Electrowetting with Electrolytes

Charles Monroe

Imperial College London

in collaboration with
Alexei A. Kornyshev (Imperial College London)
Michael Urbakh (Tel Aviv University)

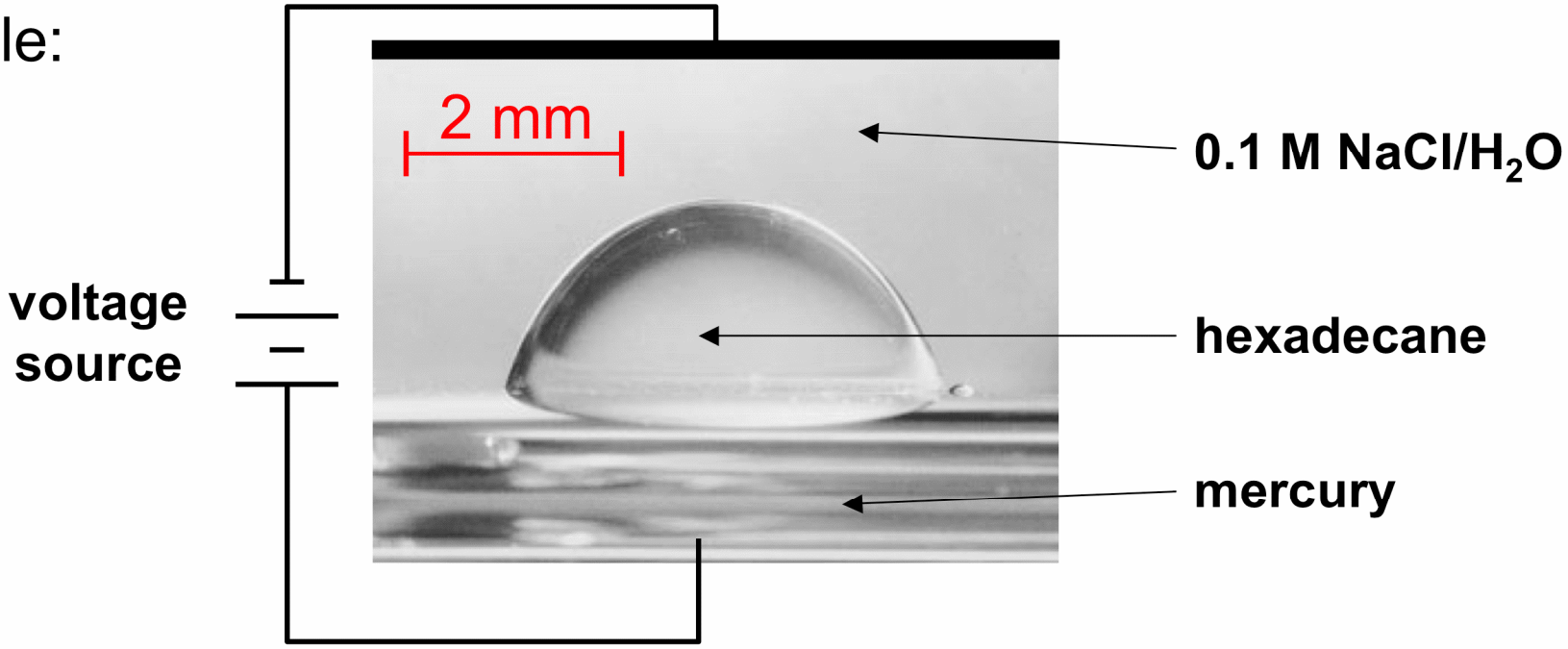
Thursday, 24 May 2007

Overview

- Electrowetting: experimental observations/applications
- Theory: physical principles of electrowetting
- Interfaces between two immiscible electrolytic solutions (ITIES)
- Small-droplet electrostatics
- Electrowetting with ITIES: predictions and experiments

The basic phenomenon

Example:



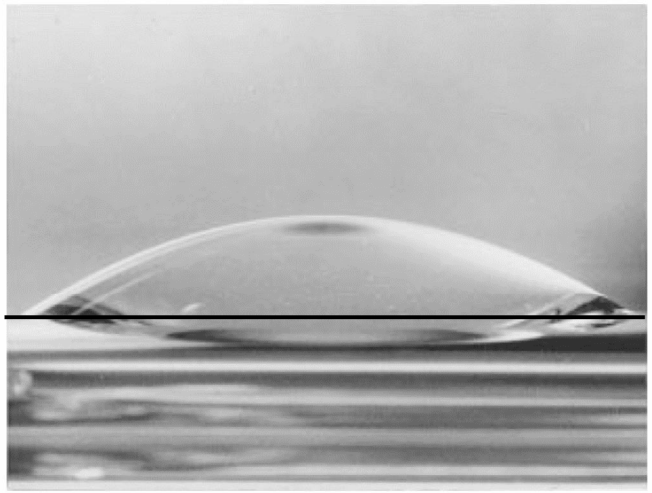
Ivosevic and Zutik, *Langmuir* **14**:1 (1998) 231

- Three phases: liquid droplet, surrounding fluid, electrode
- Electrode geometry
- Droplet shape varies with voltage

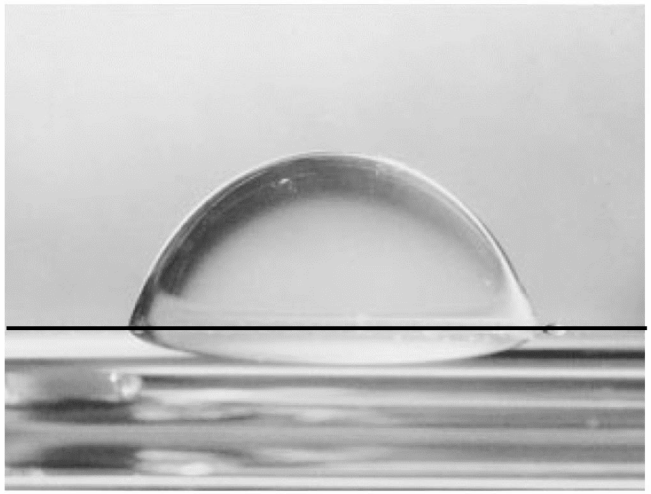
Experimental observation

potential lowers

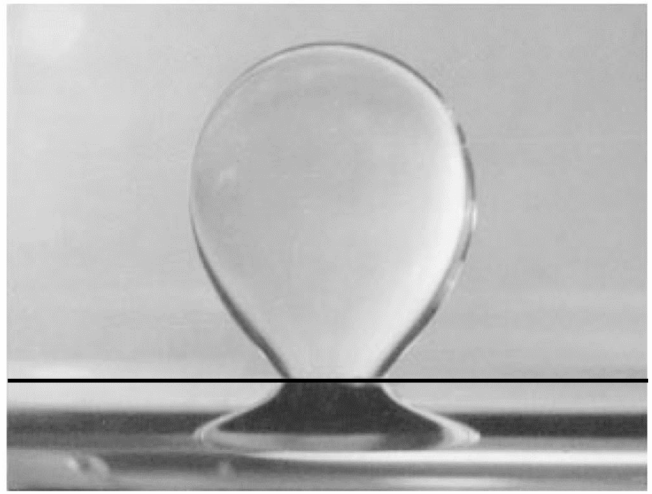
1 (OCP)



