Predrying transition on a hydrophobic surface: Statics and dynamics

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For one-component fluids, we examine the predrying phase transition between a thin and thick low-density layer in liquid on a wall repelling the fluid. This is the case of a hydrophobic wall for water. A predrying line starts from the coexistence curve and ends at a surface critical point in the phase diagram. We calculate this line numerically using the van der Waals model and analytically using the free-energy expansion up to the quartic order. We also examine the predrying dynamics of a layer created on a hydrophobic spot on a heterogeneous wall. It is from a thin to thick layer during decomposition and from a thick to thin layer during compression. Upon the transition, a liquid region above the film is cooled for decompression and heated for compression due to latent heat convection, and a small pressure pulse is emitted from the film into the liquid.

I. INTRODUCTION

Extensive efforts have been made on the wetting transitions for various liquids and walls both theoretically and experimentally [1–5]. As is well known, when a liquid droplet is placed on a wall in gas, the three-phase contact angle changes from a finite value (partial wetting) to zero (complete wetting) at a wetting transition temperature \( T_w \) on the coexistence curve. Furthermore, there is a phase transition of adsorption between a thin and thick liquid layer across a prewetting line outside the coexistence curve [1,3–9]. For one-component fluids, the line starts from the wetting transition point \( T = T_w \) on the coexistence curve and ends at a surface critical point at \( T = T^c_w \) in the \( T-n \) or \( T-p \) plane, where \( n \) and \( p \) are the density and the pressure in the surrounding gas region.

On the other hand, many authors have been interested in the structural change in the hydrogen bonding network formed by the water molecules in the vicinity of a hydrophobic surface [10–19]. We also mention many observations of surface bubbles or films on mesoscopic scales (10–100 nm thickness) on hydrophobic walls in water [20–23]. Here the attractive interaction among the water molecules arises from the hydrogen bonding. As a result, there can even be a gas region in contact with a hydrophobic surface in liquid water at ambient conditions (room temperature and 1 atm pressure).

To support this behavior, the solvation free energy \( \Delta G_{sol} \) of a hydrophobic particle with radius \( R \) in water is nearly given by \( 4\pi R^2 \sigma \) per particle for relatively large \( R(\gtrsim 1 \text{ nm}) \) [19], where \( \sigma \) is the gas-liquid surface tension.

In this paper, we examine a predrying phase transition between a thin and thick low-density layer on a hydrophobic wall in liquid. The presence of a predrying line itself is rather obvious near the critical point when the short-range interaction between the fluid and the solid wall is repulsive [5,7,24,25]. We mention an experiment by Hess et al. [26], who detected a drying transition for \( T > T^c_w \) on the coexistence curve and ends at a predrying critical point. It follows complete drying for \( T > T^c_{Ax} \) on the coexistence curve. We develop a mean-field theory based on the Ginzburg-Landau model as in the original paper [1]. Our calculations are thus performed rather close to the critical point (at \( T \sim 0.9T_c \)), where the film density is not very small compared to the ambient liquid density.

In this paper, we also study the dynamics of the wetting and drying transitions, where understanding of evaporation and condensation at the interface is still inadequate [28–30]. For example, Koplik et al. [31] performed molecular dynamics simulation to observe evaporation of a droplet and a decrease of the contact angle upon heating a wall in partial wetting. In a near-critical one-component fluid, Hegseth et al. [32] observed that a bubble was attracted to a heated wall even when it was completely wetted by liquid in equilibrium. To study such problems, we have recently developed a phase-field model for compressible fluids with inhomogeneous temperature, called the dynamic van der Waals model [33]. (See the review on various phase-field theories of fluids [34].) In our framework, we may describe the gas-liquid transition and convective latent heat transport without assuming any evaporation formula. We then numerically investigated evaporation of a liquid droplet on a heated substrate [35] and spreading of a liquid film on a cooled or heated substrate for a one-component fluid [36].

The lattice Boltzmann method has been applied to two-phase fluids also [37–39]. However, this method has not yet been fully developed to describe evaporation and condensation.

Hence this paper presents simulation results on the film dynamics using the numerical method in our previous studies [35,36]. We initially start with an equilibrium thin or thick low-density film on a wall at the bottom near the predrying transition and then cool or heat the temperature at the top. (We use “bottom” and “top” though we do not assume gravity.) Subsequently, the cell is gradually decompressed or compressed, and the predrying transition is induced in the film.

The organization of this paper is as follows. In Sec. II we will examine the static aspect of the predrying transition in the Ginzburg-Landau scheme [1,2] in the mean-field theory. In Sec. III, we will apply the dynamic van der Waals model to investigate the predrying dynamics by cooling or heating the top plate of a cylindrical cell. In Appendix B, the predrying transition will be examined near the critical point by expanding...
the free energy with respect to the density $n$ around the critical density $n_c$ up to the quartic order.

II. STATICS

A. Ginzburg-Landau model

We consider a one-component fluid in contact with a solid wall in equilibrium, where the number density $n$ is the order parameter. Assuming short-range forces and neglecting the long-range van der Waals interaction, we set up the free energy $F$ with the gradient contribution as \cite{40,41}

$$F = \int d\mathbf{r} \left[ f(n, T) + \frac{1}{2} M |\nabla n|^2 \right] + \int d\omega n,$$  \hspace{1cm} (2.1)

where the integral is in the fluid container in the first term and on the wall surface in the second term ($\int d\omega$ being the surface integral). As a function of $n$ and $T$, $f = f(n, T)$ is the Helmholtz free-energy density. In our numerical calculation, we will use the simple van der Waals form \cite{40},

$$f = k_B T n \left[ \ln \left[ n \lambda_b^3 / (1 - \nu_0 n) \right] - 1 \right] - \epsilon \nu_0 n^2,$$  \hspace{1cm} (2.2)

where $\nu_0$ is the molecular volume, $\epsilon$ is the magnitude of the attractive pair potential, and $\lambda_b = h(2\pi/mk_B T)^{1/2}$ is the thermal de Broglie length with $m$ being the molecular mass. The coefficient $M$ of the gradient free energy will be assumed to be independent of $n$ but proportional to $T$. The last term is the surface free energy expressed as the integration on the solid surface, where the second-order term of the form $M \lambda^{-2}_b (n - n_s)^2 / 2$ is neglected \cite{1}. Though it is negligible for very large $|\lambda_b|$ compared to the correlation length, it can give rise to complex surface transitions in general \cite{7,42,43}. In the literature, the so-called surface field (usually written as $h_1$) is given by $-\gamma$. For water, $\gamma > 0$ for a hydrophobic surface and $\gamma < 0$ for a hydrophilic surface. For this surface free energy, the predrying transition occurs for $\gamma > 0$, while the prewetting transition for $\gamma < 0$.

In equilibrium, the space-dependent density $n = n(\mathbf{r})$ in the bulk region is determined by

$$\mu - M \nabla^2 n = \mu_0,$$  \hspace{1cm} (2.3)

where $\mu = \partial f / \partial n$ is the chemical potential and $\mu_0$ is the chemical potential in the bulk region treated to be a given constant. The left-hand side $\mu - M \nabla^2 n$ represents the generalized chemical potential including the gradient contribution. On the wall surface we have

$$M v \cdot \nabla n = \gamma,$$  \hspace{1cm} (2.4)

where $v$ is the outward normal unit vector (from the wall to the fluid) on the wall surface.

