

Electrowetting Microfluidic Applications and Electromechanical Theory

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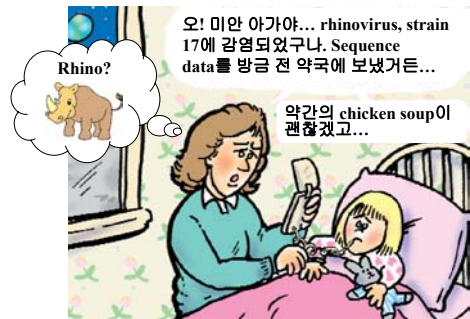
Chemistry + Mechanical Engineering

= **“Chemical Engineering”**

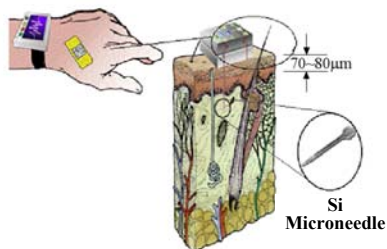
Micro-Total Analysis System (μ TAS) \approx Lab-on-a-chip



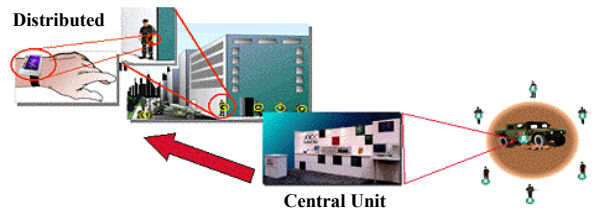
Everyone's a (future) Chemist



Wrist-mounted chem/bio assay



Wrist-mounted chem/bio assay



Microfluidics

- **Microfluidics = Microhydrodynamics + Surface Chemistry + MEMS Tech.**

$$\frac{\text{surface force}}{\text{volume force}} \propto \frac{l^2}{l^3} = \frac{1}{l}$$



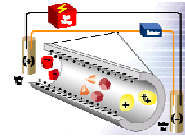
- **Central role in μ TAS**

- Transport
- Mixing
- Separation
- etc.



Liquid handling on sub-millimeter scales

- **Electroosmotic flow** – relatively high voltage \sim 1kV, slow \sim 0.1mm/s



- **Mechanical syringes and actuator** – complicated to fabricate, expensive

Liquid handling on sub-millimeter scales

- **Creation of gradient in surface tension**
 - Photonic, Thermocapillary
 - **Electric: low cost, fast delivery, relatively easy to implement.**



Surface tension in action



(National Geographic Explorer/MSNBC)

$$\frac{\text{surface force}}{\text{volume force}} \propto \frac{l^2}{l^3} = \frac{1}{l}$$



Electrowetting control of liquid droplets



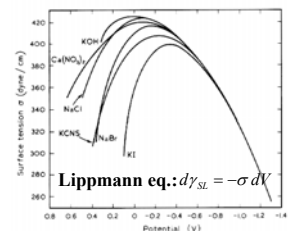
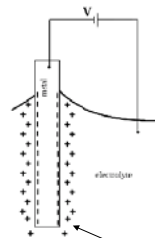
Prof. C.-J. Kim (UCLA)
(<http://simony.seas.ucla.edu/>)



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Effect of electrical charge on wetting

Electrocapillarity and electrocapillary curve



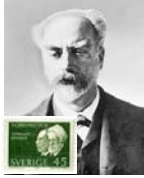
Electrical double layer

Gabriel Lippmann (1845~1921)

French Experimental Physicist



One of the first color photo "Parrot" made by Lippmann in 1891.



Nobel Prize for Physics in 1908 for producing the first color photographic plate.



