Theory of Nucleated Wetting

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We compare a new theory of nucleated wetting with experimental data for the critical liquid mixture hexadecane + acetone. Good agreement is obtained for $t \gtrsim 8\times10^{-5}$. We determine that the droplet line tension $\mathcal{L} = \mathcal{L}_0 t^x$ where $\mathcal{L}_0 \sim 1\times10^{-7}$ erg/cm and $x = 0.76\pm0.02$ while the spreading pressure $S \approx S_0 t^{\beta_1}$ where $S_0 \sim 0.007$ erg/cm^2. Theory and experiment exhibit a minimum in the nucleation data at a reduced temperature of t_m ($\approx 0.000\,22$ for an upper hexadecane-rich bulk phase of height $L = 0.56$ cm); theory predicts that t_m scales as $\sim L^{2/3(\beta_1-\beta)}$.

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In recent years there has been intense interest in the area of nonequilibrium wetting effects. Many new phenomena have been observed such as surface-directed spinodal decomposition [1], wetting during spinodal decomposition [2] (which we call "spinodal wetting"), nonequilibrium effects on wetting and adsorption [3], nucleated wetting [4,5], and metastable surface states and layering transitions [6]. This field is in a rapid state of flux where the experimental observations are still being clarified and where often no well-developed theory exists which can quantitatively explain the observations.

In a recent Letter [4] we described the new phenomenon of nucleated wetting where upon quenching a critical binary liquid mixture from the one phase region into the two phase region at time $\tau = 0$ s we observed that after an initial transient (which we attributed to spinodal wetting) the binary liquid/vapor surface entered a metastable surface state (Fig. 1) which had all of the characteristic properties of critical adsorption [7,8]. This metastable state had a surprisingly long lifetime τ_0 of many hours where the lifetime was found to depend upon the reduced temperature $t = |T_c - T|/T_c$, where T is the temperature to which the system had been quenched. At time $\tau = \tau_0$ the ellipsometric signal $\bar{\rho}$ became very noisy indicating that wetting droplets of lateral radius r and thickness h (Fig. 1, inset) had nucleated at the liquid/vapor surface. In [4] we explained the nucleation time by introducing a line tension $\mathcal{L}$ into the excess surface free energy of the droplet

$$F \approx -S\pi r^2 + \mathcal{L}2\pi r + W\pi r^2/h^2 + \Delta\rho g L V\,. \qquad (1)$$

Here the spreading pressure $S = \sigma_{\alpha v} - \sigma_{\beta v} - \sigma_{\alpha\beta}$, σ_{ij} is the surface tension between phases i and j, $W\pi r^2/h^2$ is the dispersion energy contribution [9,10], and $\Delta\rho g L V$ is the gravitational contribution with $\Delta\rho = \rho_\beta - \rho_\alpha$, g the acceleration due to gravity, L the height of the bulk α phase, and V the droplet volume. The upper (lower) liquid phase is α (β) and β droplets nucleate at the αv surface (Fig. 1). In [4] we suggested that the dominant terms in (1) were the line tension and the spreading pressure; the τ_0 data could be explained using classical nucleation theory provided that $\mathcal{L} \sim t^x$ with $x \sim 0.83$.

