Lecture 12

Electrowetting

Dynamic modulation of the wetting properties of a surface has played a key role in the manipulation of droplets, especially in the "lab-on-a-chip" systems. Electrowetting (EW) is the technique to control the wetting behavior of a droplet on surface using electric field. Over one century ago, Lippmann first discovered the phenomenon of electrocapillary,[1] that the interfacial tension of mercury in contact with an electrolyte solution changes with the voltage applied between mercury and the solution before electrochemical reactions take place (Figure 12.1a). In modern pictures, the contact angle of a electrolyte droplet decreases on a metal surface when voltage is applied. However, such device has strong drawbacks as the voltage operation window is very narrow. Nowadays, the electrowetting is mostly carried out in a device setup so-called the "electrowetting on dielectrics" (EWOD), with a thin dielectric layer sandwiched between the electrode and the droplet (Figure 12.1b). The voltage applied between the droplet and the metal electrode can be much higher than the metal-droplet system. In this lecture, we will combine our knowledge of wetting and electrostatics to explain the mechanism behind electrowetting.
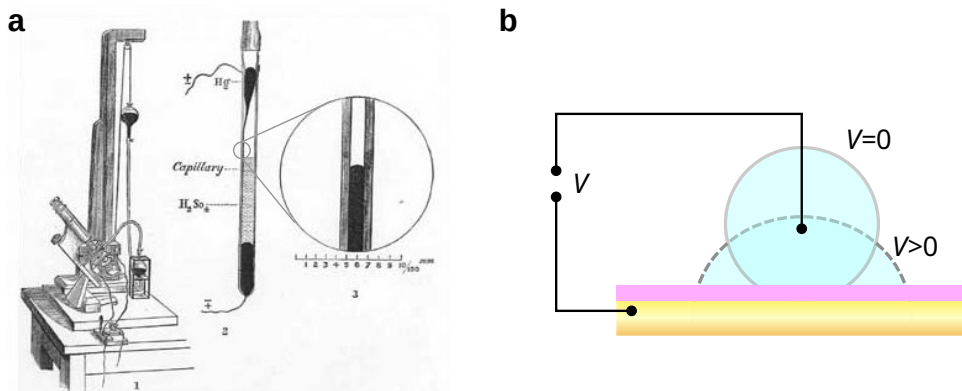

Figure 12.1: Electrowetting phenomena. (a) Initial electrocapillary experiments of Lippmann. (b) Modern application of electrowetting on dielectrics (EWOD).

12.1   Mechanism of electrowetting

From the Young-Dupré equation (2.3), $\gamma_L(1 + \cos\theta) = \Delta W_{SL}$, if θ reduces upon applied voltage, ΔW_{SL} should increase with external voltage. How can we understand the change of ΔW_{SL}? Consider an EW experiment on metal, the contact angle change can be observed up to a threshold voltage V_{th}. The current I passing through the droplet is negligible when $V < V_{th}$, which builds up the electrical double layer at the metal-liquid interface and the system behaves like a capacitor. On the other hand, when $V > V_{th}$, I linearly increase V due to electrochemical reaction, and the system behaves like a resistor (Figure 12.2)
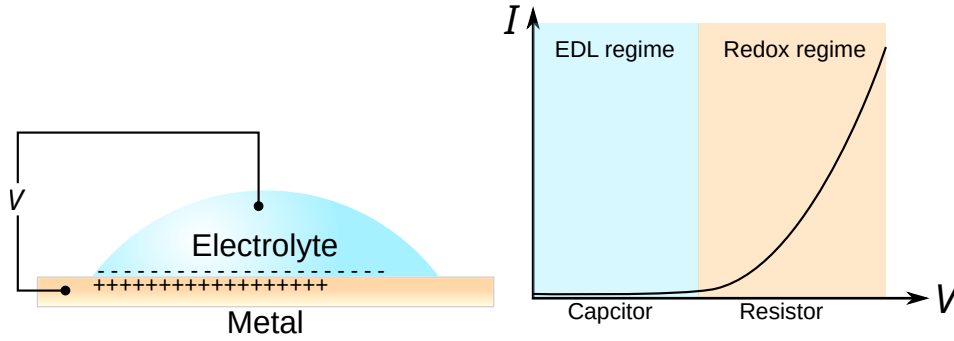

Figure 12.2: Regime of electrowetting. Left: charges accumulate at the liquid-metal interface when an bias is applied. Right: the current I remains small within the capacitor-like EDL regime, while I greatly increases after the voltage threshold is reached, turning into the resistor-like electrochemistry regime.