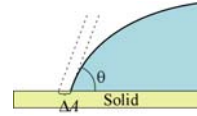
Young's equation by energy method

- The change in surface free energy due to small displacement of the liquid

$$\Delta G^s = \Delta A(\gamma_{SL} - \gamma_{SV^o}) + \Delta A \gamma_{LV} \cos(\theta - \Delta\theta)$$

- At equilibrium

$$\lim_{\Delta A \rightarrow 0} \frac{\Delta G^s}{\Delta A} = 0 \rightarrow (\gamma_{SL} - \gamma_{SV^o}) + \gamma_{LV} \cos\theta = 0$$



Contact angle change by electrocapillarity

- Young's equation: $\gamma_{LV} \cos\theta = \gamma_{SV^o} - \gamma_{SL}$

- Change of surface tension due to charge

Lippmann equation: $d\gamma_{SL} = -\sigma dV$

- Contact angle change

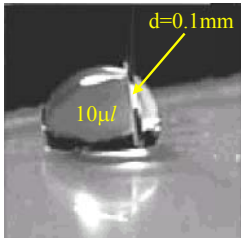
$$\cos\theta = \cos\theta_o - \frac{1}{\gamma_{LV}} \int \sigma dV; \quad \cos\theta_o = \frac{\gamma_{SV^o} - \gamma_{SL}}{\gamma_{LV}}$$

Electrocapillarity vs Electrowetting

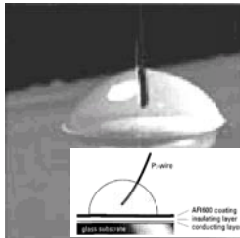
	Electrocapillarity	Electrowetting
Classification		
Surface tension	$d\gamma_{SL} = -\sigma dV$	$d\gamma_{SL} = -\sigma dV$
Surface charge	$\sigma \sim \epsilon K V$	$\sigma = \epsilon V / d$
Contact angle	$\cos\theta = \cos\theta_o - \frac{1}{\gamma_{LV}} \int \sigma dV$	$\cos\theta = \cos\theta_o + \frac{\epsilon V^2}{2\gamma_{LV} d}$ Lippmann-Young eqn.

Contact angle control by electrowetting

10^{-4} M KNO₃ droplet on Teflon AF1600/Parylene C surface

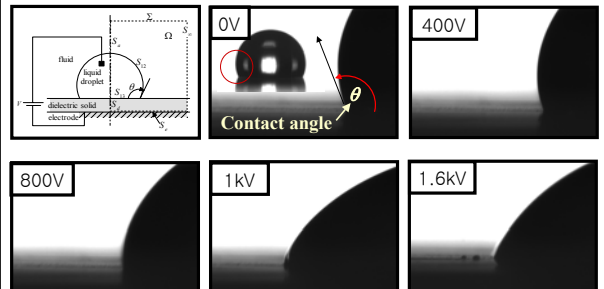


(a) 0V

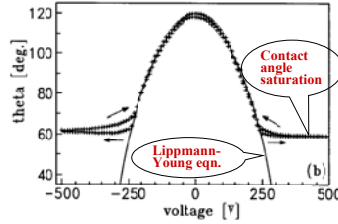


(a) 200V

Contact angle control by electrowetting



Contact angle control by electrowetting

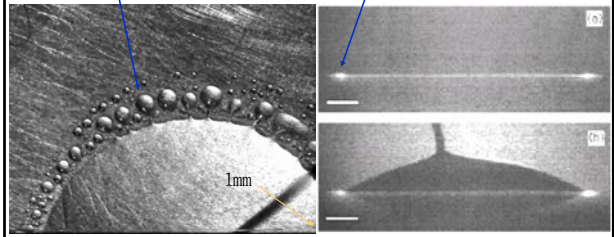


H. J. J. Verheijen et al. (Philips Res. Lab. Eindhoven, The Netherlands) (1999) *Langmuir* 15, 6616.

Contact line instability (after saturation)

Droplet ejection

Light emission from contact line



M. Vallet et al. *Eur. Phys. J. B*, 1999.

Electrocapillarity vs Electrowetting

Classification	Electrocapillarity	EW on Polymers	EW on SAMs
Capacitance	$\epsilon\kappa, \sim 10^4 \mu\text{F}/\text{m}^2$	$\epsilon/d, \sim 1 \mu\text{F}/\text{m}^2$	$\epsilon/\delta, \sim 10^3 \mu\text{F}/\text{m}^2$
Equiv. dielectric. Thickness	$\kappa, \sim 1\text{nm}$	$d, 10\mu\text{m}$	$\delta, \sim 10\text{nm}$
Specific adsorption	Influential	Electro-chemically inert	Influential
Contact angle hysteresis	moderate	Depends on polymers	In general, significant