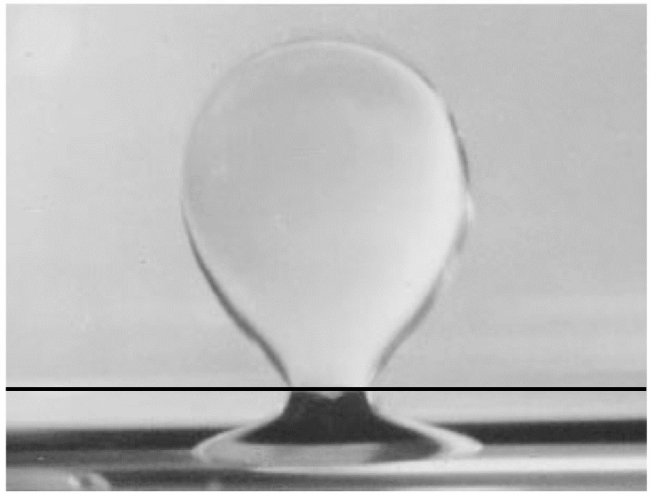
2



3



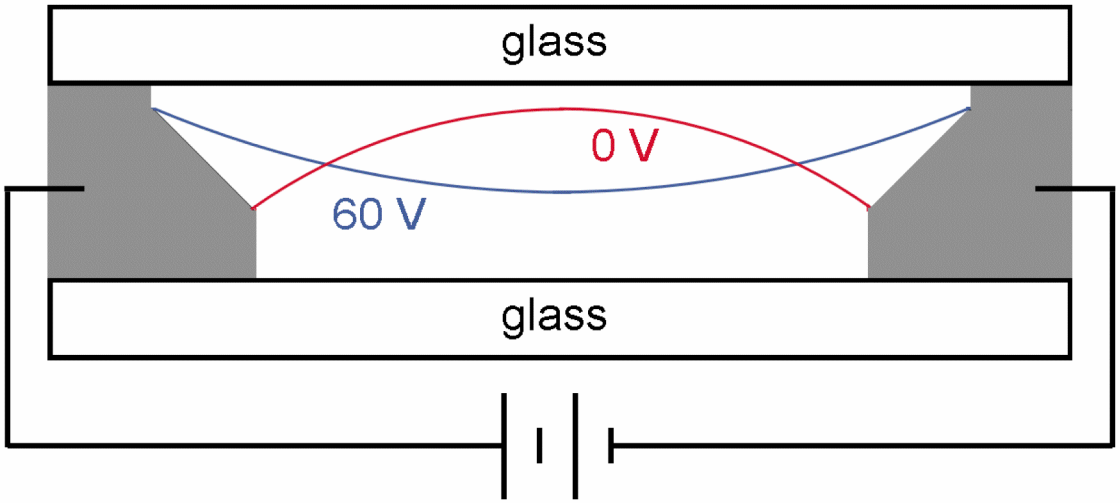
4



- Oil droplet contracts away from OCP; stays approx. spheroidal

Applications

- Liquid lenses: Varioptic (to market Jan. 2006) and Philips



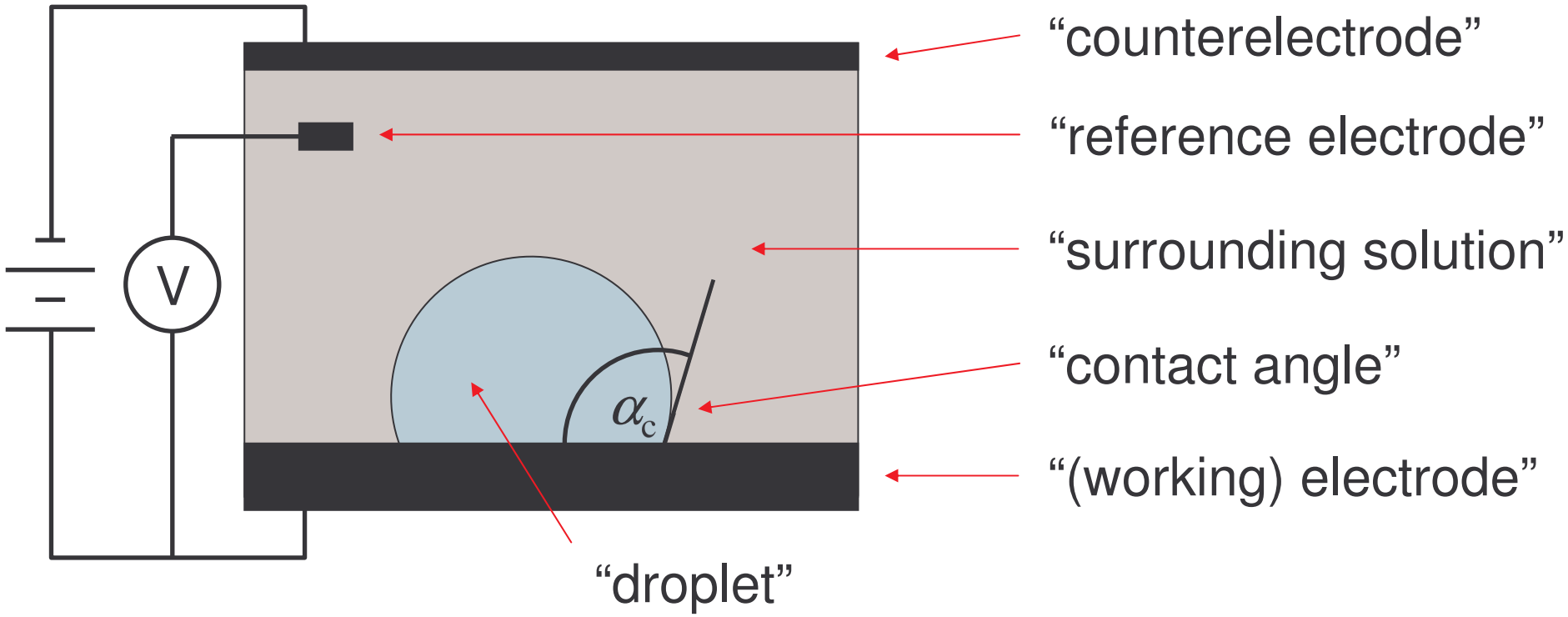
Varioptic (France) Arctic 320 data sheet, at http://www.varioptic.com/en/Arctic_320.php

- Fiber-optic switches

- Nonoptical: Microfluidic channel selection

A brief digression, and some more details

- Preliminary terminology, layout, and symbols

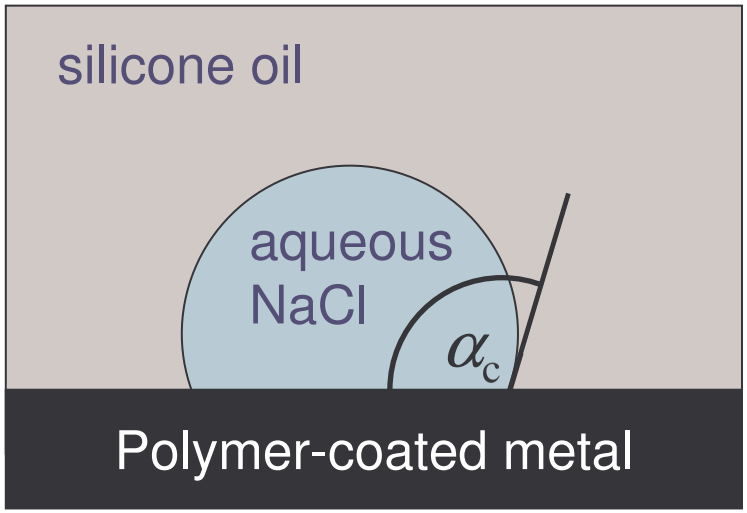


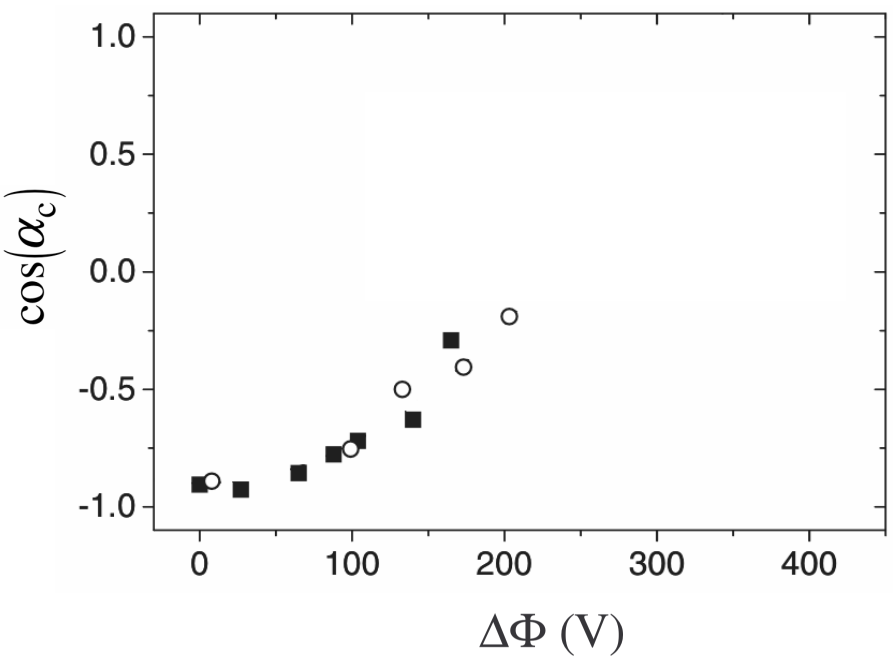
$\Delta\Phi =$ voltage drop from working to reference electrode

$\alpha_c^0 =$ contact angle at $\Delta\Phi = 0$, or "Young angle"

Observations: detailed features

- Switching oil for water leads to droplet expansion





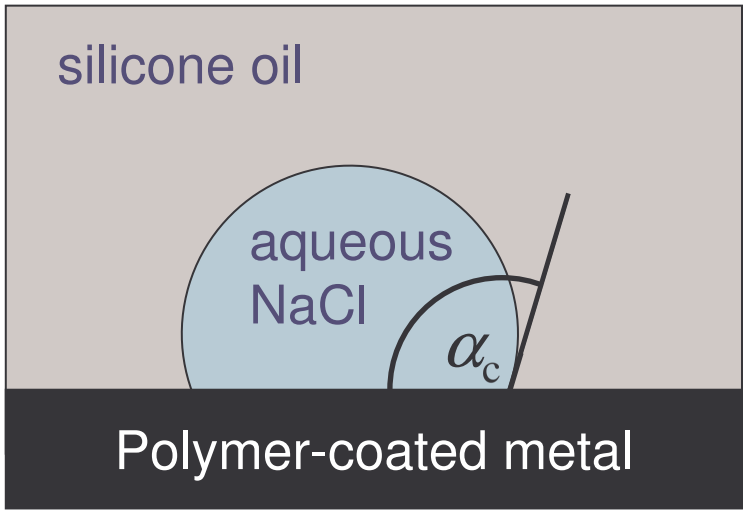
- In the low-potential limit response of contact-angle cosine is parabolic

$$\cos\alpha_c = \cos\alpha_c^0 + \tfrac{1}{2}B(\Delta\Phi)^2$$

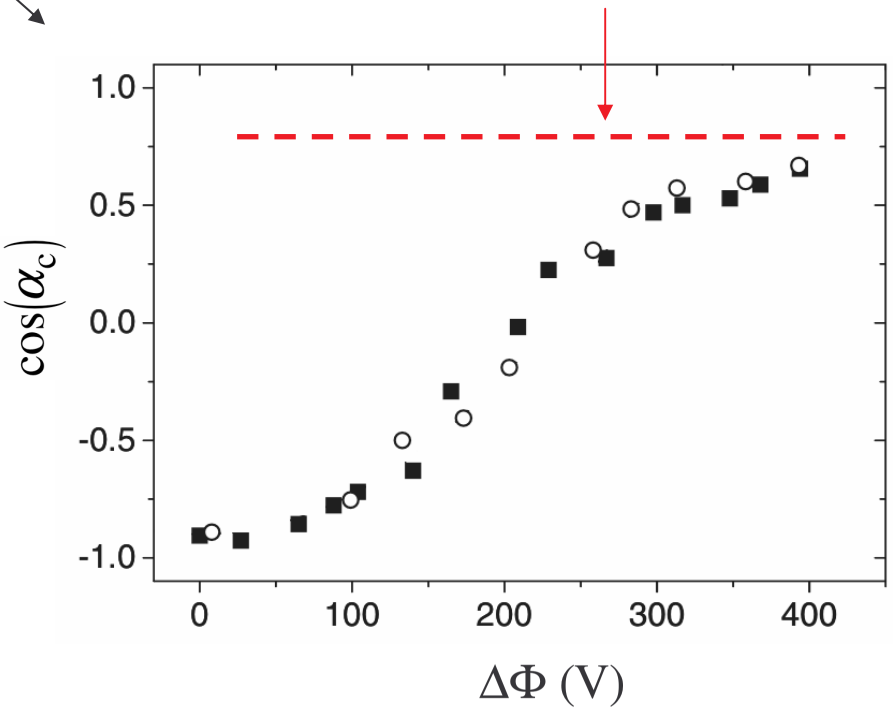
Mugele and Baret, *J. Phys. Condens. Matter* **17** (2005) R705

