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To cite this article: Y Ohmasa et al 2008 J. Phys.: Conf. Ser. 98 062026

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Critical Point Dewetting: competition between the gravity and the dispersion force

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Abstract. Near the critical temperature of an 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, and have been confirmed for many fluid systems experimentally. However, we found that liquid Se-Tl system on a quartz substrate 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 quartz wall. This result is a clear evidence of the "critical point dewetting" phenomenon. It is suggested from a theoretical consideration that the critical point dewetting takes place as a result of the competition between the long-range dispersion force and the gravity.

1. Introduction
In recent years, wetting transitions of liquid systems on substrates have attracted great interests not only for applications but also from the viewpoint of fundamental material science [1]. One of the interesting subject in this area is the influence of a long-range interatomic interactions on the wetting behavior [2]. The long-range dispersion force between the wetting film and the substrate depend strongly on their dielectric permittivity [3]. Therefore, wetting behaviors of liquid metals and semiconductors are particularly interesting subject because their dielectric permittivity depends strongly on temperature, density and composition.

In our recent works, we have studied experimentally the wetting phenomena of liquid Se-Tl system on a quartz substrate [4] [5]. Liquid Se-Tl system has a miscibility gap in the Se-rich region with a critical point at $T_c = 454^\circ C$ and $X_c = 92.05$ at.% Se [6, 7]. Liquid Se-Tl is a mixture of a semiconductor (liquid Se) and a metal (liquid Tl), and the phase-separated Se-rich and Tl-rich phases have substantially different electronic and dielectric properties [6], and dramatic changes in long-range dispersion force are expected.

We observed that a thin layer of the Se-rich liquid phase intrudes between the Tl-rich liquid phase and the quartz substrate. Surprisingly, this wetting film disappears near the critical temperature [4]. This is a completely opposite phenomenon to the Cahn’s "critical point wetting", and cannot be explained by his theory [8].

Cahn’s critical point wetting theory is based on the short-range interatomic interactions and the mean field theory. For example, when a immiscible binary liquid system (say, A-B mixture) with critical concentration is on a solid substrate, this theory predicts that one of the liquid phases (say, A-rich phase) spread over the substrate when the temperature is sufficiently close.
to the critical point. Cahn’s theoretical prediction have been confirmed for many fluid systems experimentally [1].

On the other hand, other possibilities, such as ”critical point drying”, ”critical point partial drying” and ”absence of critical point wetting”, have been discussed theoretically. The ”critical point drying” means the other liquid phase (B-rich phase) covers the substrate near the critical point, and it is a counterpart of the critical point wetting [9]. The ”critical point partial drying” and the ”absence of critical point wetting” are predicted by Ebner and Saam in 1987. Taking into account the long range interaction, they indicated that critical point wetting or drying does not necessarily occur, and, in some cases, the partial wetting state can prevail up to the critical temperature.

However, the behavior of the liquid Se-Tl system on quartz is different from the above mentioned wetting phenomena. In this case, a phase transition from complete to partial wetting takes place as the critical point is approached. This wetting phenomenon is called ”critical point dewetting” [10].

In order to interpret the observation, we constructed a model grand potential, incorporating the long-range interaction, the temperature gradient and the gravity. We found that this grand potential reproduces the observed behavior qualitatively [4]. The apparent absence of the critical-point wetting has been qualitatively explained by taking the combined effects of gravity and long-range interaction [4].

In the present article, we explain briefly our recent experimental results on the wetting behavior of liquid Se-Tl system on a quartz substrate, and its theoretical aspects.

2. Experimental
The liquid Se-Tl sample with the critical concentration (92.05 atomic % Se) was encapsulated in a rectangular quartz cell. The cell was put in a furnace with a small optical window through which one of the vertical surfaces of the cell was observed by a CCD camera (Minolta Dimage 7). The furnace was designed to control the temperature of the surface of the cell, T_{surf}, independently of that in the interior of the cell, T_{in}. Their difference, ΔT = T_{surf} − T_{in}, can be used as an external field to control the surface state. Further details of the experimental set-up and the sample preparation procedure have been given in a previous paper [4].

Since the Se-Tl sample is opaque, one can observe only the interface between the liquid sample and the wall of the quartz cell. When the liquid sample is in the partial wetting state, the three phase contact line which separates the two liquid phases is observed in the photo-images. We define the height of the three phase contact line and the bulk meniscus, h_{TPCL} and h_{bulk}, respectively, and their difference as Δh = h_{TPCL} − h_{bulk} as shown in Fig.1. On the other hand, when one of the two-phase separated liquid phases (in this case, Se-rich phase) completely wets the quartz wall and intrudes between another phase (Tl-rich phase) and the quartz wall, the three phase contact line moves downward and finally disappears. In this case, only the wetting phase is visible in the photo-images.

