

Pining phenomena of an evaporated droplet on the hydrophobic micro-textured surfaces

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1. Introduction

As like boiling, evaporation and condensation, the heat transfer mechanism with phase change is applied to the wide range of thermal hydraulic systems in the nuclear power plants. And this heat transfer mechanism is significantly influenced by the surface wetting conditions. Recently, to understand the enhancement mechanism of the heat transfer on the wetting surfaces, the phase change on the hydrophilic and hydrophobic surfaces is intensively investigated by the numerous researchers.

With the simple examples to understand the phase change on the surface wettability, we can easily consider an evaporated droplet on the surfaces. In the previous research, a droplet on a surface evaporated with the various evaporation modes [1]. During evaporation, the contact angle of a droplet is initially reduced while the contact radius of a droplet remains constant because of the pinning phenomena at the contact line of a droplet, i.e., this evaporation mode is known as the **constant contact radius (CCR)** mode. When the decreased contact angle reaches the receding contact angle, the contact radius is reduced while maintaining a constant contact angle, i.e., this evaporation mode is known as the **constant contact angle (CCA)** mode.

The emphasis of the droplet evaporation is that the transition from CCR to CCA modes is relative with the rate of the droplet evaporation, and it is markedly influenced by the surface wettability [2-4].

In this study, it is focused on the evaporation mode transition. Especially, the transition from CCR to CCA modes is investigated on the hydrophobic micro-textured surfaces. On the basis of the thermodynamics, the transition from CCR to CCA mode is theoretically analyzed. The thermodynamic model is developed to estimate the receding contact angle at the evaporation mode transition. Additionally, to compare between the theoretical model and experimental results, it is shown that the experimental receding contact angle is well-estimated by the receding contact angle with the theoretical model.

2. Thermodynamic analysis

If the states from 1 to 3 are defined as a droplet in air, an equilibrium droplet on a surface and a fully vaporized droplet, the history of the droplet can be simplified by the wetting and evaporation processes as shown in Fig. 1. Because a droplet on a surface reaches the equilibrium state rapidly enough to neglect the evaporation process, the wetting process from states 1 to 2 is dependent on isothermal and isochoric processes. Therefore, a system consisting of the droplet on the surface can be defined using the Helmholtz free energy. After the wetting process, the droplet on the surface undergoes evaporation. From state 2 to 3, if no mass transfer occurs because of external flow and temperature deviations, the droplet is diffusively evaporated by the difference in the vapor concentration and becomes fully vaporized. Because diffusive evaporation is a slow phenomenon, the temperature change due to evaporation is very small. In this case, we can assume that the evaporation process from states 2 to 3 is an isothermal and isobaric process, and that the system of the droplet on the surface can be defined by the Gibbs free energy [5].

Considering such a system, the Gibbs free energy is composed of the Gibbs free energies of the phases and interfaces:

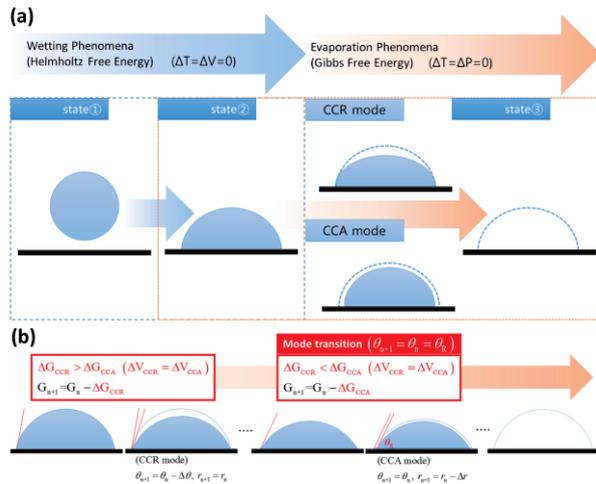


Fig. 1 History of an evaporated droplet on a surface (a) States (b) Mode transition during droplet evaporation.

$$\begin{aligned}
 G_{\text{system}} &= G_{\text{phase}} + G_{\text{interface}} \\
 &= G_L + G_V + G_S + G_{LV} + G_{SV} + G_{SL} \\
 &= (U + PV - TS)_L + (U + PV - TS)_V \\
 &\quad + (U + PV - TS)_S + (\sigma A)_{LV} + (\sigma A)_{SV} + (\sigma A)_{SL}
 \end{aligned} \quad (1)$$

where G , U , P , V , T , and S are the Gibbs free energy, internal energy, pressure, volume, temperature, and entropy of each phase, respectively. Additionally, A and σ are the interface area and surface tension between phases, respectively. Subscripts L, V and S denote the liquid, vapor, and solid phases, respectively, and subscripts LV, SV, and SL denote the liquid-vapor, solid-vapor and solid-liquid interfaces, respectively.