Observations: detailed features

- Switching oil for water leads to droplet expansion



- angle can **saturate** at large potential



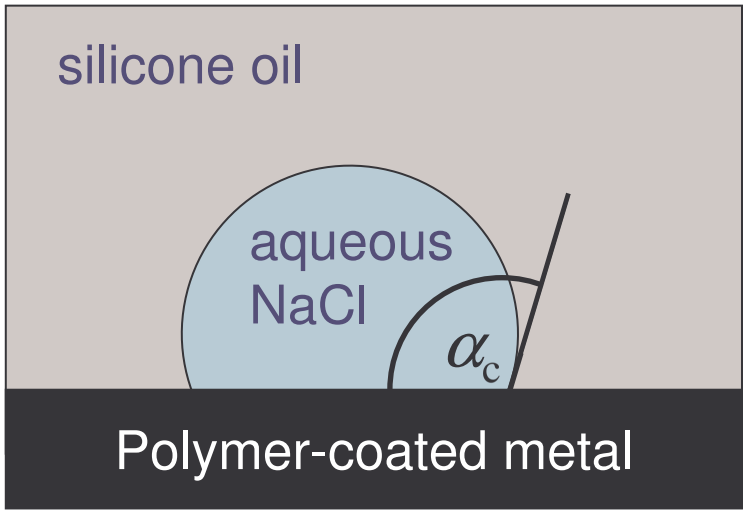
- In the low-potential limit response of contact-angle cosine is parabolic

$$\cos\alpha_c = \cos\alpha_c^0 + \tfrac{1}{2}B(\Delta\Phi)^2$$

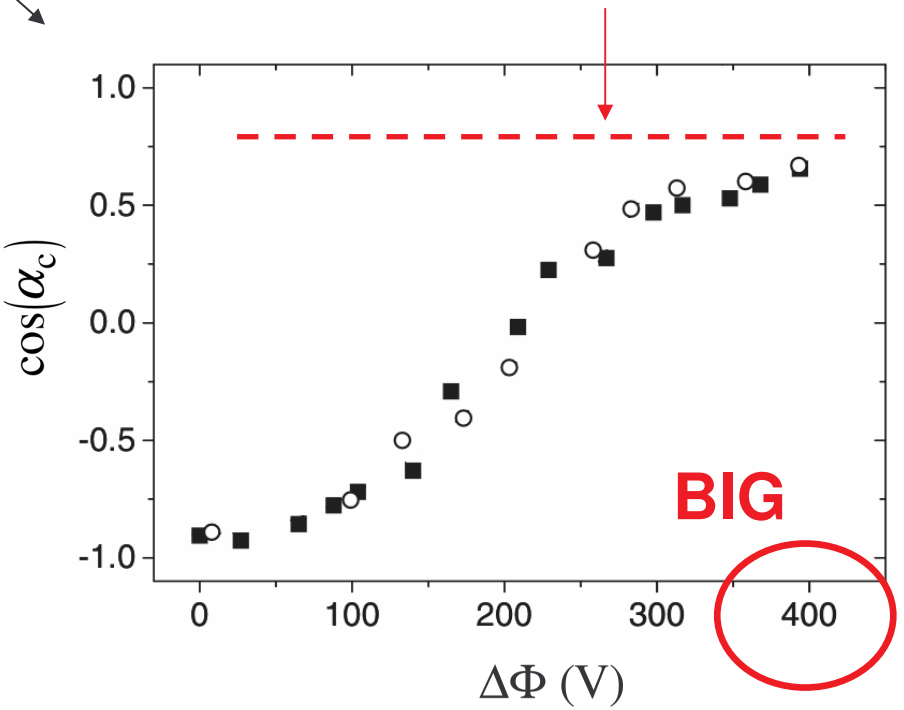
Mugele and Baret, *J. Phys. Condens. Matter* **17** (2005) R705

Observations: detailed features

- Switching oil for water leads to droplet expansion



- angle can **saturate** at large potential



Mugele and Baret, *J. Phys. Condens. Matter* **17** (2005) R705

Theoretical approach

- **Goals:**
  * What parameters control the potential response?
  * How can the voltage range of response be narrowed?
  * What about saturation?

- Shape stabilizes rapidly (~ms): *thermodynamic equilibrium*

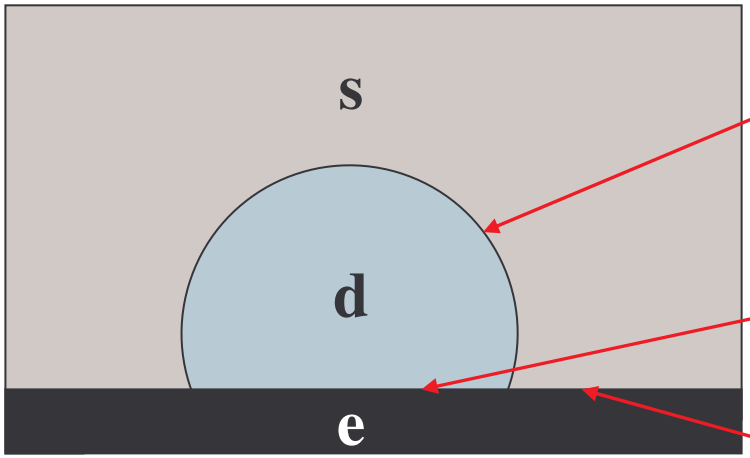
- Equilibrium is characterized by a *free-energy minimum*

- Natural treatment is through a *Lagrangian functional*, which can be minimized with respect to relevant thermodynamic variables (and with constraints), as well as with droplet shape

- But what forces contribute to the system energy?

Effect 1: Capillary action

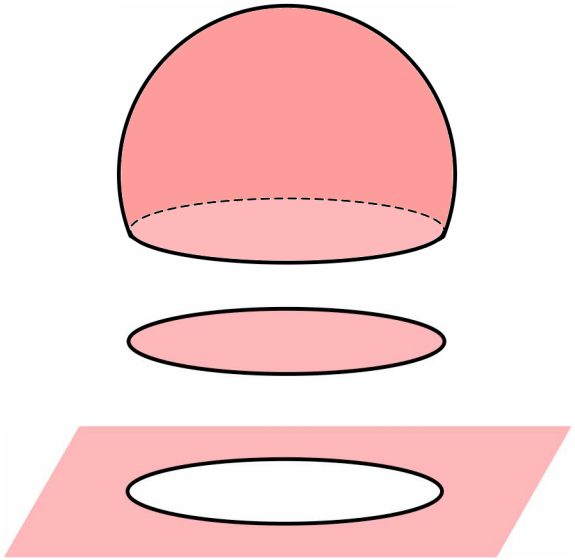
- Adhesion differs at the phase boundaries: **surface tension**



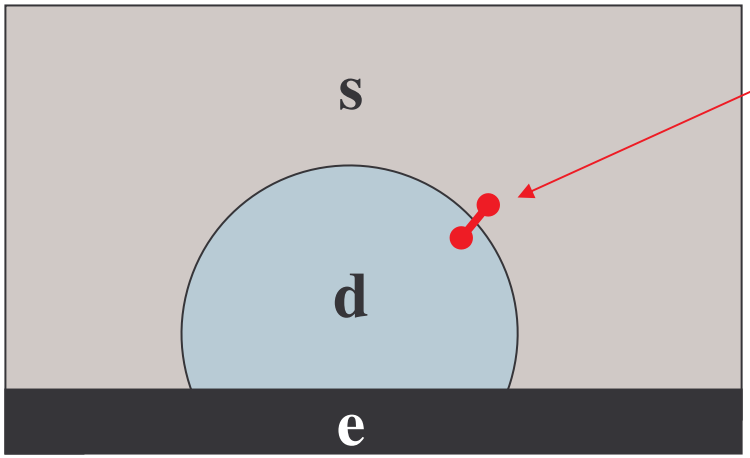
Area ds:

Area de:

Area se:



- Phases have internal cohesion, causing **mechanical force**



Pressure difference

Surface tension pushes curved interfaces:

toward no curvature:

Effect 1: Capillary action

- Euler-Lagrange formulation for small droplets

Free energy = (surface energy) + (mechanical work)

$$G = \left(\gamma_{\mathrm{de}} A_{\mathrm{de}} + \gamma_{\mathrm{se}} A_{\mathrm{se}} + \gamma_{\mathrm{ds}} A_{\mathrm{ds}}\right) + \left(V_{\mathrm{d}} \Delta p\right)$$

surface tension

area

droplet volume

Laplace pressure (multiplier)

Total electrode area fixed

$$A_{\mathrm{de}} + A_{\mathrm{se}} = \text{constant}$$

Effect 1: Capillary action

- Euler-Lagrange formulation for small droplets

Free energy = (surface energy) + (mechanical work)

$$G = \left(\gamma_{de} A_{de} + \gamma_{se} A_{se} + \gamma_{ds} A_{ds}\right) + \left(V_d \Delta p\right)$$

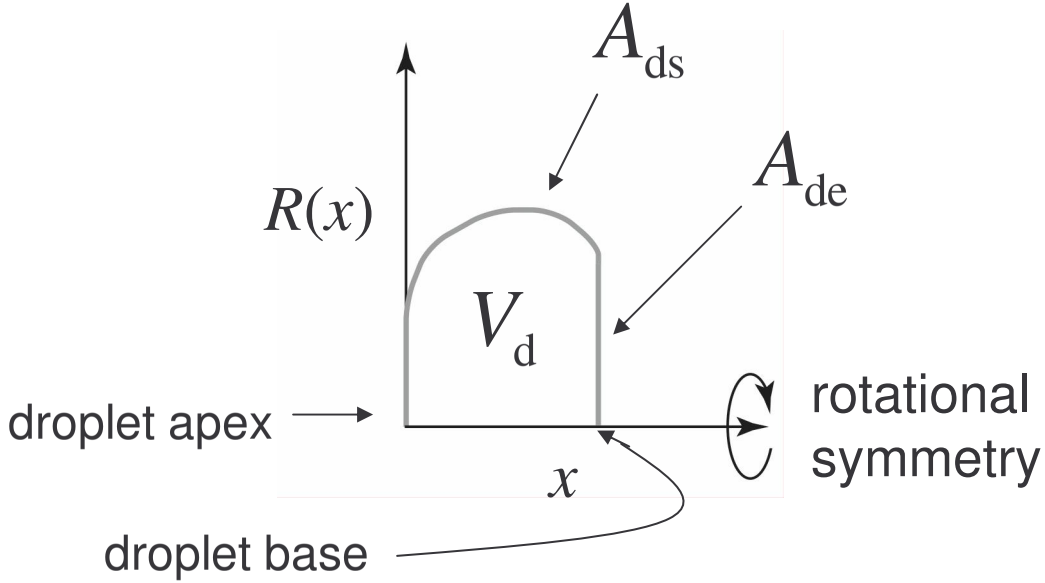
surface tension

area

droplet volume

Laplace pressure (multiplier)

- Variational minimization:



Effect 1: Capillary action

- Euler-Lagrange formula for small droplets

Free energy = (surface energy) + (mechanical work)

$$G = \left(\gamma_{\mathrm{de}} A_{\mathrm{de}} + \gamma_{\mathrm{se}} A_{\mathrm{se}} + \gamma_{\mathrm{ds}} A_{\mathrm{ds}}\right) + \left(V_{\mathrm{d}} \Delta p\right)$$

surface tension

area

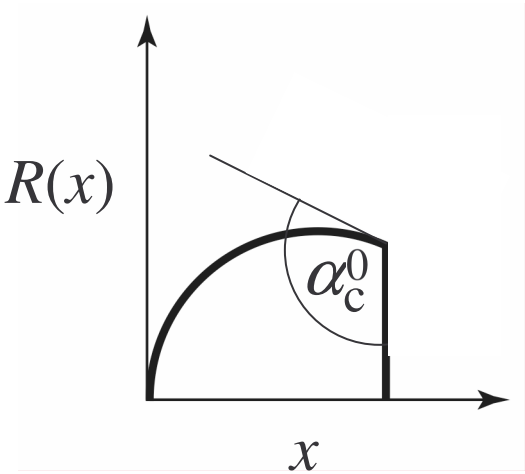
droplet volume

gauge pressure (multiplier)

