equal cation charge $F$ and droplet shape yields Boltzmann distributions in the surroundings and the droplet:

$$c_z = c_s \exp \left[ \frac{zF\Phi}{RT} \right] \quad \text{and} \quad c_d = c_d \exp \left[ \frac{zF(\Phi - \Phi_d)}{RT} \right],$$

where $\Phi_\ast$ = $\Phi_d^\text{ref}$ to simplify notation. From minimization of $G$ with respect to $\Phi$ at fixed $c_{ji}$ and shape, it follows that $\Phi$ satisfies Poisson’s equation in both liquid phases. Thus each solution obeys a nonlinear Poisson-Boltzmann equation, to be solved such that droplet-electrode interface is at $\Phi_0$ and $\Phi \rightarrow 0$ in the bulk of the surroundings; at the liquid-liquid interface, continuity of potential and electric displacement matches the distributions. Then, setting the net internal droplet charge to zero yields $\Phi_\ast$.

Before the final minimization with respect to shape, it is convenient to eliminate the arbitrary area $A_{se}$, expressing $G$ relative to a system with identical electrode geometry, but with phase $s$ only, at the same $\Phi_0$. Denote the energy of this droplet-free state $G^0$ and the relative energy $\Delta G = G - G^0$. If $\Delta G > 0$, the droplet dewets.

**Controlling parameters.**—Analysis reveals that four dimensionless parameters determine equilibrium:

$$\phi_0 = \frac{zF\Phi_0}{RT}, \quad \cos\alpha_c^0 = \frac{\varepsilon_{se} - \varepsilon_{de}}{\varepsilon_{ds}}, \quad C = \sqrt{\frac{\varepsilon_s \lambda_d}{\varepsilon_e \lambda_s}}, \quad b = \frac{R^2T^2 \varepsilon_0}{z^2F} \sqrt{\frac{\varepsilon_d \varepsilon_s}{\varepsilon_e \lambda_d \lambda_s}}.$$

Here $C$ is the square root of the ratio of specific capacitances yielded by linear Gouy-Chapman theory [22,23] for interfaces between an electrode and solution d or s, $C = (C_s^{GC}/C_d^{GC})^{1/2}$; Young’s equation relates $\cos\alpha_c^0$ to the surface tensions; the effective specific capacitance per unit surface tension is proportional to $b$. Both $b$ and $C$ depend on Debye lengths, $\lambda_j \equiv (\varepsilon_0 \varepsilon_j RT / 2F^2 z_{ji}^2 c_{ji})^{1/2}$. We also use a second dimensionless potential, $\phi_\ast = zF\Phi_\ast / RT$, at which the droplet’s local charge density is zero. Thermodynamic stability requires $0 \leq \phi_\ast / \phi_0 \leq 1$.

**Large droplets.**—In experiments the droplet radius is typically larger than a few micrometers. As shown earlier [20], when the average droplet radius $r_d > 10^3 \lambda_d$, the liquid-liquid interface maintains constant potential, excepting a small region near the three-phase contact line that contributes negligibly to both $\Delta G$ and its change with shape. Also, a plateau at $\phi = \phi_\ast$ exists over most of the droplet interior. Thus the three-phase region and interfacial curvature may be neglected in the Poisson-Boltzmann equations; geometry enters the potential dependence of $\Delta G$ through surface areas $A_{se}$ and $A_{ds}$ only.

After application of the large-droplet approximation (detailed in the supplementary notes [24]), $\Delta G$ becomes

$$\Delta G = 8bA_{de}\left[ C \sinh^2 \left( \frac{1}{2} \phi_0 - \frac{1}{2} \phi_\ast \right) - \frac{1}{2} \sinh^2 \left( \frac{1}{2} \phi_0 - \frac{1}{2} \phi_\ast \right) \right] - \cos\alpha_c^0 A_{de} + \left[ 1 - 4b f(\phi_\ast, C) \right] A_{ds} + \frac{V_d}{\gamma_{ds}} \Delta \rho,$$

in which the function $f$ is defined as

$$f(\phi_\ast, C) = \left[ (C + \frac{1}{C})^2 + 4 \sinh^2 \left( \frac{1}{2} \phi_\ast \right) \right]^{1/2} - \left( C + \frac{1}{C} \right).$$

Here $\Delta \rho$, the external pressure difference between the droplet interior and the droplet-free state, remains to be set by a droplet-volume constraint. Electrostatic contributions to $\Delta G$ are scaled by $b$; the electrostatic contribution by the ITIES is also proportional to $f$.