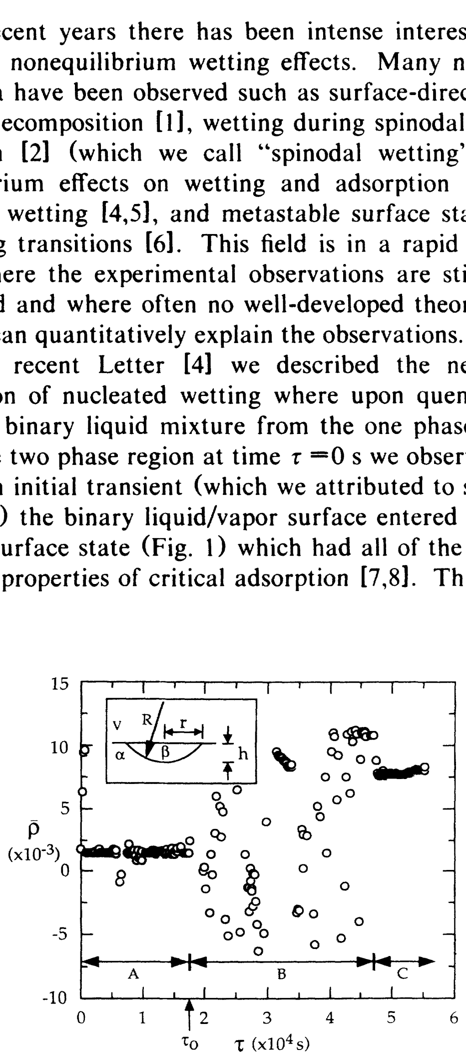

FIG. 1. Variation of the ellipsometric signal $\bar{\rho}$ as a function of time τ for a critical hexadecane+acetone sample after a temperature quench of 0.668 °C at $\tau = 0$ s. After an initial transient near $\tau = 0$ s the surface drops into a surface metastable state (region A); at $\tau = \tau_0$ wetting droplets of the heavier β phase nucleate and grow at the αv surface (region B); eventually all of the wetting droplets coalesce into a uniform film (region C). The inset shows a wetting β droplet of lateral radius r, $\alpha\beta$ radius of curvature R, and thickness h, at the αv surface.

This simple theory cannot explain recent observations at very small reduced temperatures where the nucleation time exhibits a minimum at a reduced temperature $t_m \sim 0.0002$ and then *diverges* for smaller t (Fig. 2). There are also a number of problems with the theory in [4] which stem principally from treating the parameters r and h as independent variables.

The objective of this publication is to develop a new theory of nucleated wetting, whose underlying theoretical basis is more appropriate for the physical situation, and which quantitatively describes most of the experimental observations. In the process we will be able to deduce quantitative estimates for both the magnitude and exponent of the line tension and the magnitude of the spreading pressure for the liquid mixture hexadecane + acetone. These quantities are in general very difficult to measure. The theory also predicts that the minimum in the nucleation time at reduced temperature t_m scales as $\sim L^{2/3(\beta_1-\beta)}$, where β_1 is a surface critical exponent

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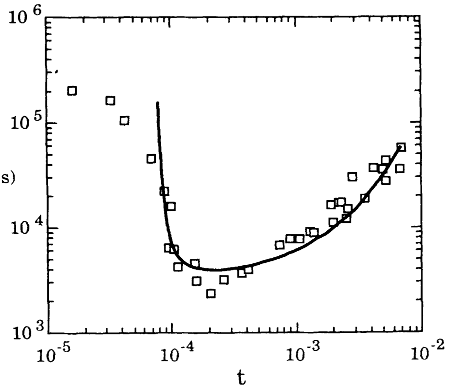

FIG. 2. Comparison of the nucleation time τ_0 as function of reduced temperature t with theory. Experimental data (open squares); theory as given by Eq. (10) (solid line). See text for details.

(≈ 0.83 [12]) and β is the usual bulk critical exponent describing the shape of the coexistence curve. We note that this new theory for the nucleation time τ_0 reduces to the form given in [4] in the limit of large $t \gg t_m$; hence one can also understand the good agreement observed previously between theory and experiment.

This new theory will again use the simple model of a nucleated wetting droplet given in (1) where we assume that the contact angle θ is very small ($R \gg r \gg h$; Fig. 1 inset) because we are above the wetting transition. In this paper we will not treat r and h as independent but instead consider a droplet of fixed volume [10],

$$V = Ah/2 = \pi r^2 h/2\,, \tag{2}$$

where we model the droplet as a spherical cap; hence the factor of $\frac{1}{2}$ in V [13]. We assume that after this droplet nucleates at the surface the local surface kinetics are sufficiently rapid that the droplet thickness readjusts itself under the influence of the surface potential to minimize F for *fixed* V. Namely, the droplet shape kinetics are much faster than the droplet growth kinetics which are determined by diffusion. This treatment is similar to the spreading kinetics of a droplet of fixed volume V on a solid surface considered by de Gennes [11]. However, de Gennes considered the *slow* spreading of a very viscous polymer droplet. In this paper we consider a low viscosity liquid mixture where the droplet is expected to acquire its "steady-state" shape very quickly.

By minimizing (1) at fixed V one obtains the following equation for h [14]:

$$\mathcal{L}\sqrt{\pi h/2V} - S + 3W/h^2 = 0\,. \tag{3}$$

For large droplet volumes $h \approx (3W/S)^{1/2}$ while for small droplet volumes near the critical droplet volume, V_c, we assume that [15]

$$h = \alpha\sqrt{W/S}\,, \tag{4}$$

where α is a volume independent dimensionless parameter which will be determined from (3) once V_c has been determined. Droplets with V greater than (less than) V_c grow (evaporate) as in normal classical nucleation theory. From (1), (2), and (4) we obtain the equation for the free energy of a *steady-state droplet* of volume V:

$$F(V) = 2\mathcal{L}\left(\frac{2\pi V}{\alpha}\right)^{1/2}\left(\frac{S}{W}\right)^{1/4} + \frac{2V}{\alpha}\left[S\left(\frac{1}{\alpha^2} - 1\right)\left(\frac{S}{W}\right)^{1/2} + \frac{\Delta\rho g L \alpha}{2}\right]. \tag{5}$$