- Variational minimization gives the optimal shape

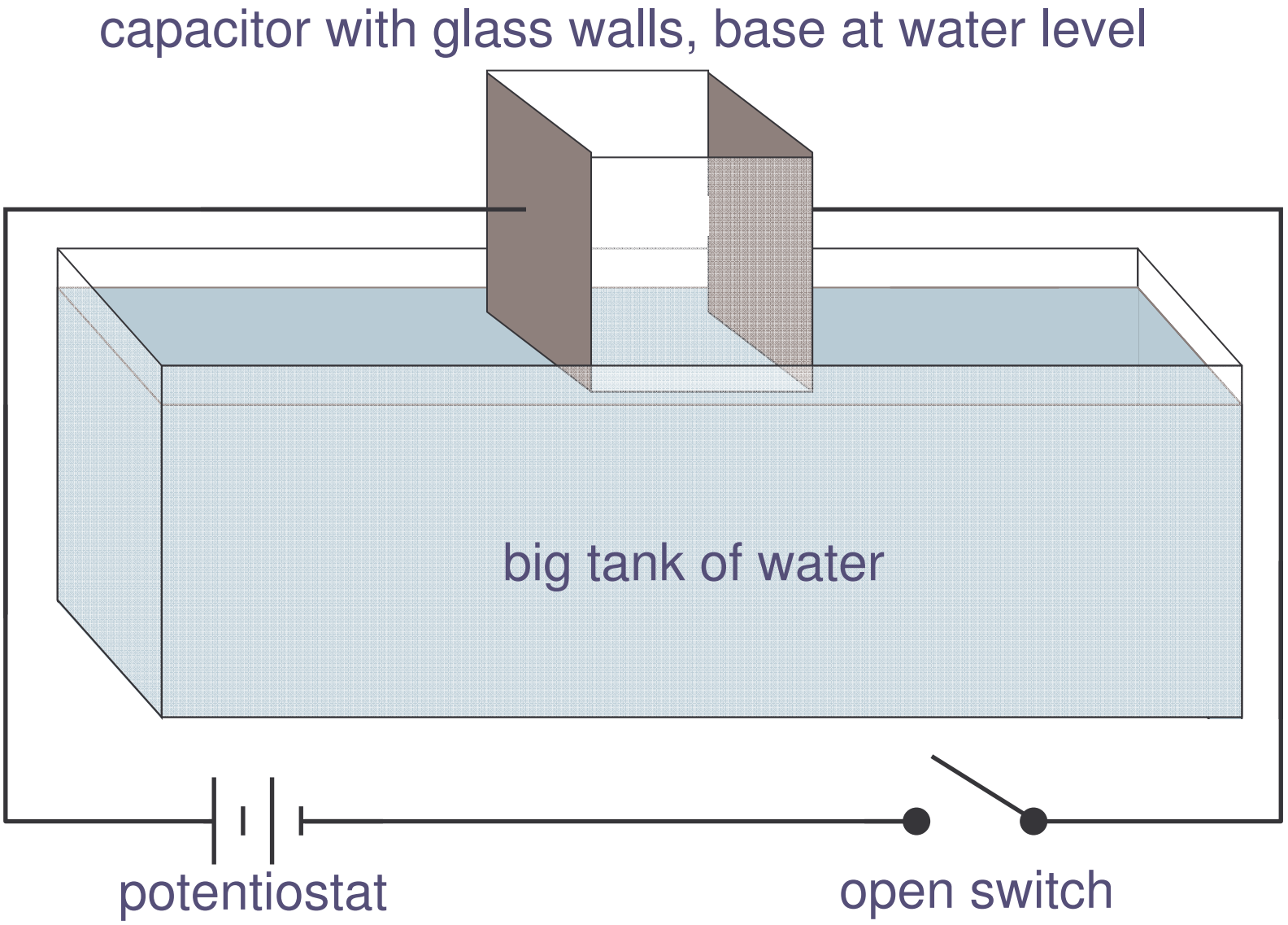
- Droplet is a *truncated sphere*

- $\cos\left(\alpha_{\mathrm{c}}^{0}\right) = \dfrac{\gamma_{\mathrm{se}} - \gamma_{\mathrm{de}}}{\gamma_{\mathrm{ds}}}$ with no voltage



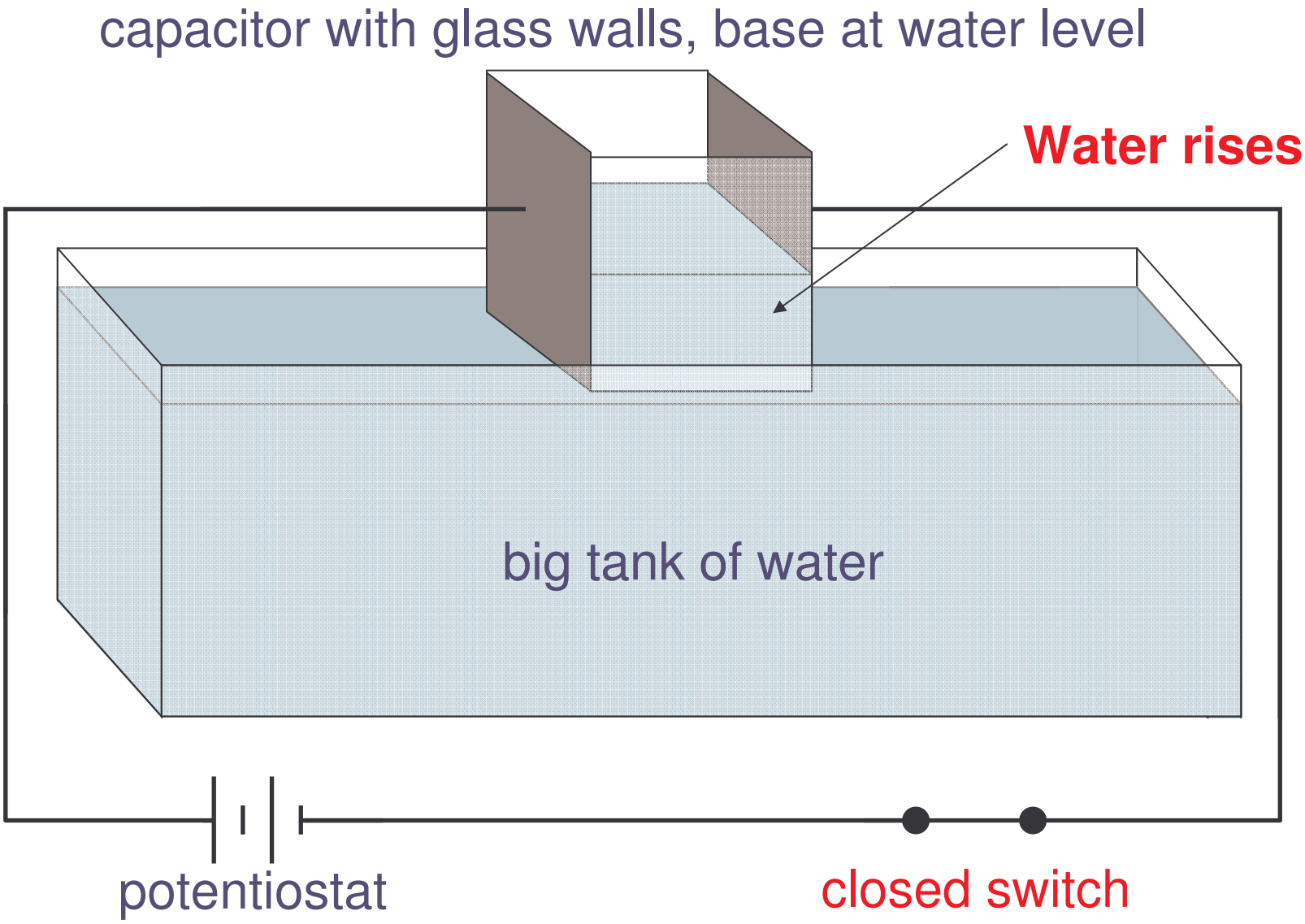
Effect 2: Dielectric suction

- Consider the following experiment (Frumkin):



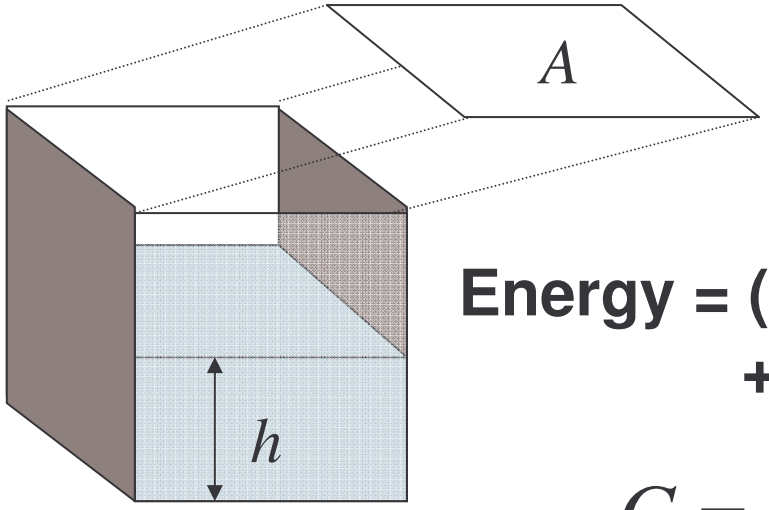
Effect 2: Dielectric suction

- Consider the following experiment (Frumkin):



Effect 2: Dielectric suction

- Frumkin's explanation is also variational in nature, and relates *shape* to *electrostatic response*



Energy = (external work by potentiostat) + (gravitational potential gain)

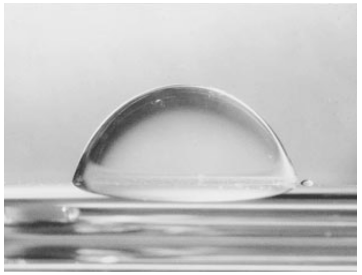
$$G = -\tfrac{1}{2} C(h) \Delta\Phi^2 + \tfrac{1}{2} \rho g A h^2$$

- Optimizing G with respect to h shows how far the water rises

- A system held at constant potential varies its internal structure to *maximize total capacitance*, subject to *mechanical constraints*

Rationalizing existing observations

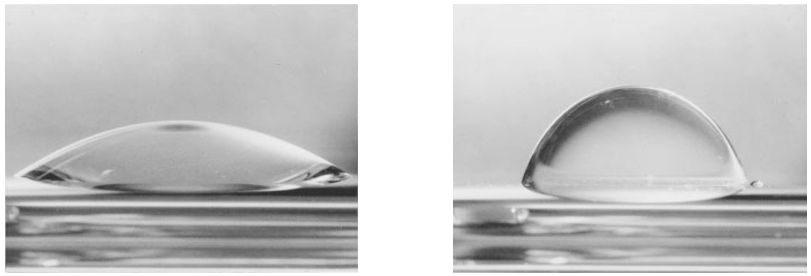
- Balance of capillary and electrostatic forces determines the electrowetting response