B. Predrying transition for $n_0 > n_s$

Let us consider an equilibrium one-component fluid in the region $z > 0$ in contact with a planar substrate with $\gamma > 0$ placed at $z = 0$. In this one-dimensional geometry, all the quantities depend only on $z$. The density $n(z)$ tends to a constant liquid density $n_0$ far from the wall. The pressure and the chemical potential far from the wall are written as $p_0$ and $\mu_0$, respectively, where $p_0 = n_0 k_B T / (1 - \nu_0 n_0) - \nu_0 e n_0^2$ for the van der Waals model (2.2). In equilibrium, we should minimize the excess grand potential $\Omega$ (per unit area) given by

$$\Omega = \int_0^\infty dz \left[ \omega + \frac{1}{2} M |n'|^2 + \gamma n_s \right],$$  \hspace{1cm} (2.5)

where $n' = dn/dz$ and $n_s$ is the surface density,

$$n_s = n(0).$$  \hspace{1cm} (2.6)

We define the excess grand potential density as

$$\omega = f - \mu_0 n + p_0,$$  \hspace{1cm} (2.7)

which vanishes far from the surface. Use of the van der Waals form (2.2) gives

$$\omega = k_B T n \ln \left[ \frac{n(1 - \nu_0 n_0)}{n_0 (1 - \nu_0 n)} \right] - k_B T \frac{n - n_0}{1 - \nu_0 n_0} - \epsilon \nu_0 n^2 - \nu_0 (0 - n_0)^2.$$  \hspace{1cm} (2.8)

Far from the wall, $\omega$ behaves as $\omega \approx \chi(n_0)(n - n_0^2)/2$ and tends to zero. We define

$$\chi(n) = \delta^2 / \partial n^2 = 1 / n^2 K_T,$$  \hspace{1cm} (2.9)

where $K_T$ is the isothermal compressibility.

In the region $z > 0$, the density profile $n = n(z)$ is determined by $\mu - M n'' = \mu_0$ from Eq. (2.3), where $n'' = d^2 n / dz^2$. We multiply this equation by $n'$ and integrate the resultant one with respect to $z$ to obtain \cite{40}

$$\omega = M |n'|^2 / 2.$$  \hspace{1cm} (2.10)

From Eq. (2.4) the boundary condition at $z = 0$ reads

$$M n'(0) = \gamma.$$  \hspace{1cm} (2.11)

On the basis of the van der Waals model (2.2), we introduce a microscopic length $\ell$ defined by

$$\ell = (M / 2k_B T v_0)^{1/2}.$$  \hspace{1cm} (2.12)

Since $\gamma > 0$ and $n'(0) > 0$, Eq. (2.10) is rewritten as

$$n'(z) = \sqrt{2 \omega(n(z))} / M = e^{-\int \omega(n(z)) / k_B T v_0},$$  \hspace{1cm} (2.13)

where $\omega$ is treated as a function of $n$ and its $T$ dependence is ignored. Using $\ell$, we integrate this equation as

$$z = \ell \int_{n_s}^{n} \frac{dn / \sqrt{\omega(n)} / k_B T v_0}{n_s}.$$  \hspace{1cm} (2.14)

From Eqs. (2.11) and (2.13) we have

$$\gamma = \sqrt{2 M \omega(n_s)} = 2 \epsilon \ell \sqrt{k_B T v_0 \omega(n_s)}.$$  \hspace{1cm} (2.15)

Using Eq. (2.13) we rewrite Eq. (2.5) as \cite{1}

$$\Omega = \int_{n_s}^{n_0} dn \left[ \sqrt{2 M \omega(n) - \gamma} + \gamma n_0 \right],$$  \hspace{1cm} (2.16)

where the integrand vanishes at the lower bound $n = n_s$ from Eq. (2.15).

Cahn \cite{1} showed that the thickness of a film of the preferred phase on a wall grows logarithmically as the surrounding fluid approaches a state on the coexistence curve. In our case, the film thickness $D$ increases logarithmically as $n_0$ approaches the liquid density on the coexistence curve $n_{cs}$, where we may take the isothermal path of approach. Here we introduce the
difference between the background chemical potential $\mu_0$ and that on the coexistence curve at the common temperature $T$:

$$\Delta \mu_0 = \mu_0 - \mu_{cx} \equiv \chi_\ell (n_0 - n_{cx}^\ell),$$  \hspace{1cm} (2.17)

where $\chi_\ell = \chi(n_{cx}^\ell)$. In Eq. (2.14), with increasing $n$, the integral around $n \approx n_{cx}^\ell$ gives $D$ for small $\Delta \mu_0$, where $n_{cx}^\ell$ is the corresponding gas density on the coexistence curve. Thus we expand the free-energy density $\gamma$ around $n_{cx}^\ell$ as

$$f \equiv -p_{cx} + \mu_{cx} n + \chi_\ell (n - n_{cx}^\ell)^2 / 2,$$  \hspace{1cm} (2.18)

where $p_{cx}$ is the pressure on the coexistence curve and $\chi_\ell = \chi(n_{cx}^\ell)$. Since $p_0 - p_{cx} \approx n_{cx}^\ell \Delta \mu_0$, we obtain

$$\Delta n_{cx} = n_{cx}^\ell - n_{cx}^\ell.$$  \hspace{1cm} (2.19)

Substitution of this relation into Eq. (2.14) yields

$$D \equiv \xi_\ell \ln[\chi_\ell \Delta n_{cx} / \Delta \mu_0],$$  \hspace{1cm} (2.20)

where $\xi_\ell = (M / \chi_\ell^2)^{1/2}$ is the correlation length in the gas phase. As $\Delta \mu_0 \to 0$, a well-defined interface appears.

In Fig. 1 we plot $\sqrt{2M \omega(n) / \xi} \ell$ vs $v_0 n$ at $T = 0.9 T_c$ for four bulk densities $n_0$, using the van der Waals model (2.8). (1) The smallest bulk density is 0.5525$v_0^{-1}$. As a result, $\omega(n)$ nearly vanishes at the coexistence gas density $n_{cx}^\ell = 0.1419 v_0^{-1}$. The gas layer thickness $D$ is logarithmically dependent on $n_0 - n_{cx}^\ell$ as in Eq. (2.20). (2) At $n_0 = 0.56 v_0^{-1}$, there are a minimum and a maximum satisfying $\partial \omega / \partial n = f' - \mu_0 = 0$. (3) At $n_0 = 0.5854 v_0^{-1}$, the two extrema merge into a point $n = n_{sc}$, at which $\partial^2 \omega / \partial n^2 \chi = 0$ holds and $n_{sc}$ coincides with the so-called spinodal density on the gas branch for the linear form of the surface free energy. (4) At $n_0 = 0.60 v_0^{-1}$, $\sqrt{\omega(n)}$ increases with decreasing $n$ in the range $n < n_0$. Then Eq. (2.15) yields a unique surface density $n_s$ for any $\gamma > 0$.

**FIG. 1.** (Color online) $\sqrt{2M \omega(n)} / \xi \ell$ vs $v_0 n$ at $T = 0.9 T_c$ for $v_0 n_0 = 0.1419$, 0.5854, 0.56, 0.5525 from below, where the smallest one is very close to the coexistence liquid density $n_{cx}^\ell = 0.5524$. Use is made of the van der Waals form (2.8).

![FIG. 1](image1.png)

As illustrated in Fig. 2, a predrying transition appears when the curve of $\sqrt{\omega(n)}$ has two extrema as in the case of $n_0 = 0.56 v_0^{-1}$ in Fig. 1. If the areas $S_1$ and $S_2$ coincide, leading to the same value of $\Omega$ in Eq. (2.16) at two surface densities $n_s = n_{c1}^\ell$ and $n_{c2}^\ell$.

**FIG. 2.** Illustration of a predrying transition, where $\sqrt{2M \omega(n)} / \xi \ell$ is plotted for $T / T_c = 0.860$ and $v_0 n_0 = 0.59407$. At $\gamma / \xi \ell = 0.05$, the areas of the regions $S_1$ and $S_2$ coincide, leading to the same value of $\Omega$.

