drops in motion
the physics of electrowetting and its applications

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Physics of Complex Fluids
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wetting & liquid microdroplets

\[ \Delta p = p_L = 2k\sigma_{lv} \]

Young equation

\[ \cos \theta_Y = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}} \]

H. Gau et al. Science 1999
electrowetting: the switch on the wettability

voltage
some applications of EW

### Tunable Lenses
(varioptic, Philips)

![Tunable Lenses](image)

Kuiper and Hendriks, APL 2004

### EW Displays
(Philips liquavista)

![EW Displays](image)

courtesy of R. Hayes

250 μm

### Micromechanical Actuation

![Micromechanical Actuation](image)

### Lab-on-a-chip

![Lab-on-a-chip](image)

Physics of Complex Fluids
Introduction

Electrowetting basics
  - Historic note
  - Origin of the EW effect
  - Electromechanical model
  - Contact angle saturation

Physical principles and challenges of EW devices

Fundamental fluid dynamics with EW
  - Contact angle hysteresis in EW
  - Contact line motion in ambient oil
  - Electrowetting driven drop oscillations and mixing flows
  - Channel-based microfluidic systems with EW functionality

Conclusion
the origin

1875: Annales de Chimie et de Physique

G. LIPPMANN. — RELATIONS

RELATIONS ENTRE LES PHÉNOMÈNES ÉLECTRIQUES ET CAPILLAIRES;

Par M. Gabriel LipPMANN,
Ancien élève de l’École Normale supérieure.

english translation: in Mugele&Baret

Gabriel Lippmann
(1845-1921)
Nobel prize 1908

1891: interferometric color photography
Lippmann’s experiment on electrocapillarity

First law—the capillary constant at the mercury/diluted sulfuric acid interface is a function of the electrical difference at the surface.

\[ \sigma = f(U) \]
Effective surface tension

capillary depression (Jurin):
\[ \Delta p_L = \frac{2\sigma \cos \theta_y}{R} = \rho g \Delta h = p_h \]

\[ \Delta h = \Delta h(U) \quad \rightarrow \quad \sigma = \sigma(U) = \sigma_0 - \alpha U^2 \]

build-up of a Debye layer

\[ E_{el} = \frac{1}{2} c U^2 \]

\[ c = \frac{\varepsilon_0 \varepsilon}{\lambda_D} \]

total free energy (per unit area):
\[ F(U) = \sigma(U) = \sigma_0 - \frac{c}{2} U^2 \]

Lippmann eq.:
\[ \rho = -\frac{\partial \sigma}{\partial U} \]

no dielectric!
modern electrowetting equation „on dielectric“

basic setup:

\[ U \]

conductive liquid
insulator
counter electrode

“Electrowetting on dielectric (EWOD)”

electrowetting equation:

\[
\cos(\theta(U)) = \cos\theta_y + \frac{1}{2} \frac{\varepsilon_0 \varepsilon}{d \sigma_{lv}} U^2
\]

electrowetting number

\[ \eta \]

low voltage: parabolic behavior
high voltage: contact angle saturation

advancing
receding

water in silicone oil

Berge 1993
Examples of EW-curves

Electrowetting equation: \[ \cos(\theta(U)) = \cos\theta_Y + \frac{1}{2} \frac{\varepsilon_0 \varepsilon}{d \sigma_{lv}} U^2 \]

Graph showing the electrowetting equation with different materials and their respective surface tensions.