- Thus we see qualitatively why the shapes are like

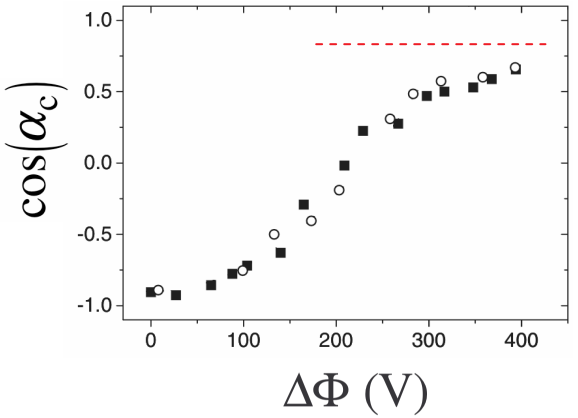
- why the potential responses are like

oil droplet in water



potential drop increases

water droplet in oil



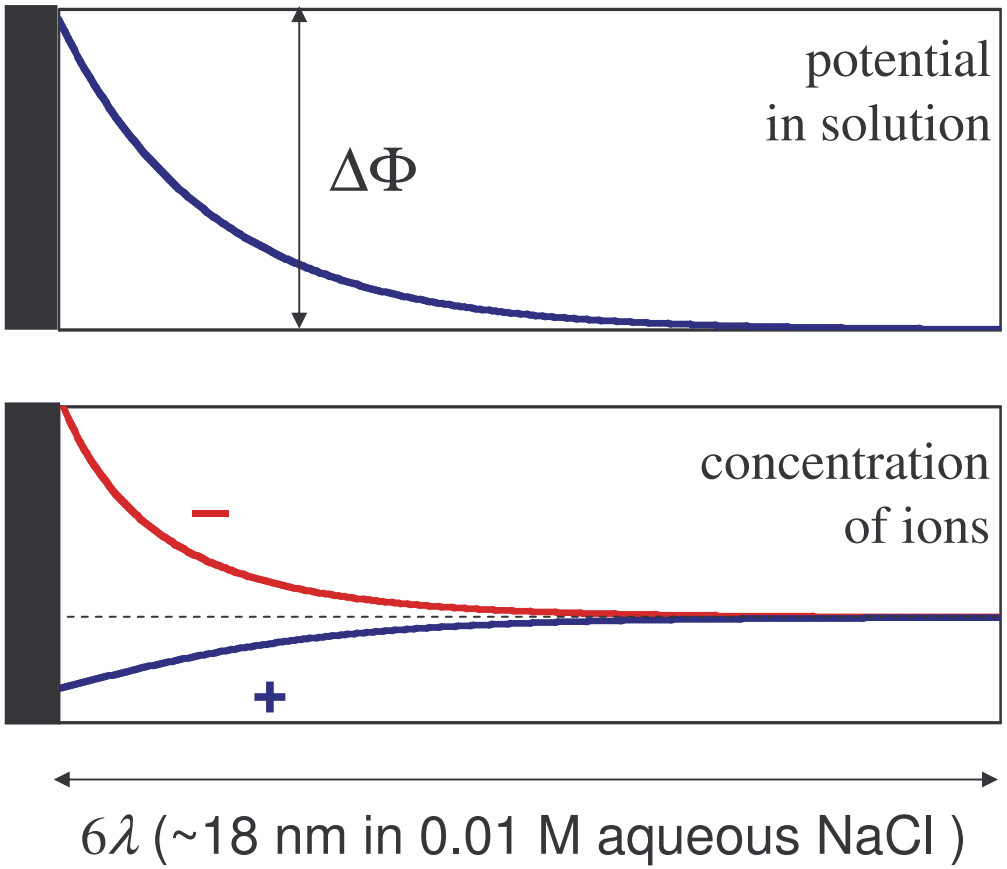
- **a sufficient variational theory might explain why**

But we also might like better control

- Higher capacitance would make shape change at lower potential
- Fields localized near the interfaces would make response less dependent on electrode geometry
- Would be better to tune capacitances without changing solvents
- All of these are achieved by **dissolving salt in both phases**

Effect 3: Charge screening/mixing

- Double layer forms in electrolyte near a polarized electrode: described by *nonlinear Poisson-Boltzmann theory*



zero-voltage
specific capacitance
(large ~0.4 F/m²)

solvent
dielectric
constant

$$\frac{C_0}{A} \propto \frac{\varepsilon}{\lambda}$$

Debye
length

$$\lambda = \sqrt{\frac{\varepsilon_0 \varepsilon RT}{2F^2 z^2 c_{avg}}}$$

(tunable)

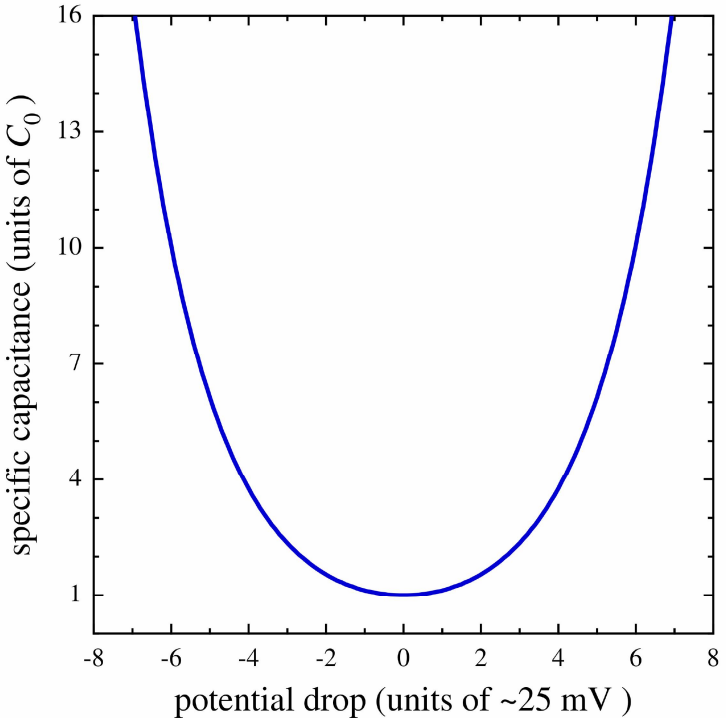
- Thermal motion (free energy of mixing) resists local charge accumulation: potential decays over a few Debye lengths

Effect 3: Charge screening/mixing

- Getting a feel for *nonlinear* double-layer capacitance

- Semi-infinite electrolytic solution contacting an equipotential plane interface (*e.g.*, a metal)

$$\frac{\text{Capacitance}}{\text{Area}} = \frac{d}{d\Delta\Phi}\sigma(\text{at surface}) = \left(\frac{\varepsilon_0\varepsilon}{\lambda}\right)\cosh\left(\frac{Fz\Delta\Phi}{2RT}\right) = C_0\cosh\left(\frac{Fz\Delta\Phi}{2RT}\right)$$



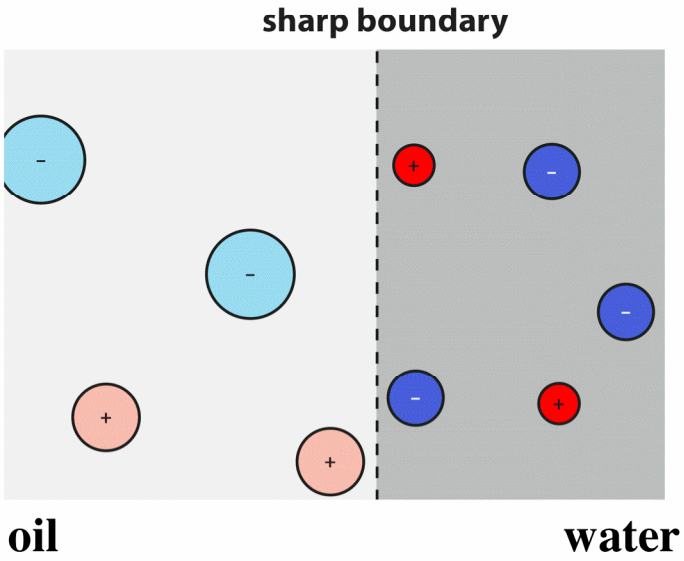
- Can think of capacitance change in terms of a potential-driven Debye length contraction

$$\frac{C}{A} = \frac{\varepsilon_0\varepsilon}{\lambda^*}$$

$$\lambda^* = \frac{\lambda}{\cosh\left(Fz\Delta\Phi/2RT\right)}$$

Properties of ITIES

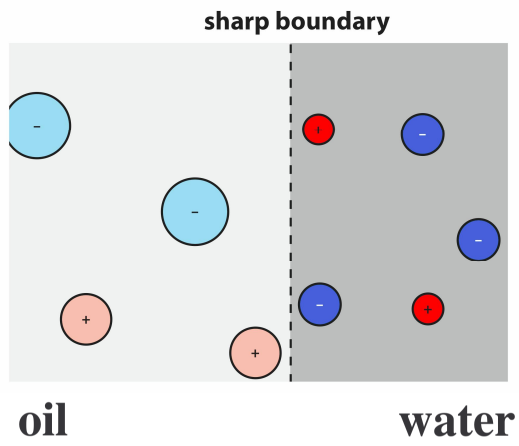
- Our system of choice: the **I**nterface between **T**wo **I**mmiscible **E**lectrolytic **S**olutions (ITIES)



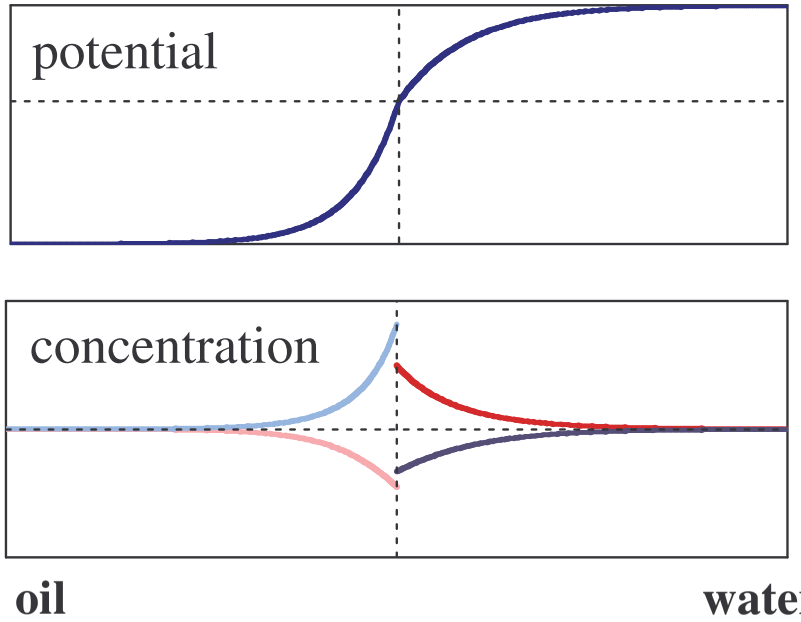
- High ionic free energies of transfer – extremely unfavorable for ions to leave their original phase

- Liquid/liquid interface also exhibits interfacial capacitance: forms “back-to-back double layers”