![FIG. 2](image2.png)

In Fig. 3 two examples of the predrying line are written for $\gamma / \xi \ell = 0.05$ and 0.1 in the $T$-$n$ plane (left) and in the $T$-$p$ plane (right), where $n$ and $p$ denote those in the bulk ($n_0$ and $p_0$). Here the predrying line merges into the coexistence line tangentially in accord with the calculation in Appendix A (where $(d \Delta \mu_0 / d T)^{-1} \propto \ln(\Delta \mu_0)$ as $\Delta \mu_0 \to 0$) [9]. In this

![FIG. 3](image3.png)
Fig. 4. (Color online) Left: (a) Predrying temperature $T_{\text{cx}}^{\text{pd}}$ on the coexistence curve and (b) predrying critical temperature $T_{\text{pd}}^{\text{c}}$ as functions of $\gamma/\epsilon \ell$. Their linear approximations are ({a'}) $T_{\text{cx}}^{\text{pd}, 0}$ and (b) $T_{\text{pd}}^{\text{c}}$ [see Eqs. (2.22) and (2.23)]. Right: (a) Predrying pressure $p_{\text{c}}^{\text{pd}}$ on the coexistence curve and (b) predrying critical pressure $p_{\text{c}}^{\text{pd}}$ as functions of $\gamma/\epsilon \ell$.

The coexistence curve and (b) predrying critical temperature $T_{\text{pd}}^{\text{c}}$ are in the range $0.7 < T < T_{\text{pd}}^{\text{c}}$. Their linear approximations are (a') $T_{\text{cx}}^{\text{pd}, 0}$ and (b) $T_{\text{pd}}^{\text{c}}$ [see Eqs. (2.22) and (2.23)]. Right: (a) Predrying pressure $p_{\text{c}}^{\text{pd}}$ on the coexistence curve and (b) predrying critical pressure $p_{\text{c}}^{\text{pd}}$ as functions of $\gamma/\epsilon \ell$.

The coefficient $M$ is independent of $n$ and is proportional to $T$ as

$$ M = T C. $$

Then $C$ and hence $\ell = (C/2v_0k_B)^{1/2}$ are independent of $n$ and $T$. However, essentially the same results were obtained even if $M$ is independent of $T$ (not shown in this paper). We give $T_{\text{cx}}^{\text{pd}}$ and $T_{\text{pd}}^{\text{c}}$ and the corresponding densities $n_{\text{cx}}^{\text{pd}}$ and $n_{\text{pd}}^{\text{c}}$.

For $\gamma/\epsilon \ell = 0.05$, we have $(T_{\text{cx}}^{\text{pd}}/T_c, v_0n_{\text{cx}}^{\text{pd}}) = (0.851, 0.601)$ and $(T_{\text{pd}}^{\text{c}}/T_c, v_0n_{\text{pd}}^{\text{c}}) = (0.943, 0.524)$. For $\gamma/\epsilon \ell = 0.1$, we have $(T_{\text{cx}}^{\text{pd}}/T_c, v_0n_{\text{cx}}^{\text{pd}}) = (0.683, 0.724)$ and $(T_{\text{pd}}^{\text{c}}/T_c, v_0n_{\text{pd}}^{\text{c}}) = (0.883, 0.606)$.

In Fig. 4 the left (right) panel displays the predrying transition temperature (pressure) $T_{\text{cx}}^{\text{pd}}(\gamma)$ ($p_{\text{c}}^{\text{pd}}(\gamma)$) on the coexistence curve and the predrying critical temperature (pressure) $T_{\text{pd}}^{\text{c}}(\gamma)$ ($p_{\text{c}}^{\text{pd}}(\gamma)$) as functions of $\gamma/\epsilon \ell$. For each $\gamma$, the predrying line is in the range $T_{\text{cx}}^{\text{pd}}(\gamma) < T < T_{\text{pd}}^{\text{c}}(\gamma)$. If $\gamma/\epsilon \ell < 1$, these temperatures are both close to $T_c$ and are expanded with respect to $\gamma$ as

$$ T_{\text{cx}}^{\text{pd}}(\gamma) = T_c(1 - A_{\text{cx}}\gamma/\epsilon \ell + \cdots), $$

$$ T_{\text{pd}}^{\text{c}}(\gamma) = T_c(1 - A_{\text{c}}\gamma/\epsilon \ell + \cdots). $$

(2.22)

(2.23)

On the basis of the van der Waals model (2.2), the coefficients $A_{\text{cx}}$ and $A_{\text{c}}$ are calculated in Appendix B as

$$ A_{\text{cx}} = \frac{9}{8} \sqrt{2}\sqrt{3} + 3, \quad A_{\text{c}} = \frac{9}{8}. $$

(2.24)

We also plot the linear approximations $T_{\text{cx}}^{\text{pd}, 0}(\gamma) = T_c(1 - A_{\text{cx}}\gamma/\epsilon \ell)$ and $T_{\text{pd}}^{\text{c}, 0}(\gamma) = T_c(1 - A_{\text{c}}\gamma/\epsilon \ell)$, which are indeed in good agreement with the numerical curves for small $\gamma \ll \epsilon \ell$. For the usual predewetting transition in the case $\gamma < 0$, the counterparts of $T_{\text{cx}}^{\text{pd}}$ and $T_{\text{pd}}^{\text{c}}$ are the wetting temperature $T_w$ on the coexistence curve and the predewetting critical temperature $T_{\text{pd}}^{\text{w}}$. As will be discussed in Appendix B, they are expanded in the forms of Eqs. (2.21) and (2.22) with $\gamma$ being replaced by $|\gamma|$.

In Fig. 5 we show the desorption $V_1d$ per unit area in the top plate and the surface density $n_1$ in the bottom plate as functions of $T_c/T_c$ for $v_0n_0 = 0.59, 0.57, 0.55, 0.53$ at $\gamma/\epsilon \ell = 0.05$. These lines are outside the coexistence curve in the $T$-$n$ plane. They change discontinuously across the predrying transition. Theoretical curve for $v_0n_0 = 0.53$ (broken line, farthest right in top panel). We also plot the linear approximations $V_1d, V_1d, V_1d$ as functions of $T/T_c$.

On each line, as $T \to T_{\text{cx}}^{\text{pd}}$, $\Gamma_{1d}$ grows logarithmically as $(n_0 - n_{\text{cx}}^{\text{pd}})D$ with $D$ being given by Eq. (2.21) upon decreasing the temperature, while $n_{\text{ld}}$ tends a well-defined limit (see the lower panel of Fig. 5). The curve for $v_0n_0 = 0.53$ is closest to the predrying criticality, so we also display its theoretical approximation from the Landau expansion in Appendix B.

In Fig. 6 we display the density profile $n(z)$ at $\gamma/\epsilon \ell = 0.05$. In the top panel we set $T/T_c = 0.93 665, 0.93 664$, and 0.92 at fixed $n_0 = 0.52 892 v_0^{-1}$, while in the bottom panel we set $v_0n_0 = 0.54 358, 0.54 357$, and 0.52 892 at fixed $T = 0.92 T_c$. In these panels, the first two curves represent the profiles just before and after the predrying transition, while the third one
values of the surface tension, we obtain $\ell \cong 3.1a_{vdw}$ and $C/2k_B \sim 10a_{vdw}^2$ [45]. In the same manner, for argon, we have $\epsilon = 0.70 \times 10^{-17}$ mJ, $v_0 = 4.11 \times 10^{-5}$ cm$^3$, and $\gamma = 9.3$ mJ/m$^2 = 0.016\epsilon \ell$ at $T = 0.92T_c$ [46], leading to $C/2k_B \sim 6.8a_{vdw}^2$.

For water, we estimate the surface field $\gamma$ by

$$\gamma \sim \sigma/n_{liq},$$

for a typical hydrophobic surface. Here $n_{liq}$ and $\sigma$ are some appropriate liquid density and surface tension. We use the above-mentioned surface tension for water and set $n_{liq} \sim n$, to obtain $\gamma/\epsilon \ell \sim 0.03$. This estimation is based on the behavior of the solvation free energy $\Delta G_{sol}$ of a large hydrophobic particle in water [19], as discussed in Sec. I.