As shown in Fig. 1a, the mode transition from CCR to CCA modes during the evaporation process is generated, and a droplet becomes fully vaporized. As the system progresses thermodynamically to reach the equilibrium state rapidly, the droplet evaporates to decrease greatly the Gibbs free energy of the system and becomes fully vaporized (state 3). On the basis of the thermodynamic view described above, pinning phenomena at the contact line can be analyzed as shown in Fig. 1b.

A droplet with CCR evaporation initially shows a marked reduction in the Gibbs free energy compared to a droplet with CCA evaporation with an equivalent evaporated volume. The mode transition from CCR to CCA is generated when the contact angle of a droplet reaches the receding contact angle. Note that the decrease in the Gibbs free energy in the CCR mode is equivalent with that in the CCA mode.

On the basis of this thermodynamic analysis, a theoretical model was developed to estimate the receding contact angle at the evaporation mode transition. When we consider the decreased volume element of a droplet during the evaporation process from n^{th} to $n+1^{\text{th}}$, the decrease in the Gibbs free energy in the CCR to CCA modes can be described, respectively, as

$$\Delta G_{n+1}|_{\text{CCR}} = G_n(V_n) - G_{n+1}(V_{n+1})|_{\text{CCR}} \quad (2a)$$

$$\Delta G_{n+1}|_{\text{CCA}} = G_n(V_n) - G_{n+1}(V_{n+1})|_{\text{CCA}} \quad (2b)$$

During the evaporation process from n^{th} to $n+1^{\text{th}}$, we consider an equivalent volume between CCR and CCA mode.

$$V_n - V_{n+1} = \Delta V = \Delta V_{\text{CCR}} = \Delta V_{\text{CCA}} \quad (3)$$

Thermodynamically, between CCR and CCA mode, a droplet evaporates in a greatly decreasing mode of the Gibbs free energy. The evaporation mode transits from CCR to CCA when the decrease in the Gibbs free energy in CCR mode is equivalent in that in CCA mode. At this transition, a droplet has the receding contact angle.

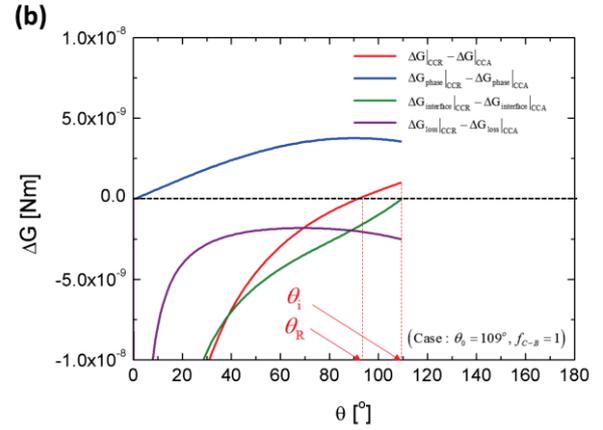
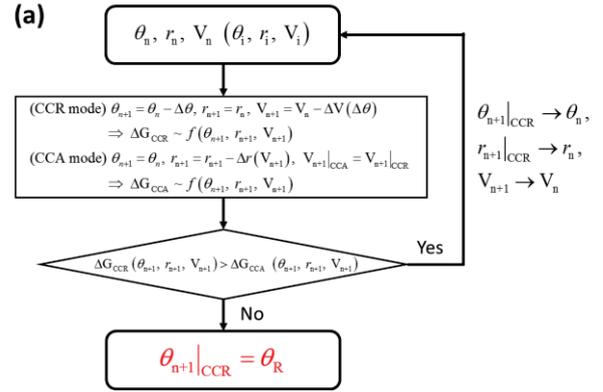


Fig. 2 (a) Flowchart of the theoretical model (b) Estimated receding contact angle on the theoretical model.

$$\begin{aligned}
 \theta_n &= \theta_R, \text{ at } \Delta G_{\text{CCR}}[\theta_n - \Delta\theta(\Delta V), r_n] \\
 &= \Delta G_{\text{CCA}}[\theta_n - \Delta\theta(\Delta V), r_n]
 \end{aligned} \quad (4)$$

where θ_n and θ_R are the contact angle of the n^{th} state during droplet evaporation and the receding contact angle at mode transition, respectively.