Electrocapillarity vs Electrowetting

Classification	Electrocapillarity	EW on Polymers	EW on SAMs
Applied voltage	0 ~ 5V	0V~1kV	0 ~ 5V
Reversibility	bad	good	bad
Dominant interaction force	Coulombic, Chemical,	Coulombic	Coulombic, Chemical

Electrowetting control of liquid droplets

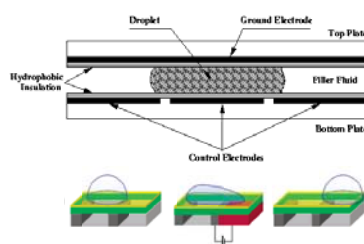


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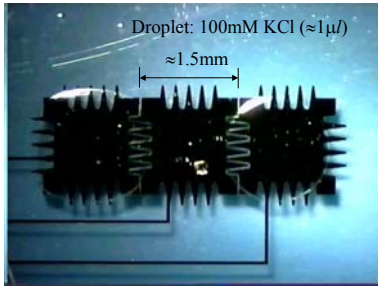
Actuation of microdroplet by electrowetting

“No need for pumps, valves, or even fixed channels.”

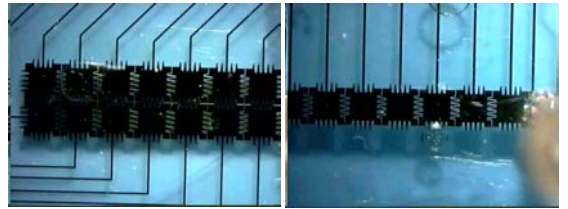


M.G. Pollack et al. (Duke U., Dept Elect. Eng.) (2000) *Appl. Phys. Lett.* 77, 1725.

Splitting of a droplet



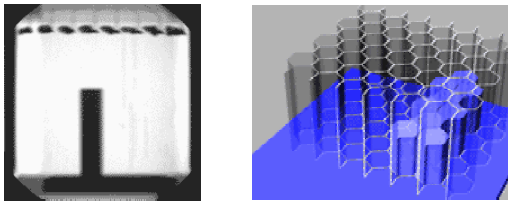
Other applications



Flow of a droplet on a 2-D array

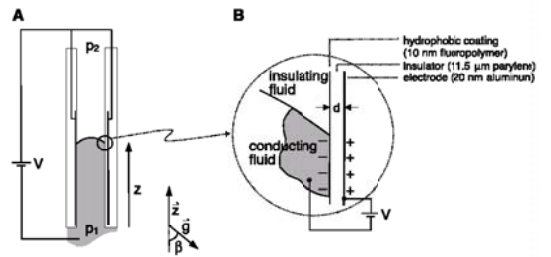
Dispensing of droplets

Liquid actuation in microcapillary



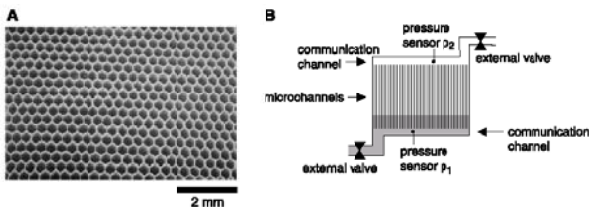
M. W. J. Prins, W. J. J. Welters, J. W. Weekamp, "Fluid Control in Multichannel Structures by Electrocapillary Pressure," Science, January 12, 2001.

Liquid actuation in microcapillary



M. W. J. Prins, W. J. J. Welters, J. W. Weekamp, "Fluid Control in Multichannel Structures by Electrocapillary Pressure," Science, January 12, 2001.

Liquid actuation in microcapillary

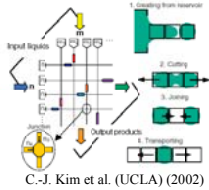


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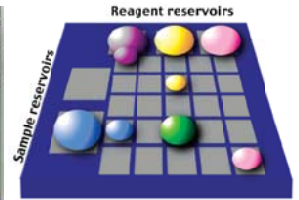
Applications

Why electrowetting for lab-on-a-chip?

