

## 시스템 내 이온수의 제한성을 고려한 전기습윤현상에 대한 연구

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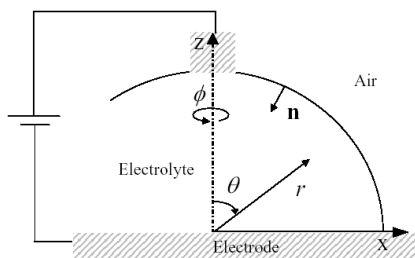
**Electrowetting phenomena including ion number constraints**

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**Introduction**

Electrowetting, the wettability change of liquid on the solid substrate by an electric field, is prevailing due to the applicability on the microfluidic devices, such as pump, lens, actuator, and so on (Quillet and Berge[1]). There may be mainly two kinds of approaches on electrowetting. The first is thermodynamic approach. Based on thermodynamics, electrowetting has been regarded as a kind of electrocapillarity. It can be represented by the Lippmann-Young equation as a typical relationship between contact angle and applied potential. On the other hand, as a complement, the possibility of electromechanical approach on electrowetting, which is based on the electric interactions and mechanical equilibrium, was suggested (Digilov[12]). With the electromechanical approach, Jones[14] and Kang[15] have recovered the Lippmann-Young equation. The wetting tension on the TCL was also obtained and analyzed on the electromechanical approach (Kang[16]). Aforementioned, the electromechanical approach can provide more concrete understanding, especially for the region near the TCL, on the electrowetting, rather than the thermodynamic approach. For the same reason, the present work is based on the electromechanical approach.

In the electromechanical approach on the usual electrolyte system, the electrostatics is governed by the Poisson-Boltzmann equation (PB). But, in a system smaller than the micron scale, the assumption of the PB for the infinite domain is not satisfied. the bulk properties are affected by the applied potential. The Poisson and Nernst-Planck equation (PNP) can be used (Daiguji et al.[11]). In this work, unknown bulk quantities are determined by the conservation of total number of each ions in the whole system, so called ion number constraints. Afterwards, the PNP with the ion number constraints will be called as the PNPC.



**Figure 1.** Electrolyte droplet on an electrode, symmetric on the  $z$  axis.

**Analysis**

For an electrolyte droplet on an electrode, being immersed in another fluid (such as air) (see Figure

1), electrostatic potential ( $\phi$ ) inside an  $z:z$  electrolyte ( $z_+ = -z_- = z$ ) droplet is governed by the Poisson-Boltzmann (PB) equation,

$$\nabla^2 \phi = \left( \frac{kT}{ze} \right) \kappa^2 \sinh \left( \frac{ze\phi}{kT} \right).$$

Here,  $\kappa^{-1} = (2z^2 e^2 n_0 / \epsilon \epsilon_0 kT)^{-1/2}$  represents the Debye length inside the droplet. On the other hand, the PNPC equation is as following,

$$\nabla^2 \phi + \frac{ez}{\epsilon \epsilon_0} \left[ A_+ \exp \left( \frac{-ze\phi}{kT} \right) - A_- \exp \left( \frac{ze\phi}{kT} \right) \right] = 0$$

$$A_+ = n_0 V / \int_V \exp \left( \frac{-ze\phi}{kT} \right) dV, \quad A_- = n_0 V / \int_V \exp \left( \frac{ze\phi}{kT} \right) dV$$

where  $n_0$  is the common initial concentration of each ion species and  $V$  is the total volume of the system. For the surface force, there are two contributions, electrostatic and osmotic interactions.

$$\mathbf{f} = \mathbf{T} \cdot \mathbf{n} = \left\{ \epsilon \epsilon_0 \mathbf{E} \mathbf{E} - \left( \frac{1}{2} \epsilon \epsilon_0 E^2 + \Pi \right) \mathbf{I} \right\} \cdot \mathbf{n}, \quad \Pi = kT \left( A_+ \exp \left( \frac{-ze\phi}{kT} \right) + A_- \exp \left( \frac{ze\phi}{kT} \right) \right) - \Pi_{standard}$$

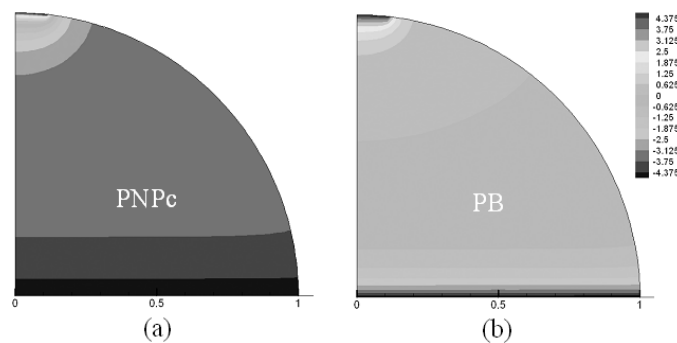
where  $\mathbf{E}$  is an electric field,  $E = |\mathbf{E}|$ ,  $\mathbf{I}$  is an isotropic tensor, and  $\mathbf{n}$  is the normal vector to the droplet surface (in this case, the direction is inward the droplet surface.).  $\Pi$  denotes the osmotic contribution. For the prediction of the deformed drop surface, it is simplified as a 2-D the cross-sectional curve near the contact point as  $x = x(z)$ . With the fixed contact point, the final second order ordinary differential equation for shape prediction can be represented as following,

$$\mathbf{n} \cdot (\mathbf{n} \cdot \mathbf{T}) = \gamma \frac{|x''|}{(1 + (x')^2)^{3/2}}, \quad x(0) = 1.0, x'(0) = 0$$