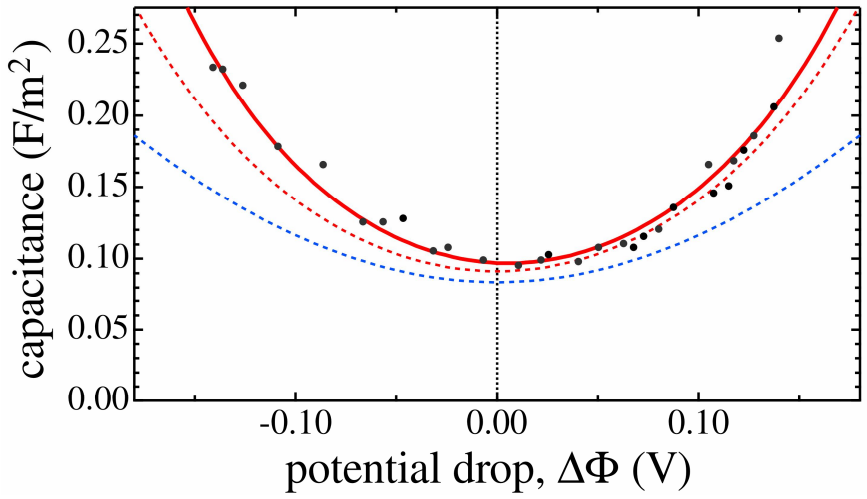
Properties of ITIES



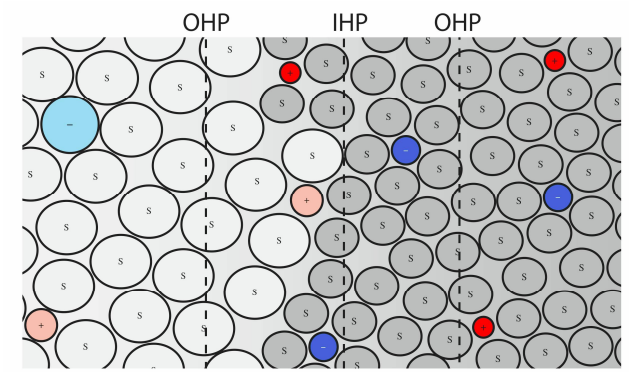
Theoretical description



- "Back-to-back double layers"



- Nanoscale mixing can be ignored



Monroe, Urbakh, Kornyshev, *J. Electroanal. Chem.* **582** (2005) 28–40

Methodology Summary

- **Theory** based in a general energy functional that includes dielectric suction, capillary action, and screening together:

$$G = \underbrace{-\sum_{j=\mathrm{d,s}} \int_{V_j} \frac{\varepsilon_0 \varepsilon_j}{2} |\nabla \Phi|^2 dV}_{\text{work by potentiostat}} + \underbrace{\gamma_{\mathrm{de}} A_{\mathrm{de}} + \gamma_{\mathrm{se}} A_{\mathrm{se}} + \gamma_{\mathrm{ds}} A_{\mathrm{ds}}}_{\text{capillary energy}} + \underbrace{\sum_{j=\mathrm{d,s}} \int_{V_j} \sum_{i=+,-} c_{ji} \mu_{ji} dV}_{\text{screening \& mixing energy (and mechanical work)}}$$

- Variation subject to constraints yields equations to describe the system response, including potential distribution, ion-concentration distributions, and droplet shape

- Why this form is reasonable

First point of discussion: electrostatics

- **Theory** based in a general energy functional that includes dielectric suction, capillary action, and screening together:

$$G = -\sum_{j=\mathrm{d,s}} \int_{V_j} \frac{\varepsilon_0 \varepsilon_j}{2} |\nabla \Phi|^2 dV + \gamma_{\mathrm{de}} A_{\mathrm{de}} + \gamma_{\mathrm{se}} A_{\mathrm{se}} + \gamma_{\mathrm{ds}} A_{\mathrm{ds}} + \sum_{j=\mathrm{d,s}} \int_{V_j} \sum_{i=+,-} c_{ji} \mu_{ji} dV$$

work by potentiostat

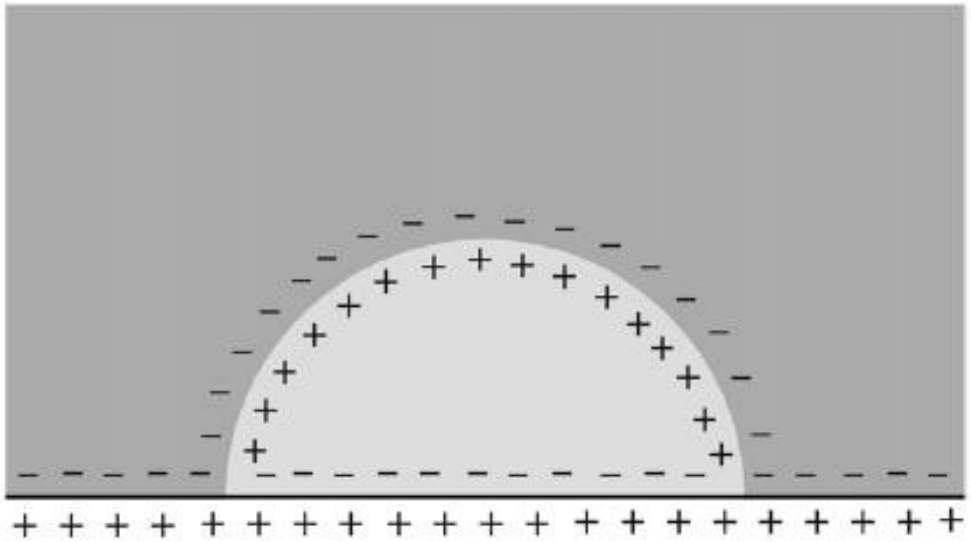
capillary energy

screening & mixing energy (and mechanical work)

- First let us fix system shape, and investigate the electrical response of droplets formed from ITIES

ITIES electrowetting: Electrostatics

- What happens to a polarized droplet with an ITIES?

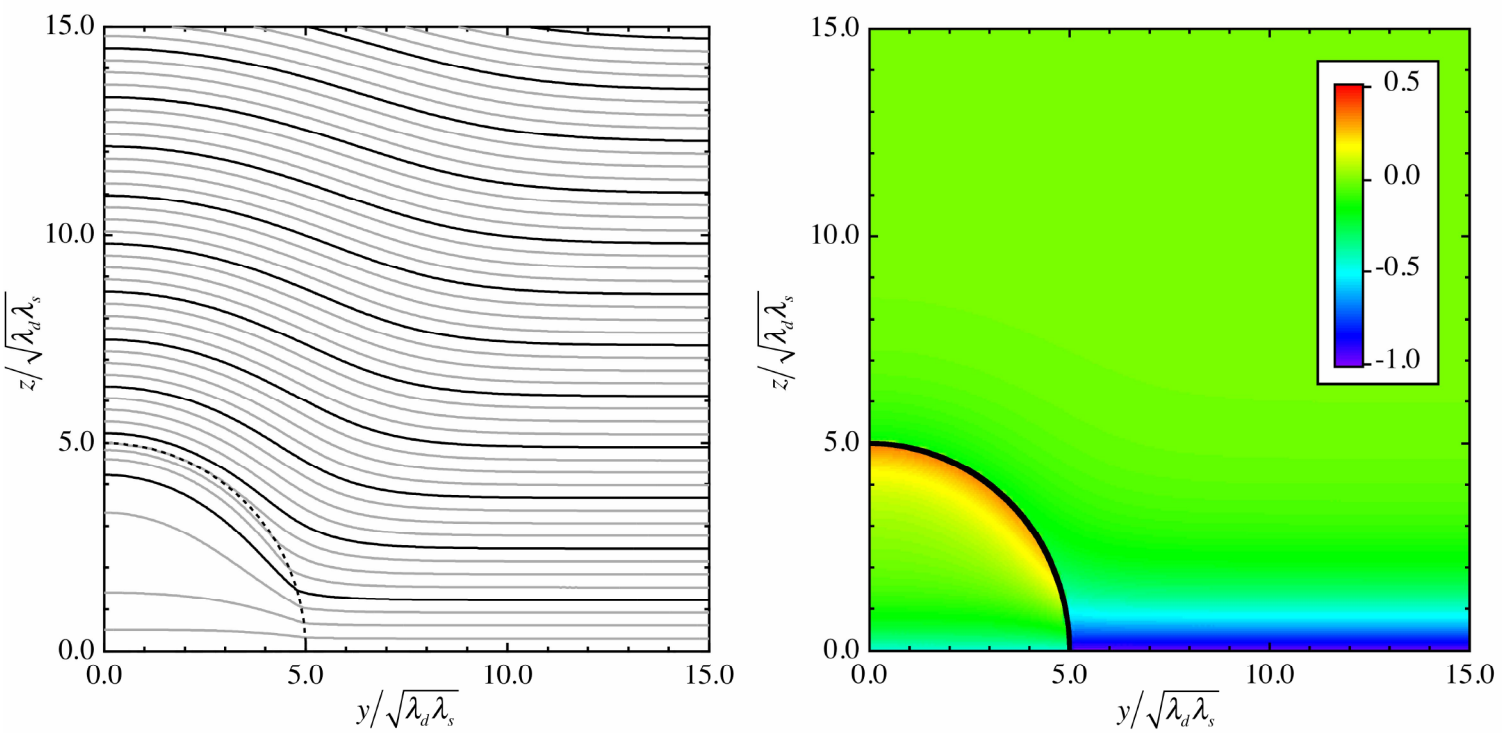


- Impermeable liquid/liquid interface: *an additional constraint on the droplet*

ITIES electrowetting: Electrostatics

- Theoretical results: Adding *charge constraint* to the functional
  Analytical solution for hemispherical droplet shape.

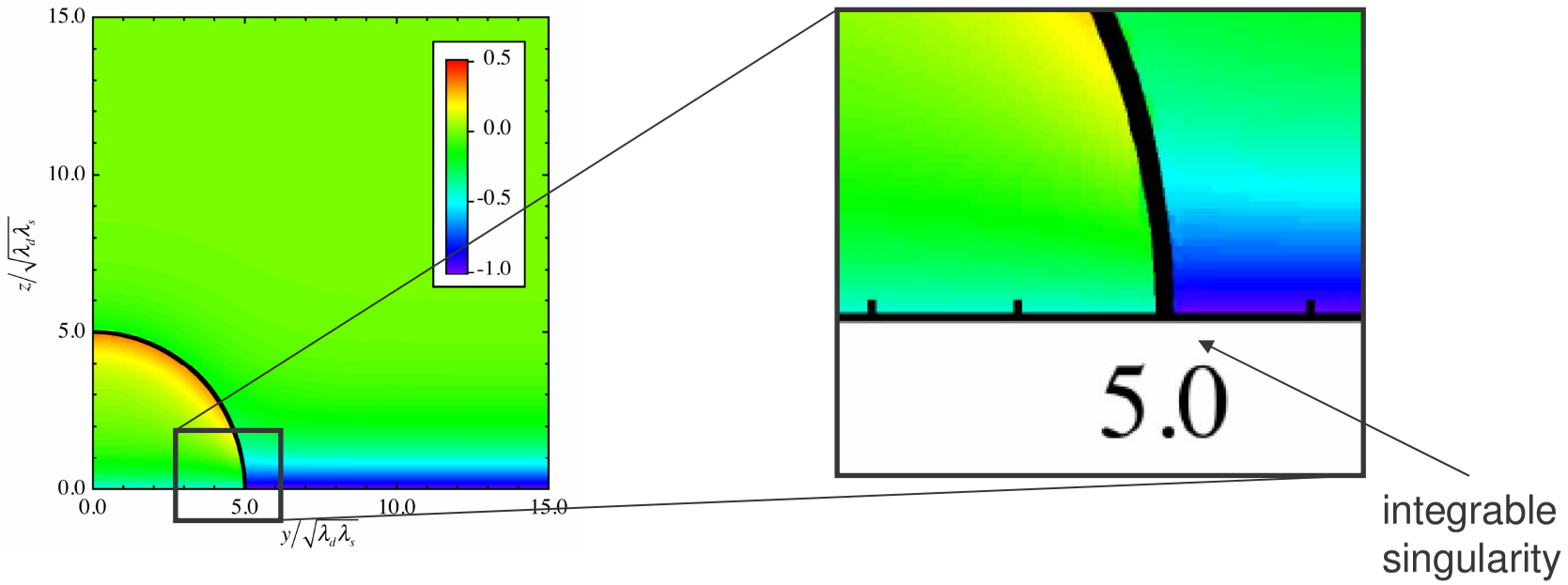
Potential distribution **Charge distribution**