In a system with a diffusively evaporated droplet on the surface, the Gibbs free energy changes of the vapor and solid phases are smaller than the energy change of the liquid phase. Also, the internal energy change is negligible in an isothermal process. When the temperature and entropy terms in Eq.1 are expressed in terms of the Gibbs free energy loss, the difference between the decreases in energy with each mode in Eq. 4 can be expressed as

$$\begin{aligned}
 &\Delta G_{\text{CCR}}|_{n+1} - \Delta G_{\text{CCA}}|_{n+1} \\
 &= [V_{n+1}(P_{n+1}|_{\text{CCA}} - P_{n+1}|_{\text{CCR}})]_L \\
 &\quad + [\sigma(A_{n+1}|_{\text{CCA}} - A_{n+1}|_{\text{CCR}})]_{LV} \\
 &\quad + \sigma_{LV} \cos \theta (A_{n+1}|_{\text{CCA}} - A_{n+1}|_{\text{CCR}})_{SL} - \Delta G_{\text{loss-CCA}} \\
 &= \Delta G_{\text{bulk}} + \Delta G_{\text{interface}} - \Delta G_{\text{loss-CCA}}
 \end{aligned} \quad (5)$$

where the decreases in the Gibbs free energy terms of the bulk, interface and loss-CCA are the decreases due to the pressure difference between the different modes,

the area difference between the different modes and the energy loss in the CCA mode respectively.

In the previous research, it has been suggested that the moving contact line causes the additional energy due to the viscous dissipation [6, 7]. And Kang and Jacobi proposed the work of adhesion w related with the energy loss at a moving contact line such as [8]

$$\frac{w}{\sigma_{LV}} = \cos \theta_0 + \left[4 \left(\frac{(2 + \cos \theta_0)(2 - \cos \theta_0)^2}{4} \right)^{2/3} - 2(1 - \cos \theta_0) \right] / \sin^2 \theta_0 \quad (6)$$

where θ_0 is intrinsic contact angle. When a droplet evaporates in the CCA mode, the contact line of the droplet moves and the energy loss at the contact line can be generated. Therefore, in this study, to estimate the evaporation mode transition, the energy loss in the CCA mode is considered with the work of adhesion.

With the assumptions that a droplet on a surface is part of sphere and it is in the Cassie-Baxter state on the hydrophobic textured surfaces, the following equations for estimating the receding contact angle at the transition from CCR to CCA mode can be described as

$$\begin{aligned} \theta_n &= \theta_R \\ \text{when } \frac{2}{3} \sigma_{LV} \pi \left(\frac{r_n}{\sin \theta_{n+1}} \right)^2 (1 - \cos \theta_{n+1})^2 \\ & (2 + \cos \theta_{n+1}) \left\{ 1 - \left[\frac{(1 - \cos \theta_n)^2 (2 + \cos \theta_n)}{(1 - \cos \theta_{n+1})^2 (2 + \cos \theta_{n+1})} \right]^{1/3} \right\} \\ & + 2 \sigma_{LV} \pi r_n^2 \left\{ \frac{\sin^2 \theta_n}{\sin^2 \theta_{n+1} \cdot (1 + \cos \theta_n)} \times \right. \\ & \left. \left[\frac{(1 - \cos \theta_{n+1})^2 (2 + \cos \theta_{n+1})}{(1 - \cos \theta_n)^2 (2 + \cos \theta_n)} \right]^{2/3} - \frac{1}{1 + \cos \theta_{n+1}} \right\} \\ & + \sigma_{LV} \pi r_n^2 \left\{ 1 - \left(\frac{\sin \theta_n}{\sin \theta_{n+1}} \right)^2 \left[\frac{(1 - \cos \theta_{n+1})^2 (2 + \cos \theta_{n+1})}{(1 - \cos \theta_n)^2 (2 + \cos \theta_n)} \right]^{2/3} \right\} \\ & \times \left(f_{C-B} \cos \theta_0 - (1 - f_{C-B}) - \frac{w}{\sigma_{LV}} f_{C-B} \right) \quad (7) \\ & = 0 \quad (\theta_{n+1} = \theta_n - \Delta\theta). \end{aligned}$$

where f_{C-B} is the roughness ratio in the Cassie-Baxter state.

3. Validation with experimental results

The proposed theoretical model is a method for determining the most thermodynamically favored process in the CCR and CCA modes during evaporation. The model describes the life of a droplet during evaporation. Therefore, to estimate the receding

contact angle, the initial contact angle must first be estimated. In this study, the initial contact angle is estimated as a function of the surface conditions using Cassie-Baxter model [9]:

$$\cos \theta_i = -1 + f_{C-B} (\cos \theta_0 + 1) \quad (8)$$

where θ_i is initial contact angle.