D. Nanobubbles on a hydrophobic spot

Drying is very sensitive to heterogeneity of the substrate as well as wetting. Here we realize bubbles in equilibrium on a heterogeneous surface with a position-dependent $\gamma$. We suppose a circular hydrophobic spot with radius $25\ell$ on the bottom surface by setting

$$\gamma(r) = 0.05\epsilon \ell \quad (r < 25\ell),$$

$$= 0 \quad (r > 25\ell),$$

where $r = (x^2 + y^2)^{1/2}$ at $z = 0$. The resultant equilibrium density $n(r,z)$ satisfies Eq. (2.3). Its boundary condition at $z = 0$ is given by $\partial n/\partial z = 0.05\gamma/M = 0.025\epsilon/k_BT v_0$ for $r < 25\ell$ and $\partial n/\partial z = 0$ for $r > 25\ell$.

Slightly above the predrying line, the top panel of Fig. 7 gives the cross-sectional density profile $n(r,z)$ at $y = 0$ for the point A in Fig. 3, where $T = 0.94T_c$, $p_0 = 0.89p_c$, and $n_0 = 0.52894v_0^{-1}$. The minimum density is $n_s = 0.40587v_0^{-1}$ at the spot center on the surface. Below the predrying line, the bottom panel of Fig. 7 gives the profile at the point B in Fig. 3, where $T = 0.92T_c$, $p_0 = 0.71177p_c$, and $n_0 = 0.52925v_0^{-1}$. The minimum density is $n_s = 0.088433v_0^{-1}$ at the spot center. These profiles are very different. To characterize the film size, we introduce the desorption of the fluid by

$$\Gamma = 2\pi \int_0^{r_0} dz \int_0^{z_0} dr [n_0 - n(r,z)],$$

(2.28)

where the gas film is well within the integration region $0 < z < z_0$ and $r < r_0$. By setting $z_0 = 15\ell$ and $r_0 = 37.5\ell$, we obtain $\Gamma = 339\ell^3 v_0^{-1}$ and $3460\ell^3 v_0^{-1}$ for the top and bottom panels in Fig. 7, respectively.

III. DYNAMICS

In this section, using the dynamic van der Waals model [33], we numerically investigate the dynamics of a thin gas layer created on the hydrophobic spot described in Eq. (2.27). We treat a one-component fluid without gravity in a temperature range $0.92 \leq T/T_c \leq 0.94$, where the gas density is 25%–30% of the liquid density (see the bottom curves in Fig. 6). Then the mean-free path in the gas $\ell_{mf}$ is not very long. For very long $\ell_{mf}$, numerical analysis based on a continuum phase-field model becomes very difficult. In our simulation, furthermore, relatively small temperature changes are applied, and heat and mass fluxes passing through the interface remain

C. Rough estimates of $C$ and $\gamma$ for water

In our continuum theory, the constant $C$ in Eq. (2.22) and the length $\ell$ in Eq. (2.12) remain arbitrary. For each fluid, we may roughly estimate their sizes with input of the experimental values of $T_c$, $n_c$, and the surface tension $\sigma$ at some temperature $T$. For example, we have $T_c = 647$ K and $n_c = 1.076 \times 10^{24}$ cm$^{-3}$ for water. Using these $T_c$ and $n_c$ in the van der Waals model calculation, we have $\epsilon = 28k_BT_c/8 = 3.0 \times 10^{-17}$ mJ and $v_0 = (3n_c)^{-1} = 31 \times 10^{-24}$ cm$^3$, from which we define the van der Waals radius by $a_{vdw} = v_0^{1/3} = 3.1$ Å. For water, an experimental surface tension is $\sigma = 9.3$ mJ/m$^2 = 0.030\epsilon/a^2$ at $T = 0.92T_c$ [44]. On the other hand, from the model (2.1) under Eqs. (2.12) and (2.21), the surface tension is numerically calculated as $\sigma_{vdw} = 0.0097\epsilon/\ell v_0$ at $T = 0.92T_c$. If we equate these experimental and numerical

is obtained close to the coexistence curve with a well-defined thick gas layer.

FIG. 6. (Color online) Normalized density profile $v_0n(z)$ vs normalized distance $z/\ell$ from a wall at $\gamma/\epsilon \ell = 0.05$. Shown are those for $T/T_c = 0.93665$ (top) and those for $v_0n_0 = 0.54358, 0.54357$, and 0.52892 at $T/T_c = 0.92$ (bottom). The first two curves from above are taken just before and after the predrying transition, while the third one close to the coexistence curve.

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density is given by

Then the total Helmholtz free-energy as

inside the prewetting line and the minimum surface density is

where $\rho$ is the initial liquid density. We set up the hydrodynamic equations for the mass density $\rho = mn$, the momentum density $\rho v$, and the entropy density $\hat{S}$ [35,36], where $m$ is the molecular mass and $v$ is the velocity field. Here $\hat{S}$ consists of the usual entropy density $ns$ and the negative gradient entropy as

where $s$ is the entropy per particle and the coefficient $C$ in Eq. (2.21) appears here. The internal energy density, written as $e$, can also contain the gradient contribution, but we neglect it for simplicity [33]. Then the total Helmholtz free-energy density is given by $e - T \hat{S} = f + M |\nabla n|^2/2$ as in the first term as given in Eq. (2.1). In our scheme, we use the entropy equation instead of the energy equation to achieve the numerical stability in the interface region. That is, with our entropy method, we may remove the so-called parasitic flow at the interface, which has been encountered by many authors [47].

We integrated the following hydrodynamic equations without gravity for $\rho$, $\rho v$, and $\hat{S}$ [35,36]:

where $\sigma$ is the van der Waals pressure. Hereafter $\nabla_i = \partial/\partial x_i$ with $x_i$ representing $x$, $y$, or $z$. The terms proportional to $C$ arise from the gradient entropy, constituting the gradient stress tensor. The $\widehat{\sigma}_{ij} = \{\sigma_{ij}\}$ in the right-hand side of Eq. (3.3) is the viscous stress tensor,

are the nonnegative entropy production rates arising from the viscosities and the thermal conductivity, respectively. On approaching equilibrium, $\dot{\epsilon}_v$ and $\dot{\epsilon}_\theta$ tend to zero, leading to vanishing of the gradients of $v$ and $T$.

The (total) energy density in the bulk is defined by

which includes the kinetic energy density. The energy-conservation equation reads [48]

If Eqs. (3.2) and (3.3) are assumed, the entropy equation (3.4) and the energy equation (3.9) are obviously equivalent. In Ref. [48], however, the entropy equation is derived from $E$ [35,36]:

and outside which $\gamma = 0$. Top: $T = 0.94T_c$, $p_0 = 0.89 p_c$, and $n_0 = 0.52894 v_0^{-1}$ at point A in Fig. 3, where the fluid is outside the prewetting line and the minimum surface density is $n_s = 0.40587 v_0^{-1}$ on the center of the spot. Bottom: $T = 0.92T_c$, $p_0 = 0.71177 p_c$, and $n_0 = 0.52925 v_0^{-1}$ at point B in Fig. 3, where the fluid is inside the prewetting line and the minimum surface density is $n_s = 0.088433 v_0^{-1}$.

FIG. 7. Equilibrium axisymmetric density profile $n(z,r)$ at $y = 0$ on a hydrophobic spot with radius $25\ell$, within which $\gamma/\ell = 0.05$ and outside which $\gamma = 0$. Top: $T = 0.94T_c$, $p_0 = 0.89 p_c$, and $n_0 = 0.52894 v_0^{-1}$ at point A in Fig. 3, where the fluid is outside the prewetting line and the minimum surface density is $n_s = 0.40587 v_0^{-1}$ on the center of the spot. Bottom: $T = 0.92T_c$, $p_0 = 0.71177 p_c$, and $n_0 = 0.52925 v_0^{-1}$ at point B in Fig. 3, where the fluid is inside the prewetting line and the minimum surface density is $n_s = 0.088433 v_0^{-1}$.

weaker. As a result, $T$ and the generalized chemical potential [the left-hand side of Eq. (2.3)] are continuous across the interface.