Teflon AF-coated ITO glass in silicone oil; AC voltage

Banpurkar et al., Langmuir 2008
EW as microdrop tensiometer

<table>
<thead>
<tr>
<th>Liquid Interface (Temperature = 23°C)</th>
<th>$\gamma_{wo}$ (EW drop tensiometer (mN/m))</th>
<th>$\gamma_{wo}$ (Du Noüy ring) (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Planar Electrode</td>
<td>Interdigitated Electrode</td>
</tr>
<tr>
<td>H$_2$O/silicone oil ($\theta_Y=169^\circ$)</td>
<td>calibration</td>
<td>calibration</td>
</tr>
<tr>
<td>H$_2$O/ mineral oil (168$^\circ$)</td>
<td>48.8± 0.5</td>
<td>47.3± 0.7</td>
</tr>
<tr>
<td>H$_2$O/ air (62$^\circ$)</td>
<td>72.4 ±0.6</td>
<td>72.0±0.2</td>
</tr>
<tr>
<td>H$_2$O/ n-hexadecane (169$^\circ$)</td>
<td>52.9±0.7</td>
<td>48.5±0.6</td>
</tr>
<tr>
<td>Aqu. Gelatin (2 %)/ mineral oil (160$^\circ$)</td>
<td>24.1±0.6</td>
<td>24.8±0.7</td>
</tr>
<tr>
<td>Aqu. Gelatin (2 %)/silicone oil (167$^\circ$)</td>
<td>20.1±0.8</td>
<td>20.4±0.8</td>
</tr>
<tr>
<td>Aqu. SDS (0.7 %)/ silicone oil (165$^\circ$)</td>
<td>7.5± 0.3</td>
<td>7.5± 0.8</td>
</tr>
<tr>
<td>Aqu. CTAB (0.1 %)/mineral oil (164$^\circ$)</td>
<td>6.5± 0.5</td>
<td>7.5± 0.8</td>
</tr>
<tr>
<td>Aqu. Triton X-100 (0.1%)/ silicone oil (163$^\circ$)</td>
<td>4.7±0.3</td>
<td>5.6±0.5</td>
</tr>
<tr>
<td>Aqu. Glycerin (50%)/ silicone oil (169$^\circ$)</td>
<td>32.8±0.8</td>
<td>35.0±0.7</td>
</tr>
<tr>
<td>Milk / silicone oil (167$^\circ$)</td>
<td>19.4±0.7</td>
<td>18.6±0.9</td>
</tr>
<tr>
<td>yeast protein (1%)/ silicone oil (167$^\circ$)</td>
<td>20.0±0.5</td>
<td>15.7±0.7</td>
</tr>
</tbody>
</table>

‡  interfacial tension measurements for nL drops consistent with bulk values

Banpurkar et al., Langmuir 2008
origin of EW

$$G = \sum_i \sigma_i A_i - \frac{1}{2} \int \mathbf{r} \cdot \mathbf{E} dV$$

$$= \sum_i \sigma_i A_i - \frac{\varepsilon_0 \varepsilon_r}{2d} A_{sl} U^2$$

$$= \sigma_{lv} A_{lv} + \left( \sigma_{sl} - \frac{\varepsilon_0 \varepsilon_r}{2d} U^2 - \sigma_{sv} \right) A_{sl}$$

Maxwell stress: $$p_{el} = -\frac{\varepsilon_0}{2} E(r)^2$$

$$\Delta p = \sigma_{lv} \cdot \kappa - \frac{\varepsilon_0}{2} E(r)^2$$

modified Young equation

modified capillary equation
local equilibrium surface profiles

1. local force balance

\[ p_{el}(x) = \frac{\varepsilon_0}{2} E(r)^2 = \gamma_{lv} \cdot \frac{h''(r)}{\sqrt{1 + h'(r)^2}} = p_{cap}(r) \]

2. free energy minimization

\[ \tilde{F} = \cos \theta_y L_{sl} + \int_B^A ds - \frac{\eta}{\varepsilon(r)} \int dV (\nabla \phi)^2 \]

iterative calculation:
- initial profile (fixed \( \theta_y \))
- field distribution (FEM)
- force balance \( \rightarrow \) refined profile
local contact angle = Young’s angle

divergent curvature near contact line: \( \kappa \sim p_{el} \sim h^{\nu} \); \(-1 < \nu < 0\)

range of surface distortions: \( \approx d_{ins} \) no contact angle saturation

(in 2-dim model)
## Experimental Verification

<table>
<thead>
<tr>
<th>$\eta$ Value</th>
<th>Image Descriptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta = 0$</td>
<td>![Images for $\eta = 0$]</td>
</tr>
<tr>
<td>$\eta \approx 0.5$</td>
<td>![Images for $\eta \approx 0.5$]</td>
</tr>
<tr>
<td>$\eta \approx 1$</td>
<td>![Images for $\eta \approx 1$]</td>
</tr>
</tbody>
</table>

- **$d = 10\mu m$**
  - ![Images for $d = 10\mu m$]

- **$d = 50\mu m$**
  - ![Images for $d = 50\mu m$]

- **$d = 150\mu m$**
  - ![Images for $d = 150\mu m$]

relation between local and apparent c.a.

\[ \cos(\theta(U)) = \cos\theta_Y + \eta \]

‡ apparent c.a. follows EW equation
equivalence of force balance & energy minimization

\[ f_{x,el} = \int_0^{\infty} \rho \cdot E_x \, dz = \frac{\varepsilon \varepsilon_0}{2d} U^2 \]

\[ f_x = \oint \Sigma T_{xk} n_k \, dA = \frac{\varepsilon \varepsilon_0}{2d} U^2 = \sigma_{lv} \eta \]

