

Critical Point Dewetting: the role of the gravity and the long-range force

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通常、2液相分離系においては、臨界点近くで片方の液相が固体基板を覆ういわゆる臨界点濡れ現象 (critical point wetting) が観測される。ところが、液体-基板間の強い長距離相互作用と重力ポテンシャルとが競合している場合、全く逆の "critical point dewetting" と呼ぶべき現象が起こりうる。我々は、液体 Se-Tl 系と石英基板の間の濡れの振る舞いを調べ、その結果、この "critical point dewetting" 現象を観測した。

Near the critical temperature of a immiscible binary liquid system, a solid substrate is usually covered completely by one of the liquid phases. This phenomenon is called the "critical point wetting", which is predicted by Cahn in 1977 [1]. He argued that the complete wetting takes place inevitably in any three-phase system when the temperature is sufficiently close to the critical point. Indeed, the critical point wetting has been confirmed for many fluid systems experimentally [2].

On the other hand, it is suggested from a theoretical consideration that the critical point wetting does not necessarily takes place when both the long-range force between the substrate and the gravity are present [3]. For example, when a wetting film (phase 2) with thickness l is present between the bulk liquid phase (phase 1) and the solid substrate (phase s), a grand potential $\Omega(l)$ per unit area can be written in the following form:

$$\Omega(l) - \Omega(0) = \sigma_{2s} - \sigma_{1s} + \sigma_{12} + W(l) + |\delta\rho g z|l, \quad (1)$$

where σ_{ij} are the surface tensions between i and j phases, $\delta\rho$ is the difference of the mass density between the two liquid phases, g is the gravitational acceleration, z is the height from the bulk meniscus and $W(l)$ is the free energy due to the long-range interaction per unit area of the wetting film. $W(l)$ depends on l as $W(l) \simeq -H/12\pi l^2$ for large l and $W(l) \simeq \sigma_{1s} - \sigma_{2s} - \sigma_{12}$ for $l \rightarrow 0$. Here, H (< 0) is the Hamaker constant. This grand potential has two minima: one is located at $l = 0$ and the other is at $l = l^* = (-H/6\pi|\delta\rho g z|)^{1/3} > 0$. The former corresponds to the non-wetting state, and the latter to the wetting state. The difference of the grand potential between these two states can be written as

$$\Omega(l^*) - \Omega(0) = \sigma_{2s} - \sigma_{1s} + \sigma_{12} + \frac{3}{2} (-H/6\pi)^{1/3} |\delta\rho g z|^{2/3}. \quad (2)$$

When $\Omega(l^*) - \Omega(0)$ is negative (positive), the wetting state is more stable (unstable) than the non-wetting state.

In the vicinity of the critical temperature T_c of the liquid-liquid phase separation, the variables in the equation (2) depend on the reduced temperature $t = (T_c - T)/T_c$ as $\sigma_{1s} - \sigma_{2s} \sim t^{\beta_1}$, $\sigma_{12} \sim t^{2\nu}$ and $-H \sim |\delta\rho| \sim t^\beta$, where $\beta_1 \sim 0.8$, $2\nu \sim 1.3$ and $\beta \sim 0.33$ are critical exponents. Therefore, $\Omega(l^*) - \Omega(0) \sim -At^{\beta_1} + Bt^{2\nu} + Ct^\beta |z|^{2/3}$, where A, B and C are positive proportional coefficients. If $C = 0$, which corresponds to the absence of the long-range interaction (i.e. $H = 0$) or gravity (i.e. $g|z| = 0$), $\Omega(l^*) - \Omega(0)$ becomes negative for a sufficiently small t because $\beta_1 < 2\nu$, and this coincides with the Cahn's prediction. On the other hand, if $C \neq 0$, the $Ct^\beta |z|^{2/3}$ term becomes dominant for $t \rightarrow 0$, and $\Omega(l^*) - \Omega(0)$ becomes positive, indicating that the critical point dewetting takes place for the system with finite $|z|$ and long-range force.