On the basis of the estimated initial contact angle with the Cassie-Baxter model, by the iterative numerical process, the receding contact angle depending on the surface conditions is estimated by the theoretical model in which the receding contact angle as a function of the surface conditions must satisfy the relation that the decrease in the Gibbs free energy in the CCR mode is equivalent to that in the CCA mode as shown in Fig. 2a and 2b.

To validate the developed model, the receding contact angle during droplet evaporation was measured on hydrophobic textured surfaces. In this experiment, textured surfaces were fabricated with various chemical compositions and geometric morphologies to investigate the relation between the receding contact angle and the surface conditions. Surfaces with intrinsic contact angle of 109° were prepared with a self-assembled monolayer coating (HeptaDecaFluoro-1,1,2,2-tetrahydrodecyltrichloroSilane), as shown in Fig. 3a. The surfaces with micro-textures were fabricated in the ranges of $0.1 < f_{C-B} < 1.0$ using photolithography and conventional dry etching, as shown in Fig. 3b. The initial and receding contact angles during the evaporation of $6.3\mu\text{l}$ deionized water droplets were measured automatically with a goniometer.

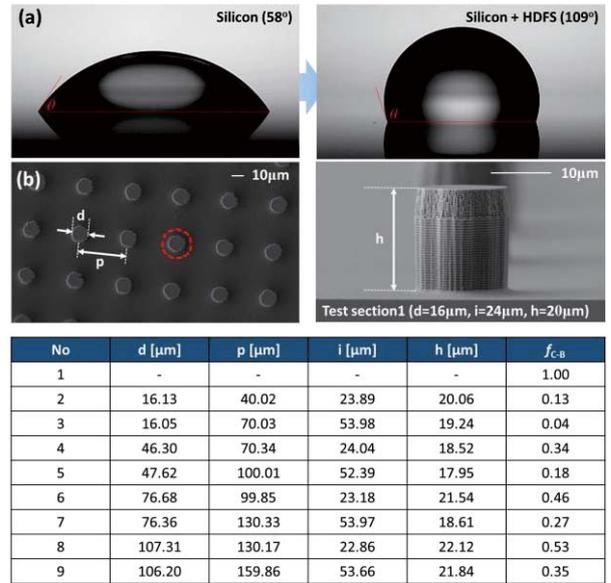


Fig. 3 (a) Intrinsic contact angle w/ and w/o self-assembled monolayer coating, (b) Geometrical morphology of micro-textured surfaces

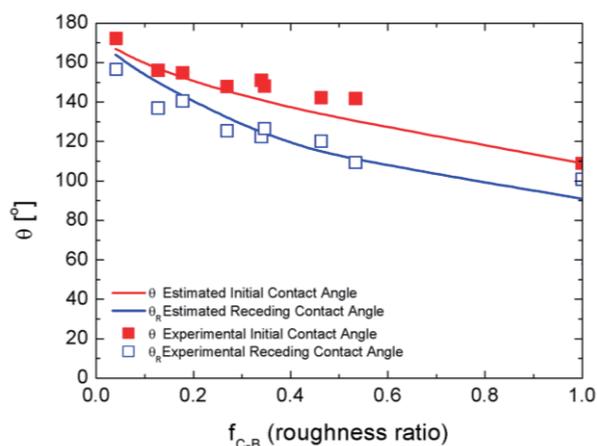


Fig. 4 Comparison between experimental and estimated (initial and receding) contact angles.

The receding contact angles on the experimental surfaces were also estimated using the proposed theoretical model as functions of the surface conditions. The initial contact angle was estimated using the wetting Cassie-Baxter model. As shown in Fig. 4, the experimental receding contact angle is well-estimate by the developed model.

4. Conclusions

This study was performed to investigate the pinning phenomena of an evaporated droplet on the hydrophobic micro-textured surfaces. The pinning phenomena at the contact line were shown theoretically to be due to the most favorable thermodynamics process that caused the Gibbs free energy to rapidly reach an equilibrium state during droplet evaporation.

The evaporation mode underwent a transition when the decrease in the Gibbs free energy was equivalent for the CCR and CCA modes. On the basis of the analysis described here, a theoretical model was developed to estimate the receding contact angle at the mode transition as a function of the surface conditions. The theoretical model to estimate the evaporation mode transition was verified by comparison between the experimental and modeled receding contact angles.

ACKNOWLEDGEMENT

This work was supported by the National Research Foundation of Korea (NRF) Grants funded by the Korean Government (MSIP) (2015R1C1A1A0203775 6). Experiments at the Pohang Light Sources were supported in part by MSIP and POSTECH.

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