- **Droplet-based microfluidic operations**
 - By programmed electric signals rather than by complex physical structures.
 - Fabrication process becomes very simple.

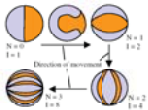
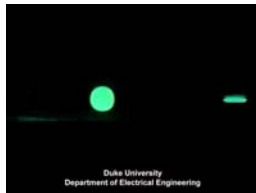
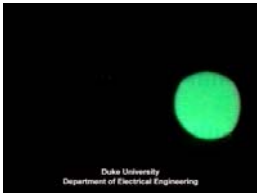


Digital microfluidics by electrowetting



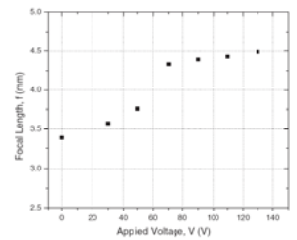
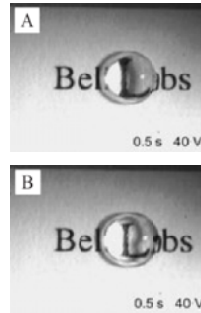
Other advantages of electrowetting
: fast liquid actuation, low power consumptions.

Mixing of droplet by electrowetting



Prof. R. B. Fair (Duke Univ.)
(<http://www.ece.duke.edu/Research/microfluidics/>)

Optical lens (1)



Yang et al. (Bell Lab.)
(2003)Adv. Mater. 15(11) 940.

Optical lens (2)

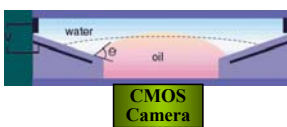


Benefits

- No moving parts, direct electric control
- Fast response (0.02s for a 5mm diameter)
- Very good optical quality
- Reduced electrical consumption

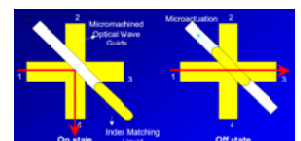
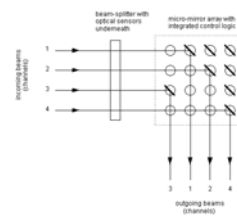
Applications

- Medical optics
- Autofocus lenses for CCD cameras
- Bar code readers



<http://www.varioptic.com/>

Optical switch for optical network



Development of Electromechanical Theory

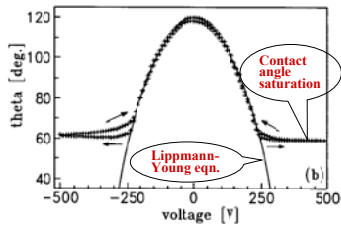
Why electromechanical approach?

- Some MEs are unfamiliar with the energy method.



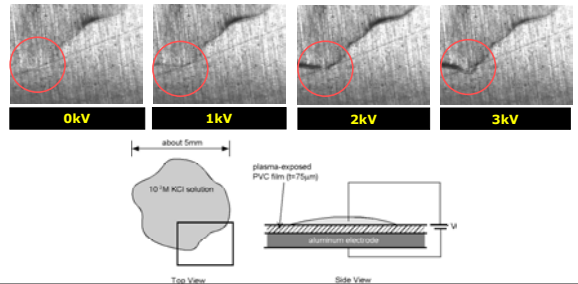
Why electromechanical approach?

- Limited validity of Lippmann–Young equation due to **contact-angle saturation**.



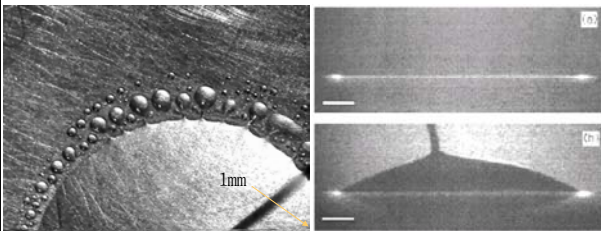
Why electromechanical approach?

- Increase of contact angle by electrowetting?