In the present work, we have studied the wetting phenomena of liquid Se-Tl system on a quartz substrate by photography and ellipsometry. Liquid Se-Tl system has a miscibility gap

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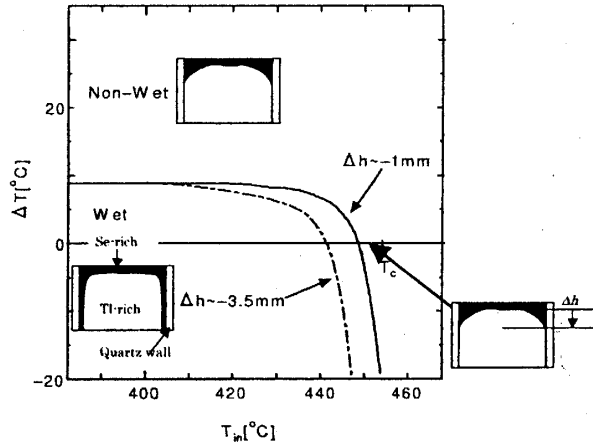


Fig.1: The wetting phase diagram on the $T_{\text{in}}-\Delta T$ plane [3], where T_{in} is the internal temperature of the bulk liquid sample and ΔT is the temperature difference between the wall temperature T_{wall} and T_{in} . The insets show schematically the shape of the two liquid phases near the quartz wall. The solid and the dot-dashed lines indicate the boundary between the wetting and the non-wetting states for $\Delta h \sim -1\text{mm}$ and $\sim -3.5\text{mm}$, respectively, where Δh is the height of the three-phase contact line measured from the bulk meniscus.

in the Se-rich region with a critical point at $T_c = 454^\circ\text{C}$ and $X_c = 92.05 \text{ at.}\%$ Se. Liquid Se-Tl is particularly interesting, because it is a unique system with combination of the large long-range force and the large mass density difference $\delta\rho$. In addition to the gravity, we introduced temperature difference ΔT between the internal temperature T_{in} of the bulk sample and the wall temperature T_{wall} as another external field to control the surface state of the system. ΔT can be used to shift the chemical potential near the surface from the two-liquid coexistence value, and this affects the wetting properties strongly. Details of the experimental set-up were described elsewhere [3].

We observed that the Se-Tl system does not show the critical-point wetting near the liquid-liquid critical point. On a contrary, when the temperature goes down from the critical point, a Se-rich wetting film intrudes between the Tl-rich bulk liquid and the silica wall. Namely, the "critical point dewetting" is observed. Furthermore, we observed that the wetting film disappears when the silica wall is slightly heated up relative to the bulk liquid sample. Figure 1 shows the observed wetting phase diagram on the $T_{\text{in}}-\Delta T$ plane. Below the phase boundary, the Se-rich wetting film covers the Tl-rich bulk liquid, while it disappears at high ΔT or at high T_{in} region. The critical point ($T_{\text{in}} = T_c$ and $\Delta T = 0^\circ\text{C}$) is located in the non-wetting region.

Near the critical temperature T_c , it is observed that the height Δh of the three-phase contact line measured from the bulk meniscus changes gradually with ΔT , and this result suggests that downward spreading of the wetting film is blocked by the gravitational potential in this temperature region.

In order to interpret the observation, we constructed a model grand potential, incorporating the long-range interaction, the temperature difference and the gravity. We found that this grand potential reproduces the observed behavior qualitatively [3]. The apparent absence of the critical-point wetting has been qualitatively explained by taking the combined effects of gravity and long-range interaction [3].

References

- [1] J. W. Cahn, J. Chem. Phys. **66** (1977) 3667
- [2] D. Bonn and D. Ross, Rep. Prog. Phys. **64** (2001) 1085, and references therein.
- [3] Y. Ohmasa, S. Takahashi, K. Fujii, Y. Nishikawa and M. Yao, submitted to J. Phys.: Condens. Matter