Maxwell stress tensor:
\[ T_{ik} = \varepsilon_0 \varepsilon (E_i E_k - \frac{1}{2} \delta_{ik} E^2) \]

force / unit length

\[ \sigma_{lv}, \sigma_{sl}, \sigma_{sv} \]

\[ f_{el} \]

\[ \hat{T}.B. \text{ Jones} \]

independent of drop shape!
reconciliation

\[ F = \sum_i \sigma_i A_i - \frac{1}{2} \int \mathbf{D} \cdot \mathbf{E} dV \]

**macroscopic picture**

\[ \approx \sum_i \sigma_i A_i - \frac{\mathcal{E}_0 \mathcal{E}_r}{2d} A_{sl} U^2 \]

\[ = \sigma_{lv} A_{lv} + \left( \sigma_{sl} - \frac{\mathcal{E} \mathcal{E}_0}{2d} U^2 - \sigma_{sv} \right) A_{sl} \]

\[ \sigma_{sl}^{\text{eff}} \]

**modified Young equation**

**electrical force / unit length**

\[ f_{el} = \int_0^{h \gg d} p_{el}(z) \, dz \]

**microscopic picture**

Maxwell stress:

\[ p_{el} = -\frac{\mathcal{E}_0}{2} E(r)^2 \]

\[ \Delta p = \sigma_{lv} \cdot \mathbf{k} - \frac{\mathcal{E}_0}{2} E(r)^2 \]

**modified capillary equation**

\[ f_{el} = \int_0^{h \gg d} p_{el}(z) \, dz \]

\[ \Rightarrow \text{both pictures are equivalent on a scale } \gg d_{\text{ins}} \]
contact angle saturation: *the* mystery of EW

what causes deviations from EW equation at high voltage?

\[
\cos(\theta(U)) = \cos\theta_Y + \frac{1}{2} \frac{\varepsilon_0 \varepsilon \U^2}{d\sigma_{lv}}
\]

diverging electric fields can cause dielectric breakdown of coating!
refined version: local breakdown at contact line

self-consistent calculation of field and surface configuration +
local breakdown upon exceeding \( V_T \)

permanent injection (or adsorption) of charges produces irreversibility and screens charges from surface beyond threshold voltage $V_T$:

\[
\gamma_{LV} [\cos \theta(V) - \cos \theta_0] = \frac{1}{2} \frac{\varepsilon_0 \varepsilon_r}{d} (V - V_T)^2
\]

‡ AC voltage suppresses ion adsorption

(Verheijen, Prins, Langmuir 1999)
contact line instability

2d Coulomb explosion: balance of capillary energy and electrostatic energy

top view:

water-silanized glass; f = 200 Hz

summary – electrowetting basics

- Contact angle reduction arises from minimization of interfacial and electrostatic energy (maximum of capacitance).

- Equilibrium shape is determined by local balance of Maxwell stress and Laplace pressure.
  - Local contact angle = Young’s angle.
  - Diverging curvature near contact line.
  - Equivalence of force balance and effective surface tension approach on scales $>> d$.

- Contact angle saturation arises from non-linearities in diverging electric fields at contact line.
  - C.A. saturation can be minimized by use of high quality substrates, AC voltage, ambient oil.
out line

- introduction
- electrowetting basics
  - origin of the EW effect
  - electromechanical model
  - contact angle saturation
- challenges and physical principles of EW devices
- FUNdamental fluid dynamics with EW
  - contact angle hysteresis in EW
  - contact line motion in ambient oil
  - electrowetting driven drop oscillations and mixing flows
  - channel-based microfluidic systems with EW functionality
- conclusion
**some applications of EW**

- **tunable lenses** (varioptic, Philips)
- **EW displays** (Philips ÷ liquavista)
- **micromechanical actuation**
- **lab-on-a-chip**

Kuiper and Hendriks, APL 2004
courtesy of R. Hayes

![EW displays](image)

250 µm
challenges for EW-based microfluidic systems

- detachment / drop generation:
  - reproducible drop size
  - high throughput

- droplet motion:
  - high speed
  - low voltage

- drop merging & splitting:
  - reproducibility
  - drop size control

- mixing:
  - high mixing speed

- contamination
  - preventing evaporation
  - controlling adsorption (e.g. proteins)
drop actuation

patterned electrodes

\[ W = \sigma_{lv} A_{lv} + (\sigma_{sl} - \sigma_{sv}) A_{sl} - \frac{\varepsilon \varepsilon_0}{2d} U^2 A_{\text{drop-\text{el}}}(x) \]

\[ \Rightarrow \vec{F} = -\nabla W = \oint_{\partial A_{sl}} \left[ (\sigma_{sv} - \sigma_{sl}) + f_{el}(r) \right] r n \, ds \]

counter-acting forces:
- bulk viscous dissipation
- contact line friction

typical design: sandwich geometry
† no wires required

pioneering work:
- 27 CJ Kim (UCLA): Cho et al. JMEMS 2003