(droplet depicted here is **very** small)

- Note potential plateau, constant liquid/liquid interface potential

Near the three-phase contact line

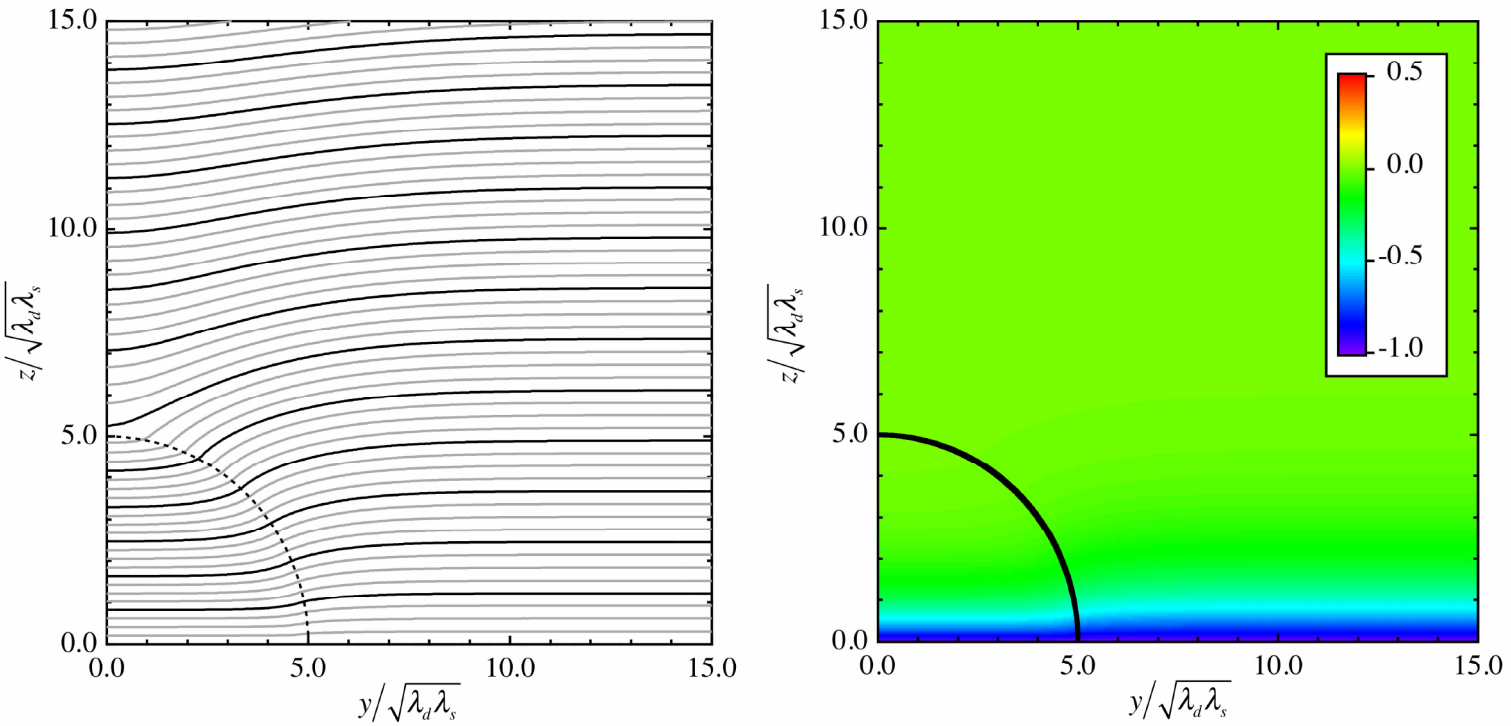


- "Edge effect" near contact line over only ~1 Debye length for all droplet sizes
- With bigger droplet volumes, charge distribution increasingly uniform at interfaces
- Contact line negligible for droplet radii > 0.3 mm

Contrast: a permeable interface

- Achieved by relaxing charge constraint

Potential distribution **Charge distribution**



- Current electrowetting models based on this physical picture, and fail to explain both droplet contraction and contact-angle saturation. Does interfacial impermeability play a role?

Methodology Redux

$$G = -\sum_{j=\mathrm{d,s}} \int_{V_j} \frac{\varepsilon_0 \varepsilon_j}{2} |\nabla \Phi|^2 dV + \gamma_{\mathrm{de}} A_{\mathrm{de}} + \gamma_{\mathrm{ss}} A_{\mathrm{ss}} + \gamma_{\mathrm{ds}} A_{\mathrm{ds}} + \sum_{j=\mathrm{d,s}} \int_{V_j} \sum_{i=1}^{n} c_{ji} \mu_{ji} dV$$

work by potentiostat

capillary energy

screening & mixing energy
(and mechanical work)

- Variation subject to constraints yields equations to describe the system response, including potential distribution, ion-concentration distributions, *and droplet shape*

ITIES electrowetting: system parameters

- In the end, four things determine the global energy minimum

$$\phi_0 = \frac{zF\Delta\Phi}{RT}$$

dimensionless **potential drop** (from the electrode to a reference in the bulk of surroundings)

$$\cos\alpha_c^0 = \frac{\gamma_{se} - \gamma_{de}}{\gamma_{ds}}$$

Young angle at zero potential

$$C = \left(\frac{C_s^{dl}}{C_d^{dl}}\right)^{1/2} = \left(\frac{\varepsilon_s c_s}{\varepsilon_d c_d}\right)^{1/4}$$

square root of the **ratio of double-layer capacitances** at droplet-electrode and surroundings-electrode interfaces

$$b = \frac{\sqrt{2R^3T^3\varepsilon_0}}{zF\gamma_{ds}}\left(\varepsilon_d\varepsilon_s c_d c_s\right)^{1/4}$$

average double-layer capacitance per unit liquid/liquid surface tension

→ system parameters that can be tuned independently to achieve desired response

ITIES electrowetting: linear response regime

- Recall observed law:

$$\cos\alpha_c = \cos\alpha_c^0 + \frac{1}{2} B \left(\Delta\Phi\right)^2$$

- Functional approach in low-potential limit returns

$$\left(\frac{RT}{zF}\right)^2 B = bC\left\{\frac{\cos\alpha_c^0\left(1+\cos\alpha_c^0\right)^2\left(1+C^2\right)+4C^2}{\left[C^2\left(3+\cos\alpha_c^0\right)+\left(1+\cos\alpha_c^0\right)\right]^2}-1\right\}$$

Contraction ($B < 0$) when the surroundings have a higher zero-voltage specific capacitance than the droplet ($C > 1$).

Spreading ($B > 0$) is only possible when $C > 1$ and $\alpha_c^0 > 130°$.

- Note role of b

Monroe, Daikhin, Urbakh, Kornyshev, *J. Phys: Condens. Matter* **18** (2006) 2837–2869

ITIES electrowetting: nonlinear response

$$8b\left[\tfrac{1}{C}\sinh^2\left(\tfrac{1}{4}\phi_0-\tfrac{1}{4}\phi_*\right)-C\sinh^2\left(\tfrac{1}{4}\phi_0\right)\right]+8b\left(A-\tfrac{1}{2}\right)f+\cos\alpha_c^0+1-2A=0$$

Free-energy minimum

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

Electrostatic energy at liquid/liquid interface

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

Droplet-charge constraint

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

Droplet geometry

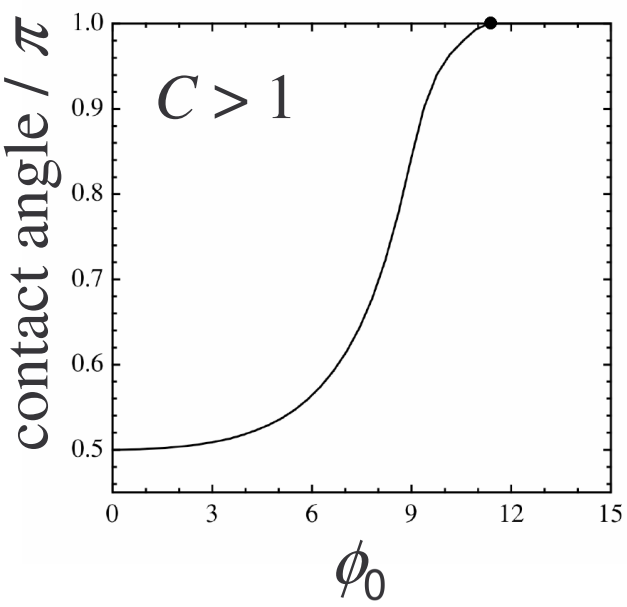
ϕ_* = Potential drop from droplet "bulk" to the bulk of the surrounding solution

Monroe, Daikhin, Urbakh, Kornyshev, *Phys. Rev. Lett.* **97** (2006) 136102

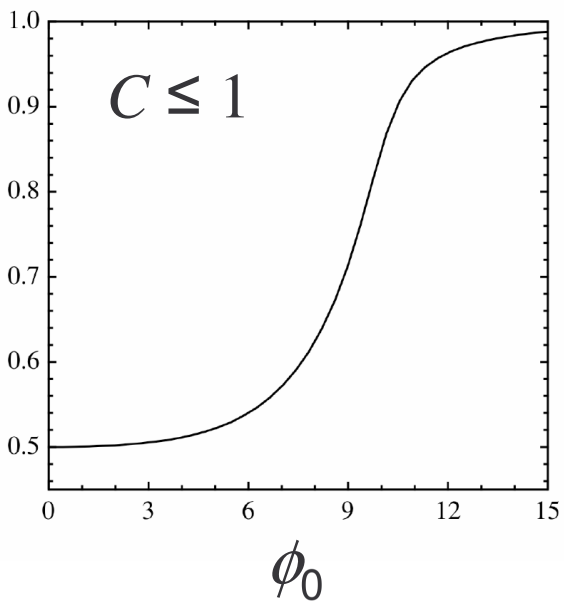
ITIES electrowetting: nonlinear response

- Three characteristic responses to voltage, determined mostly by *Young angle* and *capacitance ratio*