In our diffuse interface method, the interface thickness needs to be longer than the simulation mesh size $\Delta x$, so our system size cannot be very large. In our simulation to follow, its length is $150 \ell$. Nevertheless, our cell contains many particles about $V n_0 \sim 6 \times 10^6 \ell^3/v_0$, where $V$ is the volume and $n_0$ is the initial liquid density.

A. Hydrodynamic equations with gradient stress

We set up the hydrodynamic equations for the mass density $\rho = mn$, the momentum density $\rho v$, and the entropy density $\hat{S}$ [35,36], where $m$ is the molecular mass and $v$ is the velocity field. Here $\hat{S}$ consists of the usual entropy density $ns$ and the negative gradient entropy as

where $s$ is the entropy per particle and the coefficient $C$ in Eq. (2.21) appears here. The internal energy density, written as $e$, can also contain the gradient contribution, but we neglect it for simplicity [33]. Then the total Helmholtz free-energy density is given by $e - T \hat{S} = f + M |\nabla n|^2/2$ as in the first term as given in Eq. (2.1). In our scheme, we use the entropy equation instead of the energy equation to achieve
the space integrations of Eqs. (3.4) and (3.9) yield the time derivatives of $S_{\text{tot}}$ and $\Sigma_{\text{tot}}$:

$$
\frac{d}{dt} S_{\text{tot}} = \int dr \frac{\dot{\epsilon}_v + \dot{\epsilon}_\theta}{T} + \int da \frac{\nu \cdot \nabla T + \gamma \dot{n}}{T},
$$

(3.11)

$$
\frac{d}{dt} \Sigma_{\text{tot}} = \int da (\nu \cdot \nabla T + \gamma \dot{n}),
$$

(3.12)

where $\dot{n} = \partial n / \partial t$ and $\gamma$ can be heterogeneous as in Eq. (2.27). If there is no heat input and $\dot{n} = 0$ on the boundary walls, $S_{\text{tot}}$ continue to increase monotonically until an equilibrium state is realized.

### B. Simulation method

We suppose a cylindrical cell in the axisymmetric geometry, where our model fluid is in the region $0 \leq z \leq H$ and $0 \leq r = (x^2 + y^2)^{1/2} \leq L$. Assuming that all the variables depend only on $z$, $r$, and $t$, we perform simulations on a two-dimensional $300 \times 300$ lattice. We take the simulation mesh length $\Delta r$ equal to $\Delta x = \ell / 2$, where $\ell$ is defined in Eq. (2.12). Thus our cell is characterized by

$$
H = 150\ell, \quad L = 150\ell,
$$

(3.13)

The velocity $\nu$ vanishes on all the boundaries. The viscosities and the thermal conductivities are proportional to $n$ as

$$
\eta = \zeta = \nu_0 m n, \quad \lambda = 4k_B \nu_0 n.
$$

(3.14)

These coefficients are larger in liquid than in gas by the density ratio $n_l/n_g$ ($\sim 5$ in our simulation). The kinematic viscosity $\nu_0 = \eta/mn$ is a constant. We will measure time in units of the viscous relaxation time,

$$
\tau_0 = \ell^2 / \nu_0 = C / 2k_B \nu_0 \nu_0,
$$

(3.15)

on the scale of $\ell$. The thermal diffusion constant $D_\nu = \lambda / C_p$ is of order $\nu_0$, where $C_p$ is the isobaric specific heat per unit volume of order $k_B n$ (not very close to the critical point). The time mesh size $\Delta t$ in integrating Eqs. (3.2)–(3.4) is $0.02\tau_0$. If the dynamic equations are made dimensionless, there appears a dimensionless number given by $\hat{\sigma} = m \nu_0^2 / \ell \ell^2$ (written as $\sigma$ in Ref. [33]), where $m$ is the molecular mass. The transport coefficients are proportional to $\nu_0 \propto \hat{\sigma}^{1/2}$. In this paper we set $\sigma = 0.06$, for which sound waves are well defined as oscillatory modes for wavelengths longer than $\ell$ [33].

As the boundary conditions, we assume Eq. (2.4) for the density $n$ (even in nonequilibrium) so that $C \partial n / \partial z = 0.05 \sigma \ell / T$ on the hydrophobic spot at $z = 0$ and $\nu \cdot \nabla n = 0$ on all the other surface regions. For the velocity $\nu$, the no-slip condition $\nu = 0$ is assumed. The temperature is fixed at $T_\ell$ at the bottom $z = 0$ and at $T_H$ at the top $z = H$. The side wall is thermally insulating as $\partial T / \partial r = 0$ at $r = L$.

### C. Decompression by cooling the upper plate

We prepared the equilibrium state at $T = 0.94T_c$ in the upper plate of Fig. 7 as an initial state at $t = 0$. We then cooled the top temperature $T_H$ from 0.94$T_c$ to 0.92$T_c$, fixing the bottom temperature $T_\ell$ at 0.94$T_c$ for $t > 0$. After a very long time ($t > H^2 / 4D_\nu$), the fluid tended to a steady heat-conducting state.

In Fig. 8 we show the profiles of the temperature $T(r,z,t)$ at $r = 0$ and the density $n(r,z,t)$ at $r = L/2$ as functions of $z$ to illustrate how the top cooling and the overall decompression are realized in the cell. In the initial stage, the piston effect is operative, which has been studied theoretically [49,50] and experimentally [51–53]. In this situation, there appear a compressed thermal diffusion layer at the top and an expanded one at the bottom with thickness increasing in time as $\ell_D(t) = (D_\nu t)^{1/2}$. These boundary layers emit sound waves propagating in the cell to cause an adiabatic change outside the diffusion layers. The sound velocity in the present case is about $c = 4\ell / \tau_0$, so the acoustic traversal time over the cell is $H/c \sim 35\tau_0$. In fact, at $t = 500\tau_0$, $T$ and $n$ are flat in the middle region, where they have been changed adiabatically. In the late stage $t \gtrsim 1000\tau_0$, the layer thickness reaches $H/2$ and the thermal diffusion becomes relevant throughout the cell.
Except in the very early stage, the pressure $p$ is kept nearly homogeneous in the cell.

In our problem, we should focus on the behavior of $T$ and $p$ around the gas film on the hydrophobic spot. The film is under gradual decompression, but nearly at the initial temperature (since the bottom temperature is pinned). As a result, at $t = 1320\tau_0$, the predrying transition takes place from a thin to thick gas film. In Fig. 8 this is indicated by formation of a cool region in the liquid above the film. It is caused by the latent heat adsorption to the expanding film at the first-order phase transition (see Fig. 12 in more detail). There is no cooling outside the film region $r/L \gtrsim 0.2$.

In Fig. 9 we display the temperature $T(r,z,t)$ and the pressure $p(r,z,t)$ slightly above the film at a fixed position located at $(z/H,r/L) = (0.1,0.1)$. In the early stage $t \lesssim 300\tau_0$, we can see their oscillatory relaxations caused by sound wave traversals. Upon occurrence of the predrying transition at $t \sim 1300\tau_0$, we can see a small drop in $T$ of order $5 \times 10^{-4}T_c$ and a small peak in $p$ of order $10^{-3}p_c$ on their curves. However, the insets in Fig. 9 reveal that their behavior is somewhat complicated on a short time scale of order $50\tau_0$, because they change on arrivals of a sound wave and a velocity disturbance from the film. At long times, $T$ tends to a constant about 0.938$T_c$, but $p$ continues to decrease slowly.