The critical droplet volume V_c is determined by the condition $\partial F(V)/\partial V = 0$; therefore,

$$V_c = \frac{\pi\alpha\mathcal{L}^2\sqrt{W/S}}{2[S(1-\alpha^{-2}) - (\Delta\rho g L\alpha/2)\sqrt{W/S}\,]^2}\,. \tag{6}$$

Finally the value of α can be determined by substituting (4) and (6) into (3). We obtain

$$\alpha = \left[\frac{4S}{\Delta\rho g L}\left(\frac{S}{W}\right)^{1/2}\right]^{1/3} = \alpha_0 t^{(\beta_1 - \beta)/2}\,, \tag{7}$$

where $\alpha_0 = [4S_0(S_0/W_0)^{1/2}/\Delta\rho_0 g L]^{1/3}$, $S = S_0 t^{\beta_1}$ [16], $\Delta\rho = \Delta\rho_0 t^{\beta}$, $W = W_0 t^{\beta}$ [9], and the terms with a subscript 0 represent temperature independent amplitudes. The height of the droplet nucleation barrier is determined from (5) with $V = V_c$,

$$F(V_c) = \frac{\pi\mathcal{L}_0^2 t^{2x-\beta}}{S_0(t^{\beta_1-\beta} - C_0)}\,, \tag{8}$$

where $\mathcal{L}_0$ and x are, respectively, the amplitude and exponent of the line tension and the constant

$$C_0 = 3/\alpha_0^2\,. \tag{9a}$$

The probability of nucleating a critical droplet is $p \sim \exp[-F(V_c)/k_B T]$, where k_B is Boltzmann's constant, and therefore the nucleation time $\tau_0 \sim 1/p \sim \exp[F(V_c)/k_B T]$. A further simplification can be made in analyzing the experimental data by noting that a minimum occurs in the nucleation data τ_0 at a reduced temperature of $t_m \sim 0.0002$ (Fig. 2). This minimum in τ_0 must correspond to a minimum in $F(V_c)$; therefore from the condition that $\partial F(V_c)/\partial t = 0$ we obtain a second condition for the constant C_0:

$$C_0 = t_m^{\beta_1-\beta}\left(\frac{2x-\beta_1}{2x-\beta}\right). \tag{9b}$$

We therefore fit the nucleation data by an equation of the form

$$\tau_0 = A\exp\left\{\frac{Bt^{2x-\beta}}{\{t^{\beta_1-\beta} - t_m^{\beta_1-\beta}[(2x-\beta_1)/(2x-\beta)]\}(1-t)}\right\}, \tag{10}$$

where A, B, and x are adjustable parameters and B is related to $\mathcal{L}_0$ and S_0 by

$$B=\pi\mathcal{L}_0^2/S_0k_BT_c\,. \tag{11}$$

A nonlinear least squares fit of the τ_0 data in the range $t\geq 8\times10^{-5}$ to Eq. (10), assuming an error of $\pm20\%$ in τ_0, gave $x=0.76\pm0.02$, $A=2000\pm200$ s, and $B=90\pm20$, where the errors represent 1 standard deviation and the reduced chi squared $\chi^2=2.7$. χ^2 is sensitive to the value assumed for t_m—in our calculations we have taken $t_m=0.000\,22$ which corresponds to a minimum in χ^2. In Fig. 2 we show the good agreement between the experimental data and Eq. (10) for the parameters given above [19]. The experimental data at very small reduced temperatures below 7×10^{-5} could not be explained by (10).

According to this new theory the divergence in τ_0 at very small t occurs when the spreading pressure contribution becomes comparable to the sum of the dispersion and gravitational energies [see Eq. (1)], at which point the denominator in (10) vanishes. The moderately large χ^2 and the disagreement between theory and experiment for $t\leq7\times10^{-5}$ can probably be attributed to our very simple model of a nucleated wetting droplet. We have assumed that the contact angle is negligible and we have ignored the fact that the critical $\alpha\beta$ interface of the droplet is diffuse and diverges proportional to the correlation length ξ. Capillary wave contributions [20] have also been omitted from the free energy in (1). We note that there are some experimental difficulties at very small $t<8\times10^{-5}$, where the sample temperature drifts down very slowly towards equilibrium over many, many hours. (Far from T_c thermal equilibrium is attained in $\sim$0.5 h.) We believe this effect is due to the release of heat during mixing as the sample spinodally decomposes [21]. Such an effect is particularly important for very small reduced temperatures where the phase separation process is slow and where locally the heat of mixing can raise the temperature even closer to T_c or even back into the one phase region.