Within the electrical double layer regime, the surface charge density increases when interfacial potential ψ_0 arises. Since the EDL is confined within a thickness at the order of several nanometers, much smaller than the size of the droplet, it can be regarded as a 2D adsorption layer. According to the Gibbs-Duhem equation in Lecture 3, $SdT + Ad\gamma_{SL} + \sum_i n_i d\mu_i = 0$, where A is the contact area, n_i is numbers of ionic specie i in the EDL and μ_i is the electrochemical energy of specie i. At constant T, the change of γ_{SL} is expressed ad:

$$d\gamma_{SL} = -\sum_i \frac{n_i}{A} d\mu_i = -\sum_i \frac{i}{\Gamma_i} d\mu_i \tag{12.1}$$

where Γ_i is the 2D adsorption density of specie i. Since the electrochemical potential $\mu_i = z_i e\psi$, the differential change of γ_{SL} is then:

$$d\gamma_{SL} = -\sum_i \Gamma_i z_i e d\psi$$
$$= -\sigma_L d\psi \tag{12.2}$$

where $\sigma_L = \sum_i \Gamma_i z_i e$ is the surface charge density in the liquid phase. Using the concept of

EDL capacitance in Lecture 11, $\sigma_L = C_{EDL}\psi$, the total change of γ_{SL} is integrated as:

$$\begin{aligned}
\Delta\gamma_{SL} &= -\int_0^V \rho\,d\psi \\
&= -\int_0^V C_{EDL}\psi\,d\psi \\
&= -\frac{1}{2}C_{EDL}V^2
\end{aligned} \tag{12.3}$$

where C_{EDL} is the differential capacitance of the EDL and V is the surface potential of the electrolyte. C_{EDL} can be solved using methods such as the Debye-Hückel / Gouy-Chapman equations. Since γ_0^2 is always larger than 0, γ_{SL} decreases with the surface potential. From the definition we know $\Delta\gamma_{SL} = \gamma_S + \gamma_L - \gamma_{SL}$. Since the changes of γ_S and γ_L are negligible, $\Delta(\Delta W_{SL}) = -\Delta\gamma_{SL} > 0$. Now we can put everything together: in the EW process, applying voltage $V \rightarrow$ surface adsorption σ_L increases $\rightarrow \gamma_{SL}$ decreases $\rightarrow \Delta W_{SL}$ increases $\rightarrow \theta$ decreases. From the Young-Dupré equation we can define the quantity of electrowetting $\eta = \Delta\cos\theta = \frac{C_{EDL}}{2\gamma_L}V^2$. η_{DH} using the Debye-Hückel approximation is then:

$$\eta_{DH} = \frac{1}{2\gamma_L}\frac{\varepsilon_0\varepsilon_r}{\kappa^{-1}}V^2 \tag{12.4}$$

The change of contact angle is most prominent when the initial contact angle θ_Y, described by the Young's equation, is large. When $\kappa^{-1} = 1nm$, and V=300 mV, the theoretical contact angle change $\Delta\theta \sim 23°$ when θ_Y= 90°. However, $\Delta\theta$ becomes as large as 54° when θ_Y approaches 180°. The latter case can be achieved when the droplet is immersed in oil.

12.2 Electrowetting on dielectrics

However, we can see from the previous discussions, that such metal-electrolyte setup has certain disadvantages:

- The operational window of V is very small (at the order of 100 mV).

- The behavior of η depends strongly on the electrolyte type and concentrations.

To overcome such problems, practical electrowetting is usually performed on a dielectric layer with low surface tension (e.g. Teflon). The voltage is applied between the droplet and an electrode below the dielectric layer, and the current is usually negligible due to the extremely large resistance of the dielectric layer (Figure 12.3 left). When the external voltage is applied, the system has an effective capacitance C_{eff} (Figure 12.3 right), which consists of two capacitances in series:

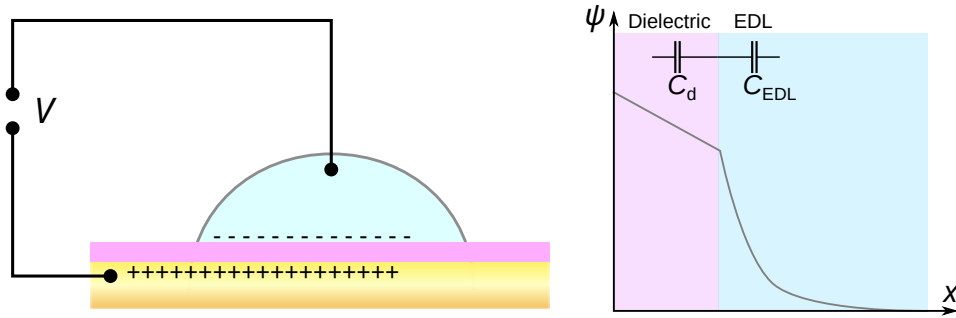$$C_{eff}^{-1} = C_{EDL}^{-1} + C_d^{-1} \tag{12.5}$$

Figure 12.3: Electrowetting on dielectrics (EWOD). Left: scheme of a typical EWOD setup. Right: effective capacitance of the EWOD system.

where $C_d = \varepsilon_0 \varepsilon_d / d$ is the geometric capacitance of the dielectric layer with relative permittivity ε_d and thickness d. As seen from our analysis in Lecture 11, C_d is usually much smaller than C_{EDL}. Therefore we can usually approximate $C_{\mathrm{eff}} \approx C_d$.