In Fig. 10 the profiles of the density $n(r,z,t)$ vs $z$ are given at $r/H = 0.1$ at three times together with their cross-sectional profiles. The increase in the film thickness is abrupt around $t = 1320\tau_0$ at the predrying transition and is very slow at $t = 2000\tau_0$. Figure 11 presents the time evolution of the surface density $n_s(r,t)$ at $r/L = 0.1$ and the excess desorption $\Delta \Gamma(t)$ defined by

$$\Delta \Gamma(t) = 2\pi \int_0^{z_D} dz \int_0^r dr \left[ (n_0(r,z) - n(t,r,z)) \right],$$

(3.16)
where \( n_0(r,z) = n(0,r,z) \) is the initial density profile and we set \( z_0 = 0.1H \) and \( r_0 = 0.25L \). The initial oscillatory relaxations arise from traversals of sound waves, while \( n_s \) decreases and \( \Gamma \) increases abruptly at the predrying transition at \( t \approx 1.3 \times 10^3 \tau_0 \). We recognize that the predrying transition from a thin to thick film occurs in a time of order \( 250\tau_0 \).

In Fig. 12 we show \( T(r,z,t) \) in gradation at \( t/t_0 = 1000, 1320, \) and \( 2000 \) around the hydrophobic spot. Since there is no clear interface here, a gas-liquid boundary is indicated by a line on which \( |\nabla n| \) is largest in the direction of \( \nabla n \). We also display the velocity \( v \) by arrows in the region with \( |v| > 10^{-4} \ell/\tau_0 \). The reference arrow below each panel represents the maximum velocity \( v_{\text{max}} \), being equal to 0.0363, 1.48, and 0.0878, at \( t/t_0 = 1000, 1320, \) and \( 2000 \), respectively, in units of \( 10^{-4} \ell/\tau_0 \). At \( t/t_0 = 1320 \), we can see an upward flow during the predrying transition in the liquid region above the expanding film. The expanding speed is of the order of \( v_{\text{max}} \). If we multiply this speed by the duration time \( 250\tau_0 \) of the transition (which is inferred from Fig. 11), we obtain a film thickness of order \( D \sim 4\ell \) in accord with the density profiles in Fig. 10. The corresponding Reynolds number around the film is about \( D|v|/v_0 \sim 0.1 \). Remarkably, the region above the film is cooled due to latent heat absorption to the film by \( 2 \times 10^{-3}T_c \). The profile at \( t = 2000\tau_0 \) is nearly stationary with \( |v| \sim 5 \times 10^{-4} \ell/\tau_0 \), where a balance is attained between condensation from the side and evaporation from the upper surface. The fluid is at rest far from the film under a constant temperature gradient.

Finally, we give the heat flux \( Q_b(r,t) = -\lambda \partial T/\partial z \) at \( z = 0 \) from the wall to the fluid at \( r = 0 \) and \( L/2 \) \( (Q_b(0,t), Q_b(L/2,t)) = (1.39, 1.13) \) at \( t = 1000 \), \( (5.71, 0.942) \) at \( t = 1320 \), and \( (0.618, 0.867) \) at \( t = 2000 \) in units of \( 10^{-4} \ell/\tau_0 \). The heat flux is much enhanced at the center during the predrying transition. In the inset of the upper panel of Fig. 8, the gradient \( |\partial T/\partial z| \) is very large at \( r = 0 \), but it is much smaller at \( r = L/2 \).

![Fig. 12](image-url) (Color online) Temperature \( T(r,z,t) \) in gradation at \( t/t_0 = 1000, 1320, \) and \( 2000 \) around the hydrophobic spot after cooling the top. On the block line, \( |\nabla n| \) is largest, indicating the film location. Arrows indicate the velocity \( v \). Their amplitudes are known from reference arrows below the middle and bottom panels. The liquid region above the film is cooled due to latent heat absorption to the film at the predrying transition. The profile at \( t = 2000\tau_0 \) (bottom) is nearly stationary, where condensation is taking from the side and evaporation from the upper surface. The colors represent \( T/T_c \) according to the color bar at the bottom.

![Fig. 13](image-url) (Color online) \( T(r,z,t)/T_c \) at \( r = 0 \) (top) and \( v_n(r,z,t) \) at \( r/L = 0.5 \) (bottom) vs \( z/H \) after heating the top from 0.92\( T_c \) to 0.94\( T_c \). Here \( t = 500, 1000, 1280, 1500, \) and 2000 from bottom for \( T \) and from top for \( v \) at \( z/H = 0.8 \). At \( t = 500\tau_0 \), thermal diffusion layers appear near the top and bottom. For \( t \gtrsim 1000\tau_0 \), the thermal diffusion extends throughout the cell. The density is increased in the lower part of the cell, resulting in a homogeneous pressure increase. Around \( t = 1280\tau_0 \), a heat spot appears above the film during the predrying transition. In the inset, the profiles of \( T \) and \( n \) at \( r = 0 \) and \( L/2 \) near the bottom are compared.
D. Compression by heating the upper plate

We prepared the equilibrium state at \( T = 0.92 T_c \) in the lower plate of Fig. 7 (at the point B in Fig. 3) as an initial state at \( t = 0 \). We then heated the top temperature \( T_H \) from 0.92\( T_c \) to 0.94\( T_c \) with the bottom temperature \( T_0 \) held fixed at 0.92\( T_c \) for \( t > 0 \).

In Fig. 13 the time evolution of \( T(r,z,t) \) at \( r = 0 \) and \( n(r,z,t) \) at \( r = L/2 \) is illustrated. As in Fig. 8, the piston effect takes place in the initial stage, but in the reverse direction. That is, at \( t = 500\tau_0 \), there appear an expanded thermal diffusion layer at the top and a compressed one at the bottom. In the late stage \( t \gtrsim 1000\tau_0 \), the thermal diffusion extends over the cell. The pressure \( p \) is nearly homogeneous in the cell and increases slowly in time above the initial value. Thus the film is under gradual compression, but nearly at the initial temperature. Occurrence of the predrying transition is indicated by formation of a heat spot in the liquid above the film at \( t = 1280\tau_0 \). It is caused by the latent heat release from the shrinking film (see Fig. 17).

Figure 14 displays the temperature \( T(r,z,t) \) and the pressure \( p(r,z,t) \) at \( (z/H,r/L) = (0.1,0.1) \) as in Fig. 9. The adiabatic process takes place in the early stage. The predrying transition occurs at \( t \sim 1280\tau_0 \), where \( T \) and \( p \) exhibit a small peak of order \( 2 \times 10^{-4} T_c \) and \( 2 \times 10^{-3} p_c \), respectively, with a duration time about 50\( \tau_0 \). Their detailed behavior can be seen in the insets of Fig. 14. At long times, \( T \) tends to 0.9216\( T_c \), but \( p \) continues to increase slowly.

In Fig. 15 the profiles of \( n(r,z,t) \) vs \( z \) are given at \( r/H = 0.1 \) at three times together with their cross-sectional profiles. The film thickness decreases gradually around \( t = 1000\tau_0 \) and is stationary at \( t = 2000\tau_0 \). Figure 16 gives the time evolution of the surface density \( n_s(r,t) \) at \( r/L = 0.1 \) and the excess desorption \( \Delta \Gamma(t) \) defined in Eq. (3.16). Here, \( n_s(r,t) \) increases abruptly around \( t = 1000\tau_0 \) as in Fig. 11. However,
Finally, we give the heat flux $Q_b(r,t) = -\lambda \frac{\partial T}{\partial z}$ at $z = 0$ from the wall to the fluid at $r = 0$ and $L/2$. That is, $(-Q_b(0,t), -Q_b(L/2,t)) = (1.24, 1.22)$ at $t = 500$, $(44.2, 0.870)$ at $t = 1280$, and $(1.02, 0.871)$ at $t = 1500$ in units of $10^{-3} \epsilon / \nu_0 \tau_0$. The heat flux is much enhanced at the center during the predrying transition. In the inset of the upper panel of Fig. 13, we can see that $\partial T / \partial z$ is large at $r = 0$ and is much smaller at $r = L/2$.