Why electromechanical approach?

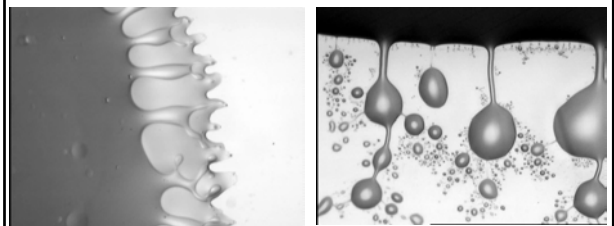
- Mechanism of the contact line instability?



M. Vallet *et al.* *Eur. Phys. J. B*, 1999.

Why electromechanical approach?

- Mechanism of the contact line instability?

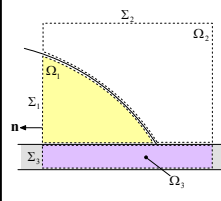


Why electromechanical approach?

- Limited validity of Lippmann–Young equation due to **contact-angle saturation**.
- Mechanism of the contact line instability?
- An alternative approach is necessary to analyze the complex phenomena.

Essence of the electromechanical theory

- Use of Gauss theorem and the Maxwell stress tensor.



$$\mathbf{F} = \int_{\Omega} \mathbf{f} dV = \int_{\Sigma} \mathbf{T} \cdot \mathbf{n} dS$$

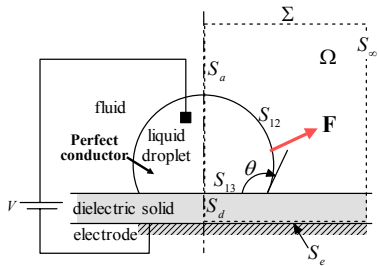
$$\mathbf{f} = \rho_f \mathbf{E} - \frac{1}{2} E^2 \nabla \varepsilon \quad (\text{Korteweg-Helmholtz force density})$$

$$\mathbf{T} = -\frac{1}{2} \varepsilon E^2 \mathbf{I} + \varepsilon \mathbf{E} \mathbf{E} \quad (\text{Maxwell stress tensor})$$

$$W_{el} = -\mathbf{F} \cdot \mathbf{e}_x \quad (\text{wetting tension})$$

$$\cos \theta = \cos \theta_0 + \frac{W_{el}}{\gamma} \quad (\text{modified Young's equation})$$

Direct integration of Maxwell stress



$$\nabla^2 \varphi = 0$$

$$\mathbf{F} = \int_{S_{12}+S_{13}} \mathbf{T} \cdot \mathbf{n} dS$$

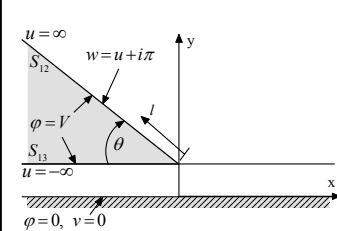
$$\mathbf{T} = -\frac{1}{2} \varepsilon E^2 \mathbf{I} + \varepsilon \mathbf{E} \mathbf{E}$$

Maxwell stress tensor

Note: Effect of electrical double layer is neglected.

Analysis of potential problem

Schwarz-Christoffel transformation



$$Z = \int_{i\pi}^w (e^{w'} + 1)^\alpha dw' + i\pi$$

$$Z = x + iy$$

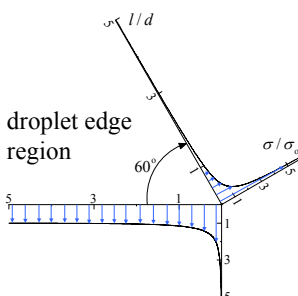
$$w = u + iv = u + i \left(\frac{\pi}{V} \right) \varphi$$

$$\mathbf{T} \cdot \mathbf{n} = \left(-\frac{1}{2} \varepsilon E^2 \mathbf{I} + \varepsilon \mathbf{E} \mathbf{E} \right) \cdot \mathbf{n}$$

$$= \frac{\varepsilon E^2}{2} \mathbf{n} = \frac{\sigma^2}{2\varepsilon} \mathbf{n}$$