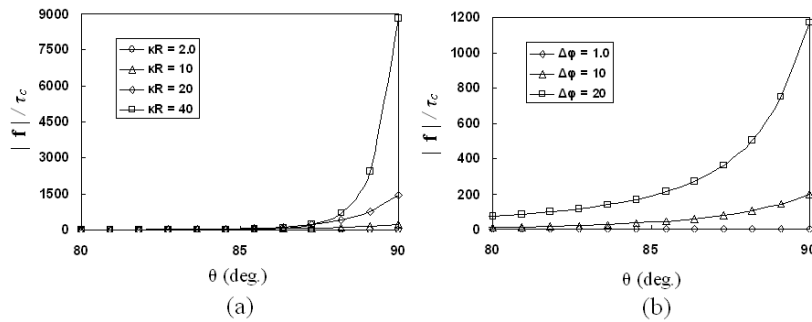
where,  $\mathbf{n}$  is an outward normal vector,  $\mathbf{T}$  is a stress tensor,  $\gamma$  is a liquid-gas interface tension.

## Results and discussion

Potential distribution was obtained from two governing equations PB and PNPC. Potential contours are shown in the figure 2 for the case of  $\kappa R = 10$  and  $\Delta\phi = 10$ .

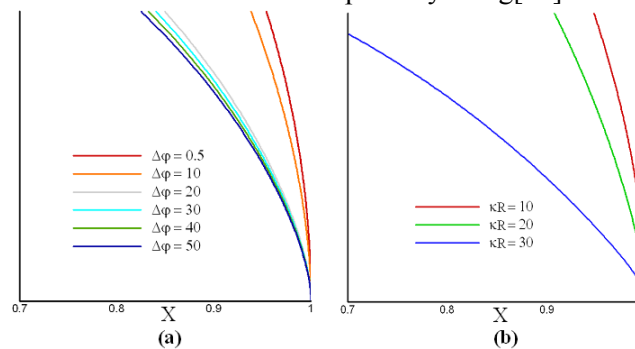


**Figure 2.** Potential contours inside the droplet based on two governing equations. In both the cases,  $\kappa R = 10$ ,  $\Delta\phi = 10$  ( $\phi_{top} = 5$ ,  $\phi_{bottom} = -5$ ). (a) Based on the PNPC equation. (b) Based on the PB equation.



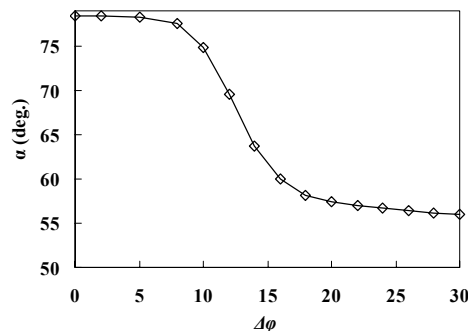
**Figure 3.** The distribution of the normalized magnitude of total surface force along the drop surface near the TCL. Symbols indicate the results for different (a)  $\kappa R$  (under the constant  $\Delta\varphi = 10$ ) and (b)  $\Delta\varphi$  (under constant  $\kappa R = 10$ ). Normalizing factor ( $\tau_c$ ) denotes the characteristic electric stress.  $\theta$  is an angle measured from the z-axis.

Figure 3 shows the distribution of the magnitude of total surface force along the drop surface for different  $\kappa R$  and  $\Delta\varphi$ , with respect to the azimuthal angle near the TCL region. The normalizing factor is the characteristic electric stress (at  $25^\circ\text{C}$ ,  $R = 1\text{mm}$ ,  $\tau_c \sim O(10^{-7})\text{N/m}^2$ ). In the usual cases ( $\kappa R \sim O(10000)$ ), the surface force can be regarded as a point force focused on the contact point. Young and Lippmann equation was derived based on this assumption by Kang[15].



**Figure 6.** Deformed shapes for different parameters. (a) external voltage ( $\Delta\varphi$ ) (constant  $\kappa R = 10$ ) (b) the ratio of the Debye length and the radius ( $\kappa R$ ) (constant  $\Delta\varphi = 10$ )

From the surface force distribution, deformed shape was predicted with a uniform surface tension ( $\tau_c R / \gamma = 0.00623$ ). In the Figure 6, according to  $\Delta\varphi$  and  $\kappa R$ , the curve for drop shape near the TCL is plotted. Remarkably, the curves for different external voltages are converged to a certain shape.



**Figure 7.** Macroscopic contact angle with respect to the variation of external voltage.

To conform this relation, we have calculated the macroscopic contact angle with different  $\Delta\varphi$  (See the Figure 7). The macroscopic contact angle was measured from the tangential line to the zero-stress

point ( $z = 0.201235 \sim 2l_D$ ). Contact angle is almost saturated according to the increase of an external voltage. It is similar to the experimental result qualitatively (Verheijen and Prins[13]).

### Concluding remarks

The present work was performed to elucidate the effect of the finiteness of ions on the charge-related wetting system. The geometric effect of the upper electrode was neglected. The shape of droplet near the contact line was simplified to a 2-dimensional curve with a fixed contact point and microscopic contact angle. The deformation of the droplet was approximated to be just a variation of the curvature of curve by surface force. The finiteness of ions in a closed system, like electrolyte droplet, can be modeled by the PNPC equation. Using the PNPC equation, the curve for contact angle saturation was predicted originally in theory and numerical approach. Consequently, the finiteness of ions can be a reason for the contact angle saturation in electrowetting for nano-sized, closed system.

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