To retrieve $\phi_\ast$, one sets the surface charges on the droplet-surroundings and droplet-electrode interfaces to be equal and opposite, yielding

$$A(\phi_\ast, \phi_0, C) = C \sinh \left( \frac{1}{2} \phi_0 \right) /\sinh \left( \frac{1}{2} \phi_0 - \frac{1}{2} \phi_\ast \right) \left[ \left( C + \frac{1}{C} \right)^2 + 4 \sinh^2 \left( \frac{1}{2} \phi_\ast \right) \right]^{1/2},$$

where $A = A_{de}/A_{ds}$ is the ratio of surface areas bounding the droplet. This relates the droplet geometry to $\phi_\ast$, making Eq. (3) a function of shape parameters only.

**Potential dependence of contact angle.**—The droplet shape is retrieved by minimization of Eq. (3) with $V_d$ fixed. This yields a Young-Laplace equation, which shows the droplet to be a truncated sphere and that $\Delta \rho = -2\gamma_{ds}(1 - 4bf)/r_d$. For a truncated sphere, $\alpha_c$ relates to the interfacial areas by

$$\cos\alpha_c = 2A(\phi_\ast, \phi_0, C) - 1.$$

As a result, $\Delta G$ in Eq. (3) becomes a simple function of the contact angle. Minimization of $\Delta G$ with $\alpha_c$ gives
At fixed applied potential, with \( f(\phi_*,C) \) given by Eq. (4) and \( A(\phi_*,\phi_0,C) \) by Eq. (5), this is an equation in the single unknown \( \phi_* \). Once \( \phi_* \) has been found from Eq. (7), \( \alpha_c \) is returned from Eqs. (5) and (6).

Equations (4)–(7) constitute our central result. These four governing relationships describe how the contact angle between an ITIES and a planar electrode, \( \alpha_c \), depends on the applied potential \( \phi_0 \). Equilibrium is determined by three system characteristics: \( b \), \( C \), and \( \alpha_c^0 \).

**Results and discussion.**—Our analysis differs from conventional electrowetting in the assumptions regarding droplet charge. Theories to date have assumed that a net charge accumulates in the droplet with applied potential [6]. But in electrowetting with an ITIES, ions cannot leave the droplet—it always maintains zero net charge. Potentials cause equal and opposite space charges inside the droplet [cf. Fig. 1]. Unusual results here owe mainly to this distinction.

Also, in other analyses the essential potential drop is often taken to occur at the droplet-electrode interface, primarily lowering interfacial energy there. This leads to a prediction of droplet spreading with rising potential. In contrast, with an ITIES, potentials can lower the interfacial energy to a similar extent at every phase boundary: droplets may spread or contract.

Differences in energy lowering at the droplet-electrode and surroundings-electrode interfaces define the direction of contact-angle variation. This is clarified in the limit of low potential, where Eq. (7) reduces to Eq. (1) [20], with \( B(b,C,\alpha_c^0) \) given by [25]

\[
B = \frac{\pi^2 F^2 b C}{R^2 T^2} \left[ \cos \alpha_c^0 (1 + \cos \alpha_c^0)^2 (1 + C^2) + 4C^2 \right] - 1. 
\]

The sign of \( B \) is determined by \( C \) and \( \alpha_c^0 \). Contraction (\( B < 0 \)) occurs whenever the surroundings have a higher Gouy-Chapman capacitance than the droplet (\( C > 1 \)). Spreading (\( B > 0 \)) is only possible when \( C < 1 \).

Also, \( \alpha_c^0 \) must be obtuse for spreading. To see why, consider separately the capillary and electrostatic contributions to \( \Delta G \). Capillary energy is minimal at \( \alpha_c^0 \). Electrostatic energy is minimal at the angle which maximizes overall capacitance. Minimal \( \Delta G \) is realized at an angle between these two minima. If \( C > 1 \), the electrostatic minimum is at \( \alpha_c = 180^\circ \) (dewetting) because the surroundings have a higher specific capacitance than the droplet interior. Thus, applied potentials always cause contraction. But if \( C < 1 \), the electrostatic minimum lies at \( 0 < \alpha_c < 180^\circ \) (partial wetting), because net droplet electroneutrality inhibits the space-charge accumulation within it as it spreads. When \( C < 1 \), the capacitance-maximizing angle is smaller than \( \alpha_c^0 \) only if \( \alpha_c^0 > 130^\circ \).