Important assumption: $\varepsilon_{\text{substrate}} = \varepsilon_{\text{air}}$

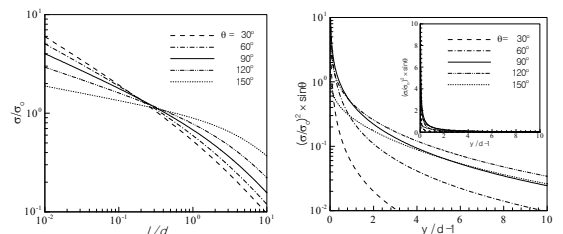
Charge distribution at the surface



$$\sigma = \varepsilon |E_x - iE_y| = \frac{\varepsilon V}{e} \left| \frac{i}{dz/dw} \right|$$

$$\frac{\sigma}{\sigma_0} = \begin{cases} 1/(e^u - 1)^\alpha, & \text{on } S_{12}, \\ 1/(1 - e^u)^\alpha, & \text{on } S_{13}. \end{cases}$$

Maxwell stress acting on surface

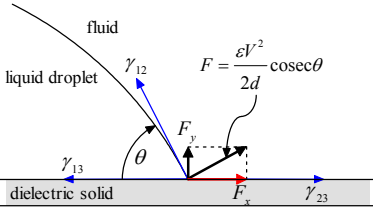


Charge distribution

Maxwell stress

Surface force and wetting tension

$$F = \int_{S_{12}} \frac{\sigma^2}{2\epsilon} dl = \frac{\epsilon V^2}{2d^2} \int_{S_{12}} \frac{1}{(e^u - 1)^{2\alpha}} dl = \frac{\epsilon V^2}{2d} \operatorname{cosec} \theta$$

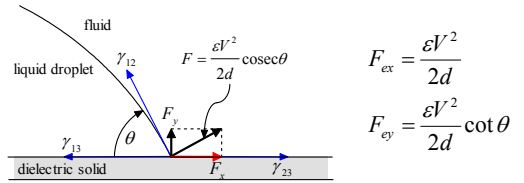


$$F_x = \frac{\epsilon V^2}{2d}$$

$$F_y = \frac{\epsilon V^2}{2d} \cot \theta$$

Derivation of Lippmann–Young eqn.

- Conventional electrowetting equation is recovered.



$$F_{ex} = \frac{\epsilon V^2}{2d}$$

$$F_{ey} = \frac{\epsilon V^2}{2d} \cot \theta$$

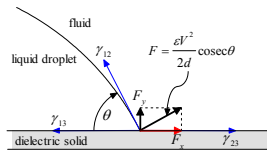
$$\gamma_{12} \cos \theta = \gamma_{23} - \gamma_{13} + \frac{\epsilon V^2}{2d} ; \text{Lippmann-Young eqn.}$$

(Langmuir 2002, 18, 10318)

Origin of electrowetting phenomena

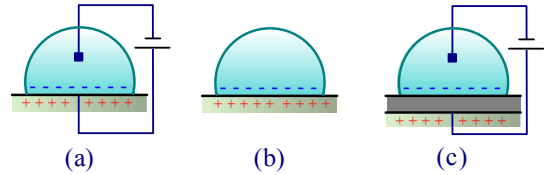
- Electrowetting originates from wetting tension, rather than from change of surface energy.
- Roll of the vertical force should be explained.

$$F_x = \frac{\epsilon V^2}{2d}, \quad F_y = \frac{\epsilon V^2}{2d} \cot \theta$$



Note: Effect of interfacial shape is not considered.