On a dielectric layer, the contact angle change is then:

$$\eta_{\mathrm{EWOD}} = \frac{1}{2\gamma_{\mathrm{L}}} \frac{\varepsilon_0 \varepsilon_d}{d} V^2 \tag{12.6}$$

Typically in the EWOD setup, Teflon with $\varepsilon_d = 2.1$ and $d \approx 1 \ \mu$m are used. Therefore V can be applied up to the order of 10^2 V before breakdown of the dielectric layer. Although theoretically the contact angle should constantly decrease when V is applied, in experiments people usually observe that θ saturates at an angle θ_{s} (ca. $30° \sim 80°$ depending on the system). This phenomenon is known as the contact angle saturation and poses as one of the challenges in EWOD applications. The exact cause of contact angle saturation is not well-understood. Some theories ascribe such phenomena to the diverging electric fields at the three-phase contact line (TCL) at low contact angles. When ε_{s} is reached, the electric field strength at the TCL is extremely high which causes several nonlinear effects at the boundary, each individually causes the contact angle saturation. A detailed discussion can be found in Ref. [2].

One method to compensate for the effect of contact angle saturation, is to use a system with very high initial contact angle θ_{Y}. As discussed previously, this can be achieved in a water-oil system. A few techniques have made use of such setup. For instance, the electrowetting display. A pixel of an EW display unit consists of transparency aqueous electrolyte solution, hydrophobic dielectric layer and transparent electrode (such as indium tin oxide, ITO), and a colored oil droplet (Figure 12.4 a). Before applying the external voltage, the colored oil (small surface tension) wets the dielectric layer and the display unit appears as dark. By increasing V, the interfacial work ΔW_{SL} between the aqueous solution and the dielectric layer increases and oil is depleted from the dielectric surface, making the display unit bright (Figure 12.4 b). A great advantage of EW display is its ultra low energy cost, since theoretically only a few amount of energy is need to charge the capacitors in the EWOD setup, and can be used for long-term display applications.

Another application of EWOD is to drive droplets in a lab-on-a-chip instruments,[3] where

a

Aqueous Electrolyte Solution

$V=0$

Colored oil

Hydrophobic Dielectrics

Transparent Electrode

White light
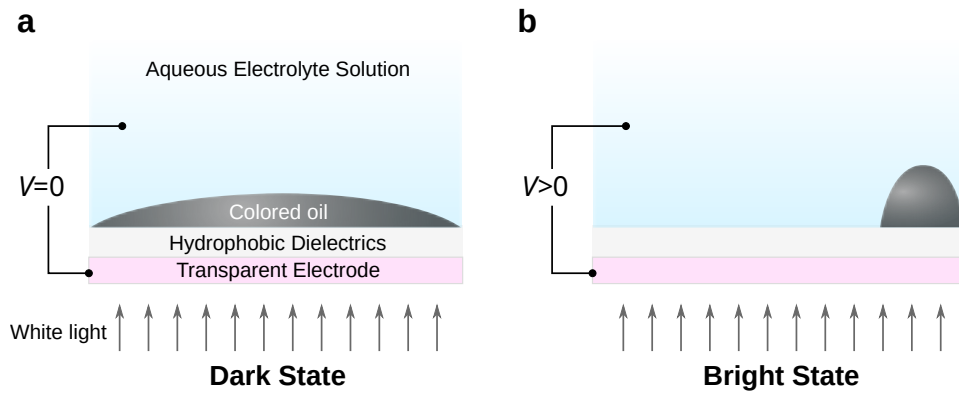
Dark State

b

$V>0$

Bright State

Figure 12.4: Operation modes of an EW display unit at (a) dark state with $V = 0$ and (b) bright state with $V > 0$.

the droplet is sandwiched between dielectric layer with a grid of electrodes. By sequentially applying voltage to the neighboring electrodes, motion of the droplet on the dielectric surface can be achieved.

References

(1) Bard, A. J.; Faulkner, L. R.; Leddy, J.; Zoski, C. G., *Electrochemical methods: fundamentals and applications*; Wiley New York: 1980; Vol. 2.

(2) Mugele, F.; Baret, J.-C. *J. Phys. Condens. Matter* **2005**, *17*, R705–R774.

(3) Shen, H.-H.; Fan, S.-K.; Kim, C.-J.; Yao, D.-J. *Microfluidics and Nanofluidics* **2014**, *16*, 965–987.