The theory also rationalizes a more extreme effect—dewetting of droplets at high potential. For \( C > 1 \) there is a limiting potential above which no physical solution to Eq. (7) exists. If the potential exceeds \( \phi_0^{\text{max}}(b,C,\alpha_c^0) \),

\[
\phi_0^{\text{max}} = 2\cosh^{-1}\left[ 1 + \frac{C(1 + \cos \alpha_c^0)}{4b(C^2 - 1)} \right], \quad C > 1, \quad \alpha_c^0 > 130^\circ. 
\]

The free-energy minimum lies above the accessible range of contact angles and the droplet dewets. This follows from Eq. (7) because \( \phi_* \to 0 \) as \( \alpha_c \to 180^\circ \) (\( A \to 0 \)). When \( C \leq 1 \) the droplet remains at the surface, in the regime of partial wetting, at all applied potentials; the contact angle in these cases saturates toward dewetting.

Figure 2 compares three results yielded by Eqs. (4)–(7) to the small-potential approximations provided by Eqs. (1) and (8). Each was calculated with \( b = 0.005 \), corresponding to a nitrobenzene-water ITIES with 0.01M solutions. Figure 2(a) shows two cases with \( \cos \alpha_c^0 = 0 \), typical of conductive substrates. Contraction occurs for both \( C = 0.817 \), representing an aqueous droplet, and \( C = 1.225 \), an organic droplet. The former approaches dewetting asymptotically and the latter dewets as predicted by Eq. (9). Departures from linearity are already clear above \( \phi_0 = 3 \) (~80 mV at room temperature). Figure 2(b) presents the surprising results for \( C = 0.5 \) and \( \cos \alpha_c^0 = -0.8 \). The nonlinear theory predicts spreading, which slows, and then reverses, as \( \phi_0 \) rises.

A striking difference between the nonlinear and linear theories appears at moderate potential. Each nonlinear
result in Fig. 2 has an inflection point—the onset of contact-angle saturation—near \( \phi_0 = 8 \) (\(-200 \text{ mV}\)). Inflection points arise because the depth of the minimum in electrostatic energy increases exponentially with \( \phi_0 \). At small \( \phi_0 \), the electrostatic and capillary contributions to \( \Delta G \) are of similar magnitude. But above a moderate value of \( \phi_0 \), determined mainly by \( b \), the electrostatic energy outweighs the capillary energy, and the tendency to maximize capacitance dominates the contact-angle response. The transition manifests as an inflection.

For all combinations of parameters, the contact-angle change with rising \( \phi_0 \) falls into one of the three categories shown on Fig. 2. Although adjusting \( b \) changes the potentials at which dewetting and inflection occur, the shapes of response curves are set primarily by \( C \) and \( \alpha_0^0 \). Figure 3 provides a phase diagram that shows the type of contact-angle response as a function of \( C \) and \( \alpha_0^0 \).

Concluding remarks.—The presented phase diagram and dependence of inflection-point positions on \( b \) both suggest qualitative experimental tests. Given a pair of solvents, one can vary \( C \) or \( b \) independently by choosing salt concentrations; one can vary \( \alpha_0^0 \) either by changing electrode materials or by adding neutral surfactants.

Several effects of lesser importance were ignored here. Experiments suggest that limited ion penetration can affect the capacitance of ITIES. But if \( c_d \) and \( c_i \) are \( \leq 0.01 M \), the assumption of an impermeable interface applies [26,27]. Buoyancy, nonidealities, thin-film forces, and dielectric breakdown were neglected, and the large-droplet approximation is unjustified when the three-phase contact line has radius less than \( \left( \lambda_d \lambda_i \right)^{1/2} \). These effects can all be added to the general functional in the supplement [24].

For electrowetting with ITIES, nonlinear double-layer charging and ionic impermeability of the liquid-liquid interface control how applied potentials lead to contact-angle saturation and droplet dewetting. The analysis presented here provides surprising predictions that can be explored in the laboratory, and, after verification, used to design microfluidic or electro-optical devices.

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