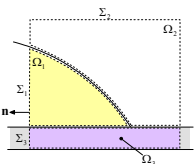
Generalization of Theory



Electromagnetic momentum conservation

- Force on a volume Ω : $\mathbf{F}^\Omega = \int_{\Omega} \mathbf{f} dV = \int_{\Sigma} \mathbf{T} \cdot \mathbf{n} dS$
- Maxwell stress with osmotic pressure:

$$\mathbf{T} = -(\Pi + \frac{1}{2} \epsilon E^2) \mathbf{I} + \epsilon \mathbf{E} \mathbf{E}; \quad \Pi = 2n^\infty kT [\cosh \beta \phi - 1]$$
- A vector identity: $\int_{\Sigma} (\mathbf{n} \cdot \mathbf{E}) \mathbf{E} dS = \int_{\Omega} [\mathbf{E} (\nabla \cdot \mathbf{E}) + \mathbf{E} \cdot \nabla \mathbf{E}] d\Omega$



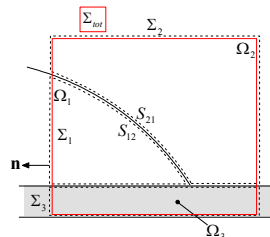
$$\nabla \cdot \mathbf{E} = -\nabla^2 \phi = \frac{\kappa^2}{\beta^2} \sinh \beta \phi$$

(Poisson–Boltzmann equation)

$$\int_{\Sigma} \left\{ \left[\Pi + \frac{1}{2} \epsilon E^2 \right] \mathbf{I} - \epsilon \mathbf{E} \mathbf{E} \right\} \cdot \mathbf{n} dS = 0$$

Surface force and wetting tension

$$\mathbf{F}_{tot} = \mathbf{F} + f'_y \mathbf{e}_y = -f'_y \mathbf{e}_y - \int_{S_{12} + S_{21}} \mathbf{T} \cdot \mathbf{n} dS = \int_{\Sigma_{tot}} \mathbf{T} \cdot \mathbf{n} dS$$



$$f_x = \frac{\epsilon_3 (V - \phi_{13})^2}{2d} + \frac{4\epsilon_1 \kappa_1}{\beta^2} \left[\cosh \frac{\beta \phi_{12}}{2} - 1 \right] - \frac{\epsilon_3 (V - \phi_{23})^2}{2d} - \frac{4\epsilon_2 \kappa_2}{\beta^2} \left[\cosh \frac{\beta \phi_{23}}{2} - 1 \right]$$

(Langmuir 2003, 19, 5407)

Surface force and wetting tension



$$W_{el}^{(I)} = 8kT \left(\frac{n_{1s}}{\kappa_1} - \frac{n_{2s}}{\kappa_2} \right) \left[\cosh \frac{\beta v}{2} - 1 \right]$$

Note:

$$\cos \theta = \cos \theta_0 + \frac{W_{el}}{\gamma}$$



$$W_{el}^{(II)} = \left\{ \frac{8n_{1s}kT}{\kappa_1} [\cosh \frac{\beta \phi_{1s}}{2} - 1] - \sigma_1 \phi_{1s} \right\} - \left\{ \frac{8n_{2s}kT}{\kappa_2} [\cosh \frac{\beta \phi_{2s}}{2} - 1] - \sigma_2 \phi_{2s} \right\} + (\sigma_1 - \sigma_2) \phi_0$$

Geometry dependent term.
(Langmuir 2003, 19, 6881)



$$W_{el}^{(III)} = \frac{\epsilon_2}{2d} [(V - \phi_{1s})^2 - (V - \phi_{2s})^2] + 8 \frac{n_{1s}kT}{\kappa_1} [\cosh \frac{\beta \phi_{1s}}{2} - 1] - 8 \frac{n_{2s}kT}{\kappa_2} [\cosh \frac{\beta \phi_{2s}}{2} - 1]$$

Benefits of the electromechanical theory

- Familiar to MEs
- **Easy and clear;** requires understanding only on the Maxwell stress tensor.
- Suitable for numerical calculations for complex situations.
- Can handle dynamic problems.

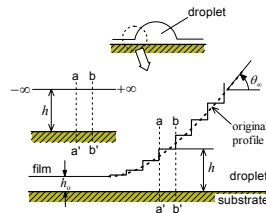


Usefulness

Validity of the Derjaguin approximation on the Frumkin–Derjaguin approach

Validity of the Derjaguin approximation ...