IV. SUMMARY AND REMARKS

We summarize our main results:

(1) In Sec. II, for one-component fluids, we have examined the predrying transition on a hydrophobic wall in the mean-field theory. We have assumed the Ginzburg-Landau free energy for the number density $n$ in the bulk and the surface free energy linear in $n$ with $\gamma$ representing the interaction between the wall and the fluid. Depending on the sign of $\gamma$, a line of prewetting or predrying appears in the gas or liquid side of the coexistence curve. If $\gamma$ is small, the line is close to the critical point as in Eqs. (2.22) and (2.23). In numerical analysis in Figs. 3, 5, and 6, we have set $\gamma = 0.05 \epsilon$ [where $\epsilon$ is defined in Eq. (2.2) and $\ell$ in Eq. (2.12)]. For water, a rough estimation yields such an order of magnitude of $\gamma$. For real systems it is desirable to measure $\gamma$. In Sec. II D, we have numerically realized a localized film on a hydrophobic spot in Eq. (2.27), where a thin film is above a predrying line at $T = 0.94T_c$ and a thick one is below it at $T = 0.92T_c$.

(2) In Sec. III, we have investigated the time evolution of a localized film on the hydrophobic spot in the axisymmetric geometry. Starting with the equilibrium films in Fig. 7, we have numerically integrated Eqs. (3.2)–(3.4) after a change of the top temperature from $0.94T_c$ to $0.92T_c$ in Sec. III C and from $0.92T_c$ to $0.94T_c$ in Sec. III D. Cooling at the top leads to a pressure decrease, while heating at the top leads to a pressure increase. We have found abrupt temporal changes in the surface density $n_s(t)$ and the excess desorption $\Delta \Gamma(t)$ at the predrying transition as in Figs. 11 and 16. Most markedly, the liquid above the film is cooled for compression and is heated for compression due to latent heat convective transport from the growing or shrinking film, as shown in Figs. 8, 12, 13, and 17. A small pressure pulse is emitted from the film to propagate through the cell, as shown in Figs. 9 and 14. This pulse could be detected experimentally [53].

We give some remarks:

(1) A predrying line as well as a prewetting line can readily be derived near the critical point for a small surface field $\gamma$, as shown in Appendix A. It is then of great interest where we can find a predrying line for water on a given hydrophobic wall in the phase diagram.

(2) In future work, we should examine the role of the long-range van der Waals interaction [2, 4–6, 8, 24] on the predrying phase transition. It should crucially influence the thickness.

(3) In future work, we should also include the second order term $M^2(n - n_s)^2/2$ in the surface free energy [1, 42]. Using density functional theory, Kuipers and Blokhuis [43] recently obtained molecular expressions for the two surface parameters $\gamma$ and $\lambda_s$ ($b_1$ and $g$ in their notation), both of which sensitively influence the wetting and drying behavior.
(4) For water, a small amount of impurities can strongly promote phase transitions due to the solvation effect [27], though we have treated pure one-component fluids only. As a solute, we may add a noncondensable gas (such as CO₂), hydrophobic particles, or ions in water. Such impurities can strongly affect the formation of surface bubbles or films on a hydrophobic wall in water [20–23]. We will report shortly on how the predrying line is shifted downward with increasing the solute concentration.

(5) If the mesh length Δx = ℓ/2 is a few Å, our system length is on the order of several ten nanometers, and the particle number treated is of order 10⁷–10⁸ (see the beginning of Sec. III). Our continuum description should be imprecise on the angstrom scale. Thus examination of our results by very large-scale molecular dynamics simulations should be informative. We should also investigate how our numerical results can be used or modified for much larger film sizes.

(6) Phase changes inevitably induce a velocity field carrying heat and mass. It has been crucial during the predrying transition. We have found a steady flow around the film at long times in Figs. 12 and 17. In our previous simulation [36], a steady circular liquid film was realized on a homogeneous wall in the complete evaporation-condensation balanced. It evaporated to vanish for stronger heating, while it expanded for weaker heating or for cooling.

(7) We should study the two-phase hydrodynamics such as evaporation or boiling, where the hetrogeneity of the wall is crucial, as exemplified in this paper. In fluid mixtures, a Marangoni flow decisively governs the dynamics with increasing the droplet or bubble size even at very small solute concentrations [54].

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APPENDIX A: DRYING AND PREDRYING NEAR THE COEXISTENCE CURVE

The drying and predrying transitions change over in a narrow region around the reference point (T_n₁) = (T^d(c)(γ), n^c(T^d(c)(γ))) on the coexistence curve for a given γ > 0. The liquid branch of the coexistence curve is expressed as n = n^c(T). The temperature deviation is written as

\[ \Delta T = T - T^d(c)(γ). \]  

From Eq. (2.27) Δμ₀ is the following linear combination,

\[ \Delta μ₀ = \chi^d \left[ n₀ - n^c \left( \frac{dT^d(c)(γ)}{dT} \right) \right], \]  

which vanishes on the coexistence curve n₀ = n^c(T) to linear order in the deviations. For γ < 0, the following results can also be applicable to the wetting and prwetting transitions if liquid and gas are exchanged.

We rewrite the relation T = T^d(c)(γ) between T and γ into the equivalent relation γ = γ^d(c)(T). Then, for Δμ₀ = 0, the integral in Ω becomes

\[ \int_{n^d_1}^{n^c} d\gamma \sqrt{2Mω(n)} = γ^d(c)(T)Δn_1, \]  

where we allow ΔT ≠ 0 and Δn₁ = n^d(c) – n^c. Let Ω^d(c) and Ω^c be the value of Ω for a thick film (n₁ = n^d(c)) and a thin film (n₁ = n^c), respectively, in the limit Δμ₀ → 0. The difference (ΔΩ) = Ω^d(c) – Ω^c is equal to that between the areas S₂ and S₁ in Fig. 2 so that

\[ (ΔΩ) = (γ^d(c) – γ)c Δn₁ / (dT^d(c)/dγ). \]  

Since dT^d(c)/dγ < 0, the wall is completely (partially) dried by the gas phase if T is higher (lower) than T^d(c)(γ) on the coexistence curve.

Next, we suppose small positive Δμ₀. Since ω(n) behaves as in Eq. (2.19) for small Δμ₀, there arises a singular contribution in the integral in Eq. (2.16), which is proportional to Δμ₀ ln(aΔn₁/Δμ₀). Here Δn₁ = n^d(c) – n^c. Note the formula \[ f \int dx[(Δx)^2 + Δe] = 1 + Δe/2 + Δ ln((4Δe)/e) + \cdots \] for 0 < e ≪ 1 to derive it. For small ΔT and Δμ₀, the difference ΔΩ = Ω^d(c) – Ω^c is equal to the potentials for thick and thin films consists of two contributions as

\[ ΔΩ = (ΔΩ)c + (ξ^d Δn₁/Δμ₀) ln \left( \frac{ξ^d Δn₁}{Δμ₀} \right), \]  

where the first term is given by Eq. (A4). The predrying curve is determined by the condition ΔΩ = 0, which starts from the reference point on the coexistence curve and extends outside it. The derivative dΔμ₀/dT along the predrying line behaves as

\[ \frac{dT^d(c)}{dT} \frac{dΔμ₀}{dγ} = \left( \frac{ξ^d Δn₁}{Δμ₀} \right) ln(ξ^d Δn₁/Δμ₀), \]  

where the denominator in the right hand side grows logarithmically as Δμ₀ → 0. This result is well known for a prewetting line [9]. However, in the presence of the long-range van der Waals interaction, it follows the relation Δμ₀ ∝ (ΔT^γ) with c ≃ 1.5 [4].