3. Results and Discussion
Figure 2 shows the observed wetting phase diagram on the T_{in}-ΔT plane. It is observed that the Se-Tl system does not show the critical point wetting. Indeed, the critical point (T_{in} = T_c and ΔT = 0°C) is located in the non-wetting region. On a contrary, when the temperature is decreased from the critical point along the Line (A) in the figure, 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 with keeping T_{in} constant (Lines (B) and (C)).
We observed that the Se-rich wetting film intrudes gradually with decreasing $\Delta T$ when $T_{\text{in}}$ is close to the critical temperature $T_c$ (Line (C)), while it spreads suddenly when $T_{\text{in}}$ is much lower than $T_c$ (Line (B)). This trend can be confirmed quantitatively by measuring $\Delta h$ as a function of $\Delta T$ and $T_{\text{in}}$. Figure 3 shows the $\Delta T$-dependence of $\Delta h$ at various $T_{\text{in}}$. When $T_{\text{in}}$ is close to $T_c$, $\Delta h$ moves downward gradually with decreasing $\Delta T$. On the other hand, when $T_{\text{in}}$ is far below $T_c$, $\Delta h$ drops suddenly. This result suggests the importance of the gravity near the critical temperature $T_c$, i.e. the downward spreading of the wetting film is blocked by the gravitational potential in this temperature area.

These experimental results are explained by using a model grand potential, $\Omega(l)$, as a function of the thickness of the wetting film $l$, taking into account the long-range dispersion force, the temperature difference $\Delta T$ and the gravity. In the present article, however, we restrict ourselves to the homogeneous temperature conditions, or $\Delta T = 0$.

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

Here, $\sigma_{ij}$ are surface tensions between i and j phases. The subscripts 1, 2 and s represent the Ti-rich phase, the Se-rich phase and the quartz substrate, respectively. $W(l)$ is the free energy due to the long-range interaction, which has the form

$$W(l) \sim \begin{cases} -H/12\pi l^2 & \text{(for large)} \\ \sigma_{1s} - \sigma_{2s} - \sigma_{12} & \text{(} l \to 0 \text{)} \end{cases}.$$  

where $H (< 0)$ is the Hamaker constant. $\delta \rho$ is the difference of the mass density between the two liquid phases, $g$ is the gravitational acceleration, and $z$ is the height from the bulk meniscus. The term $|\delta \rho g z| l$ in the equation (1) is the gravitational potential.
This grand potential (1) has two minima: one is located at \( l = 0 \) and the other is at \( l^* = \left( \frac{-H}{6\pi|\delta\rho g z|} \right)^{1/3} \). The minimum at \( l = 0 \) corresponds to the non-wetting state, and that at \( l = l^* \) to the wetting state. The minimum at \( l = l^* \) is formed as a result of competition between the long-range force \( W(l) \) and the gravitational potential. The former is a decreasing function of \( l \), and prefers thicker wetting film, while the latter term prefers thinner wetting film.

The difference of the grand potential between the wetting and the non-wetting states can be written as

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

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 \( -H \sim |\delta\rho| \sim \delta_C \sim t^\beta \), where \( \beta_1 \approx 0.8, 2\nu \approx 1.3 \) and \( \beta \approx 0.33 \) are the critical exponents. Therefore, the \( t \)-dependence of the grand potential can be written as

\[
\Omega(l^*) - \Omega(0) \sim -At^{\beta_1} + Bt^{2\nu} + C|z|^{2/3}t^\beta,
\]

where \( A, B, C \) and \( D \) are positive proportional coefficients.

Figure 4 shows a schematic picture of \( t \)-dependence of each term in equation (3). When the reduced temperature \( t \) approaches the critical point \( t = 0 \) from the large-\( t \) region, the \( At^{\beta_1} \) term (dotted line) first intersects the \( Bt^{2\nu} \) term (dashed line), and \( \Omega(l^*) - \Omega(0) \) changes its sign from positive to negative, indicating that the wetting state \( l = l^* \) is more stable than the non-wetting state \( l = 0 \). This corresponds to the Cahn’s critical point wetting transition.

However, when \( t \) approaches further to the critical point, \( At^{\beta_1} \) term (dotted line) intersects the \( C|z|^{2/3}t^\beta \) term (solid line), and \( \Omega(l^*) - \Omega(0) \) changes from negative to positive again. This corresponds to the “critical point dewetting”.

It should be noted that the appearance of the critical point dewetting is a result of the interplay between the gravity and the long-range force. Indeed, if either the gravity or the long-range force is absent, i.e. \( g|z| = 0 \) or \( H = 0 \), the term \( C|z|^{2/3}t^\beta \approx (-H)^{1/3}(g|z|)^{2/3} \) becomes zero, and the intersection of the solid and the dotted lines does not occur down to \( t = 0 \).

We have also taken into account the temperature difference \( \Delta T \) and studied the phase boundary between the wetting and non-wetting states where \( \Omega(l^*) - \Omega(0) \) crosses zero. From this analysis, we found that the wetting phase diagram (Fig.2) and the temperature dependence of the three-phase contact line (Fig.3) can be explained qualitatively [4].

4. Summary
In the present work, we studied the wetting phenomena of liquid Se-Tl system on a quartz substrate, and found that this system does not show the critical point wetting near the liquid-liquid critical point, but shows the “critical point dewetting” phenomenon. It is suggested from a theoretical consideration that the critical point dewetting takes place as a result of the competition between the long-range dispersion force and the gravity.

Acknowledgments
The authors are grateful to Mr. Y. Nishikawa Mr.K.Tanaka for their collaborations on the experiment. This work is partially supported by the Grant-in-Aid for Scientific Research on Priority Area “Soft Matter Physics” and “Science of Ionic Liquids” from the Ministry of Education, Culture, Sports, Science and Technology, and the Grant-in-Aid for the 21st Century COE “Center for Diversity and Universality in Physics” from the Ministry of Education, Culture, Sports, Science and Technology.
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