Frumkin–Derjaguin approach (base on the DLVO theory)



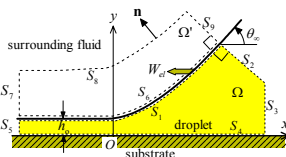
$$\cos \theta_\infty = 1 + \frac{1}{\gamma} \int_{h_0}^{\infty} \pi_1(h) dh = 1 + \frac{V_1(h_0)}{\gamma}$$

$$V_1^o(h_0) = \frac{\epsilon \kappa}{2} [2\phi_1 \phi_2 \text{csch} \kappa h_0 - (\phi_1^2 + \phi_2^2) (\coth \kappa h_0 - 1)]$$

$$V_1^s(h_0) = \frac{\epsilon \kappa}{2} [2\phi_{1s} \phi_{2s} \text{csch} \kappa h_0 + (\phi_{1s}^2 + \phi_{2s}^2) (\coth \kappa h_0 - 1)]$$

Validity of the Derjaguin approximation ...

Electromechanical approach



$$\cos \theta = \cos \theta_0 + \frac{W_{el}}{\gamma}$$

$$W_{el} = -\mathbf{F} \cdot \mathbf{e}_x$$

$$\mathbf{F} = -\int_{S_1} \mathbf{T} \cdot \mathbf{n} dS - \int_{S_2} \mathbf{T} \cdot \mathbf{n} dS$$

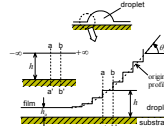
Validity of the Derjaguin approximation ...

Frumkin–Derjaguin approach (base on the DLVO theory)

$$\cos \theta_\infty = 1 + \frac{1}{\gamma} \int_{h_0}^{\infty} \pi_1(h) dh = 1 + \frac{V_1(h_0)}{\gamma}$$

$$V_1^o(h_0) = \frac{\epsilon \kappa}{2} [2\phi_1 \phi_2 \text{csch} \kappa h_0 - (\phi_1^2 + \phi_2^2) (\coth \kappa h_0 - 1)]$$

$$V_1^s(h_0) = \frac{\epsilon \kappa}{2} [2\phi_{1s} \phi_{2s} \text{csch} \kappa h_0 + (\phi_{1s}^2 + \phi_{2s}^2) (\coth \kappa h_0 - 1)]$$



Electromechanical approach

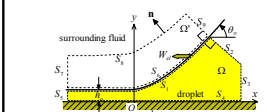
$$\cos \theta = \cos \theta_0 + \frac{W_{el}}{\gamma}$$

$$W_{el} = -\mathbf{F} \cdot \mathbf{e}_z$$

$$W_{el}^o = \frac{\epsilon \kappa}{2} [2\phi_1 \phi_2 \text{csch} \kappa h_0 - (\phi_1^2 + \phi_2^2) (\coth \kappa h_0 - 1)]$$

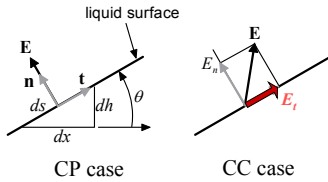
$$+ \frac{\epsilon \kappa}{2} \phi_2^2 (\cos \theta_0 - 1) \quad \text{electrocapillary term}$$

$$W_{el}^s = \frac{\epsilon \kappa}{2} (\phi_{1s}^2 - \phi_{2s}^2) (\coth \kappa h_0 - 1) + \frac{\epsilon \kappa}{2} \phi_{1s}^2 (\cos \theta_0 - 1)$$



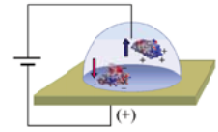
Validity of the Derjaguin approximation ...

- For constant potential (CP) case, valid for *all* the contact angles with minor correction.
- For constant charge (CC) case, **significant error due to existence of tangential stress.**



Some of current issues on electrowetting

- Reduction of actuation voltage: now, normally $\sim 30V$
- Delay of saturation angle by AC voltage (dielectrophoresis, Prof. Jones in U. Rochester)
- Mechanism of contact angle saturation.
- Contact line instability (droplet ejection)
- Minimization of protein adsorption by additives.



Concluding remarks

- Electrowetting has many advantages for microfluidic actuation of liquids such as
 - ✓ fast
 - ✓ low energy consumption
 - ✓ digitized operations
- An electromechanical framework on electrowetting is established.