APPENDIX B: CALCULATIONS NEAR THE CRITICAL POINT

We examine the predrying transition near the critical point in the mean-field theory. The surface free-energy density is linear in n as in Eq. (2.1). The density n and the temperature T are assumed to be close to their critical values n_c and T_c. We expand the Helmholtz free-energy density f = f(n, T) in powers of the density deviation \[ ψ = n - n_c \] up to the quartic order as

\[ f(n, T) = f_c(T) + μ_c(T)ψ + \frac{a_0}{2} ψ^2 + \frac{a_0}{4} ψ^4, \]  

where a₀, b₀, and c₀ are positive constants.
where \( f_s(T) = f(n_c, T), \mu_s(T) = \mu(n_c, T), \) and
\[
\tau = T/T_c - 1 \quad \text{(B2)}
\]
is the reduced temperature. We assume \( \tau < 0. \) Then the liquid and gas densities on the coexistence line are \( n_c + \psi e \) and \( n_c - \psi e, \) respectively, with
\[
\psi e = (a_0 |\tau|/u_0)^{1/2}. \quad \text{(B3)}
\]
In the van der Waals model in Eq. (2.22) [40], \( T_c = 8\varepsilon/27k_B, \)
\( n_c = \nu_0^{-1}/3, \) and
\[
a_0 = 2\nu_0, \quad u_0 = 9\nu_0^{3/2}. \quad \text{(B4)}
\]
With the Landau expansion (B1), \( \psi \) in Eq. (2.7) is written as
\[
\omega = \frac{u_0}{4}(\psi - \psi_0)^2(\psi^2 + 2\psi_0 \psi + 3\psi_0^2 - 2\psi_0^2), \quad \text{(B5)}
\]
where \( \psi_0 = n_0 - n_c \) is the value of \( \psi \) far from the wall assumed to be small. The derivative \( \omega' = \partial \omega/\partial n \) is equal to the chemical potential deviation \( \mu = \mu_c \) written as
\[
\omega' = u_0(\psi - \psi_0)(\psi^2 + \psi_0 \psi + \psi_0^2 - \psi_0^2). \quad \text{(B6)}
\]
Here we introduce a dimensionless surface field \( \hat{\gamma} \) by
\[
\hat{\gamma} = \gamma(2/u_0 M)^{1/2} \psi e^2 = \sqrt{\frac{3}{8} \psi e^2 |\tau|}, \quad \text{(B7)}
\]
where the second line is the result of the van der Waals model. For each \( \hat{\gamma} \) and \( \psi_0/\psi e, \) the condition (2.15) yields the equation for the surface density deviation \( \psi e = n_0 - n_c \) (which is smaller than \( \psi_0 \)) in the form
\[
(\psi_0 - \psi e)(\psi e^2 + 2\psi_0 \psi e + 3\psi_0^2 - 2\psi_0^2)^{1/2} /\psi e^2 = \hat{\gamma}. \quad \text{(B8)}
\]
As illustrated in Fig. 2, this equation has two solutions: \( \psi e = n_0^L - n_c \) and \( \psi e = n_0^H - n_c, \) corresponding to the two surface densities at the predrying transition.

First, we take the limit \( n_0 \to n_0^L \) or \( \psi e \to \psi e \) on the prewetting line, where the film thickness grows as in Eq. (2.21) but \( \psi e = n_0^L - n_c, \) and \( \hat{\gamma} \) tend to finite limiting values. From Eq. (B8) we obtain \( \hat{\gamma} = |\psi e^2 /\psi e^2 - 1| \) in this limit. Since \( \psi e < -\psi e \) and \( \psi e > \psi e \) we find
\[
\psi e^L = n_0^L - n_c = -\psi e(1 + \hat{\gamma})^{1/2}, \quad \psi e^H = n_0^H - n_c = \psi e(1 - \hat{\gamma})^{1/2}. \quad \text{(B9)}
\]
The equal area requirement \( S_1 = S_2 \) in Fig. 2 yields
\[
(1 + \hat{\gamma})^{3/2} - (1 - \hat{\gamma})^{3/2} = 2, \quad \text{(B10)}
\]
whose square gives \( 3\hat{\gamma}^2 - 1 = (1 - \hat{\gamma}^2)^{3/2}. \) Again taking the square of this equation, we find \( \hat{\gamma}^2 + 6\hat{\gamma}^2 = 3, \) which is solved to give
\[
\hat{\gamma} = \sqrt{2\sqrt{3} - 3} = 0.68125. \quad \text{(B11)}
\]
Therefore, as \( T \to T_D^\psi(\gamma) \), the two surface densities at the predrying transition are \( \psi e^L \approx -1.2966\psi e \), and \( \psi e^H \approx 0.5646\psi e \). From Eq. (B7), the predrying value of \( \gamma \) on the coexistence curve is written as
\[
\gamma e(T) = \frac{2}{3}(2\sqrt{3} - 1)^{1/2}|\tau|/\ell. \quad \text{(B12)}
\]
We then obtain the coefficient \( A_{\psi c} \) in Eq. (2.25).

Second, we seek the value of \( \gamma \) at the predrying critical point, denoted by \( \gamma c(T) \). Since \( \psi e(\partial\omega/\partial n) = 0 \) at \( n = n_c, n_s \) coincides with the spinodal density on the gas branch so that
\[
\psi s = n_s - n_c = -\psi e/\sqrt{3}. \quad \text{(B13)}
\]
Then from Eq. (2.15) we find
\[
\gamma c(T) = 8|\tau|/\ell/9. \quad \text{(B14)}
\]
From the additional condition \( \omega' = 0 \) at \( \psi = \psi e, \) Eq. (B7) yields the bulk density deviation \( \psi e \) in this case as
\[
\psi e = n_0 - n_c = 2\psi e/\sqrt{3}, \quad \text{(B15)}
\]
which is larger than \( \psi e \) as it should be. For each small \( \gamma \), the reduced temperature \( \tau \) and the density deviation \( n_0 - n_c \) are given by \( \tau^L = -9\gamma/8\ell \) and \( 4|\tau^H|/3\sqrt{3}\nu_0, \) respectively, at the predrying critical point. We then obtain the coefficient \( A_{\psi c} \) in Eq. (2.25).

Our calculation results are applicable to the prewetting transition near the critical point, where \( \gamma, \psi e, \) and \( \psi e \) are small negative quantities. To use the above relations, we should set \( \psi e = -(a_0 |\tau|/u_0)^{1/2} \) and replace \( \psi e \) by \( |\gamma|/\ell |\) in the comment below Eq. (2.24) on \( T_w \) and \( T_c^\mathrm{pw} \).

We should note that Papatzzacos [55] obtained the wetting angle \( \theta_w \) in partial wetting for the linear surface free energy in Eq. (2.1) and the bulk free energy in Eq. (B1) (see Ref. [37] also). In our notation, the drying angle \( \theta_d = \pi - \theta_w \) satisfies
\[
(1 + \hat{\gamma})^{3/2} - (1 - \hat{\gamma})^{3/2} = 2 \cos \theta_d, \quad \text{(B16)}
\]
where the fluid is on the coexistence curve. The above equation becomes \( \hat{\gamma}^6 + 6\hat{\gamma}^4 + 3\hat{\gamma}^2(1 - 2\cos(2\theta_d)) = \sin^2(2\theta_d). \) Setting \( \beta = 3^{-1/2} \) and \( \sin(2\theta_d) = \beta(1 - \cos(2\theta_d)), \) we solve this equation to obtain
\[
\hat{\gamma} = 2\sin(\pi/2 - \theta_d)\sqrt{\cos(\beta(1 - \cos(2\theta_d))), \quad \text{(B17)}}
\]
where \( \sin(x) \) gives the sign of \( x. \) For \( \gamma > 0, \) we have the complete drying limit \( \theta_d \to 0 \) (or \( \theta_w \to \pi \)) as \( T \to T_D^\psi = T_c(1 - A_{\psi c}\gamma/\ell + \cdots) \) from below. For \( \gamma < 0, \) we have the complete wetting limit \( \theta_d \to 0 \) (or \( \theta_w \to \pi \)) as \( T \to T_w = T_c(1 - A_{\psi c}\gamma/\ell + \cdots) \) from below.

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