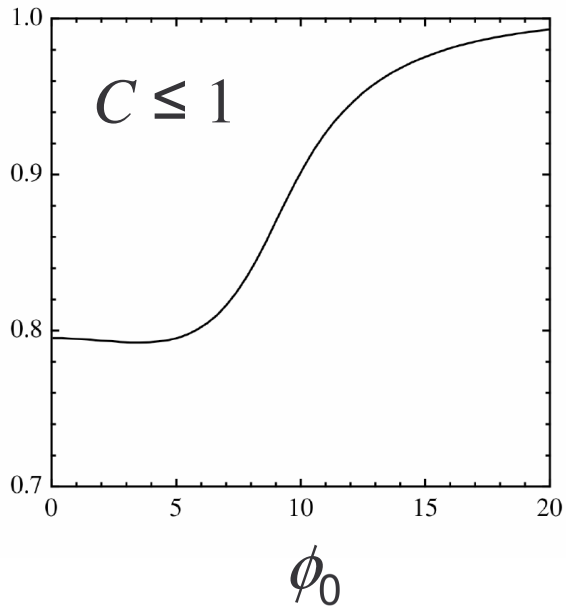
initial angle > 130°



I contraction until dewetting



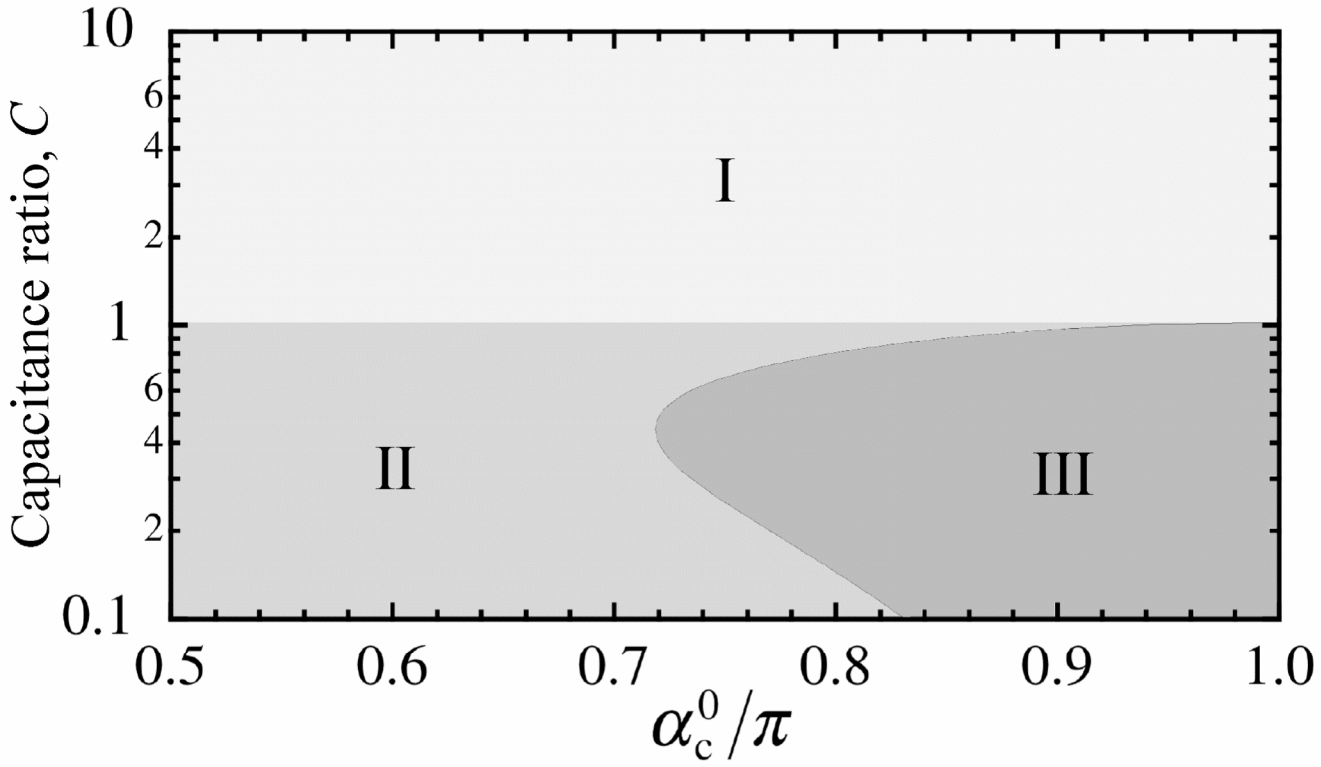
II contraction until saturation



III expansion, then contraction and saturation

ITIES electrowetting: results

Phase diagram



Characteristic responses:

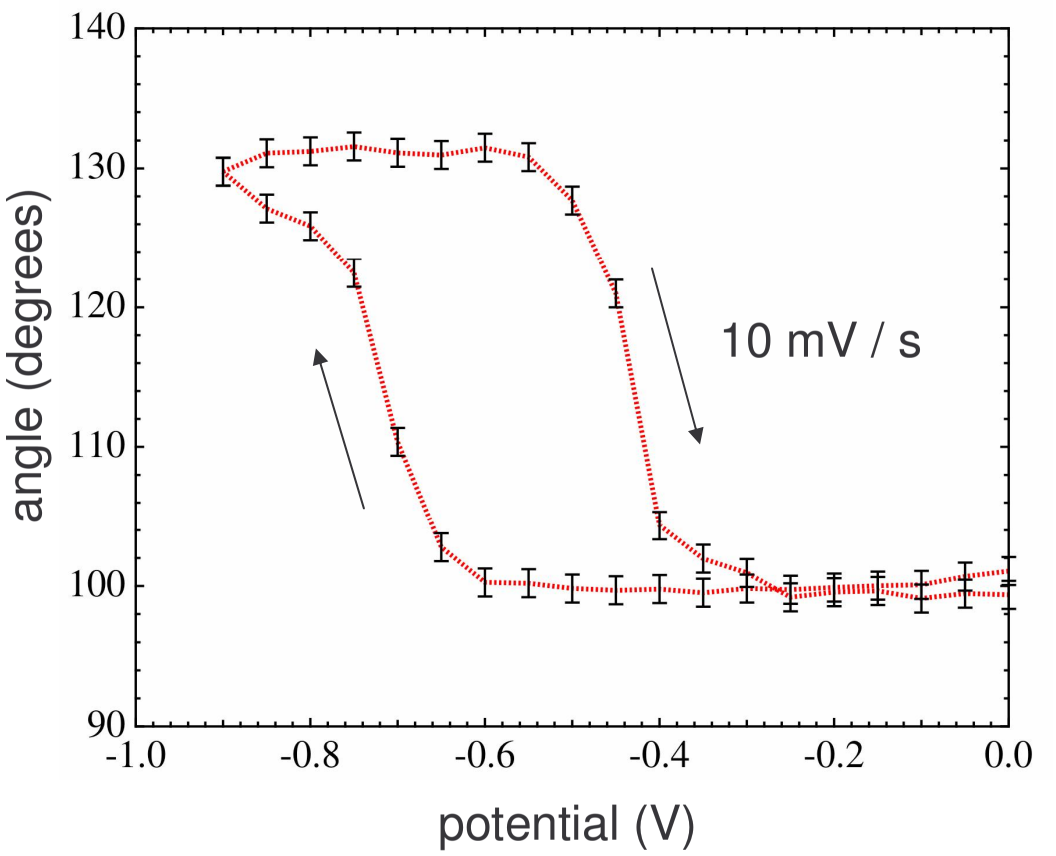
I Angle rises until dewetting

II Angle rises until saturation

III Angle initially falls, but reverses, with eventual saturation.

ITIES electrowetting: dynamics

0.5 M LiCl (aq) / 0.01 M TBA^+TPB^- (in dichloroethane) / gold

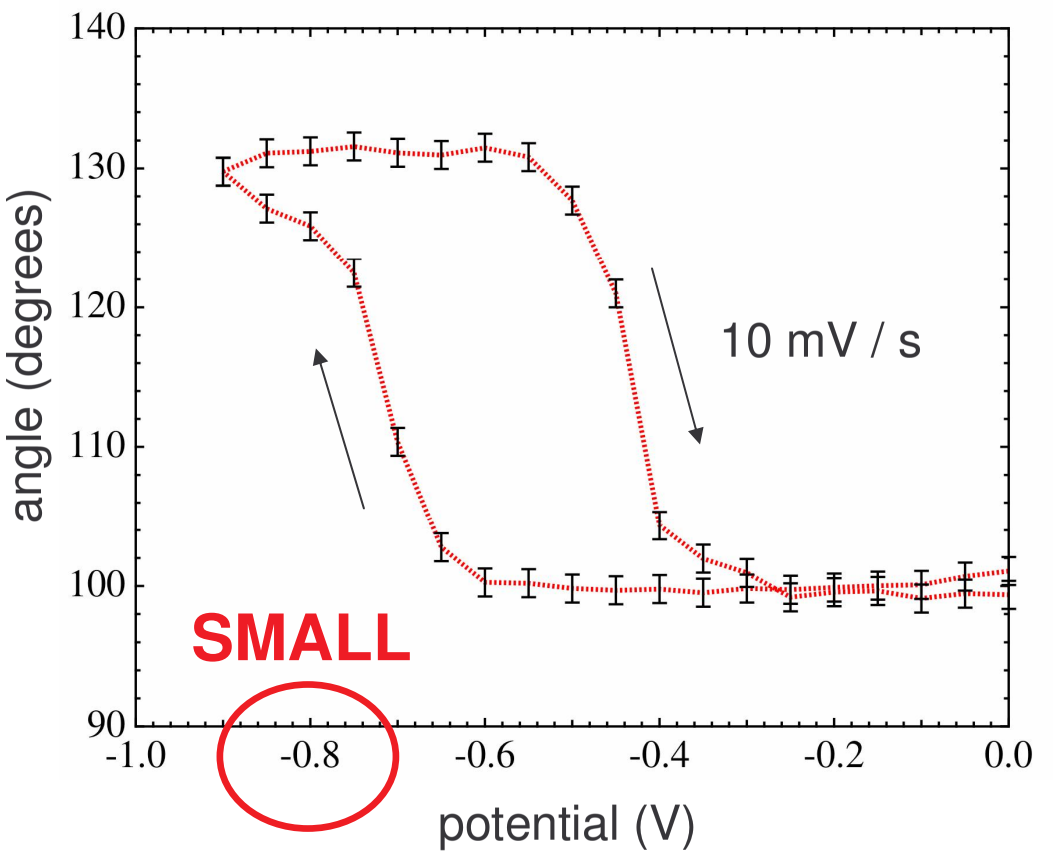


Source: Alice Sleightholme, Kucernak group

- General parameter dependences agree, but *hysteresis*

ITIES electrowetting: dynamics

0.5 M LiCl (aq) / 0.01 M TBA^+TPB^- (in dichloroethane) / gold



Source: Alice Sleightholme, Kucernak group

- Note the factor of 100 reduction in operating voltage

Conclusions

- Electrowetting systems involve a complex interplay of effects: capillary, electrostatic, and electrochemical

- Advantageous electrical properties of ITIES could improve existing electrowetting-based devices

- Design equations show what system parameters can be varied to control the contact-angle response

- ITIES angles change dramatically at potentials ~ 2-3 orders of magnitude smaller than pure-dielectric systems

Acknowledgments

- Leverhulme Trust Interchange Grant

- Laboratory Facilities: Dr. Anthony Kucernak

- Experimental Data: Alice Sleightholme