This theory enables us to determine a number of parameters which are in general very difficult to measure. From (9a) and (9b) we determine that $S_0\sim0.007$ erg/cm^2 where for our hexadecane + acetone sample we have used $\Delta\rho_0=0.0375$ g/cm^3 [22], $L=0.56$ cm, and $W_0\sim2.9\times10^{-16}$ erg [23]. Similarly from (11) we determine that $\mathcal{L}_0\sim1\times10^{-7}$ erg/cm using $T_c=304.265$ K. The magnitude of $\mathcal{L}_0$ is qualitatively similar to line tensions found in other liquid systems [24] determined using different techniques. The approximate size of the nucleated droplets can also be calculated. From (4) and (7) the critical droplet thickness is temperature independent with $h_c=\alpha_0(W_0/S_0)^{1/2}\sim38$ nm, while near the nucleation minimum at t_m the critical droplet radius $r_c\sim560$ nm [using (2) and (6)]. This droplet has a diffuse $\alpha\beta$ interface as $\xi\sim40$ nm [23] and a small contact angle, $\theta\sim4°$. Unfortunately hexadecane+acetone and also most polar liquid mixtures are not ideal candidates for testing this theory as they exhibit a rather complicated dispersion energy curve as a function of depth into the liquid [23,25]. In the calculation above we have used an effective Hamaker constant determined from the dispersion force curves when $h\sim30$–40 nm [23].

It has been suggested that $\mathcal{L}\sim k_BT/\xi\sim t^{\nu}$ using an argument similar to Widom [26] for the critical interfacial tension. If we assign $x=\nu$ then (10) does not fit the experimental data ($\chi^2\sim2000$). We believe the problem is related to the presence of a noncritical ($\sim$0.5 nm) and a critical correlation length ($\xi\sim t^{-\nu}$) for the nucleated droplet. It seems possible that $\mathcal{L}$ might scale as t^{ν} near a tricritical point where the vapor phase has been replaced by a critical phase.

In conclusion, we have proposed a new theory of nucleated wetting which gives better agreement with experimental observations over a wider reduced temperature range. This new theory predicts that the reduced temperature t_m scales as $\sim L^{2/3(\beta_1-\beta)}$; it allows us to determine estimates of the magnitude and exponent for the line tension and the magnitude for the spreading pressure for the critical liquid mixture hexadecane+acetone. Further extensions to this theory are required to account for nonzero contact angles, the diffuse $\alpha\beta$ interface, a more realistic description of the dispersion energy, droplet growth, and coalescence.

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[10] For spherical cap-shaped droplets the spreading pressure and droplet volume take the forms given in (1) and (2) in the limit of small contact angles, namely, for $R\gg r\gg h$. A spherical cap-shaped droplet is, however, only an approximation for the real shape of the droplet. For large V the droplet takes the form of a pancake where it is parabolic near the perimeter and of constant thickness

$\sim(W/S)^{1/2}$ far from the perimeter [11]. The dispersion energy can then be approximately demarcated into a line tension energy near the perimeter and an energy $\sim W\pi r^2/h^2$ away from the perimeter. The later energy is only an approximation at small V. With this form we ensure that $h\sim(W/S)^{1/2}$ at large V as required [see Eq. (3)].

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[14] As $V=\pi r^2 h/2$, Eq. (3) is in reality the two-dimensional Laplace equation with the inclusion of the dispersion energy, namely, $S=\mathcal{L}/r+3W/h^2$.

[15] Physically this assumption implies that h is determined by the local potential. This is expected to be valid for our situation where $R\gg r\gg h$.

[16] What is the temperature dependence of the spreading pressure S? According to the Cahn argument [17], $S=\sigma_{\alpha v}-\sigma_{\beta v}-\sigma_{\alpha\beta}=S_0 t^{\beta_1}-\sigma_0 t^{\mu}$ below the wetting transition T_w, while above T_w the equilibrium spreading pressure, denoted S_e, is *zero*. For our situation we are above T_w and therefore have a nonequilibrium spreading pressure. The key question in determining the temperature dependence of S is: What is the metastable surface tension $\sigma_{\alpha v}$(meta)? We argue below that $\sigma_{\alpha v}$(meta) has the same temperature dependence as the equilibrium surface tension $\sigma_{\alpha v}$(equil) below T_w; therefore, $S=S_0 t^{\beta_1}-\sigma_0 t^{\mu}$ ($\sim t^{\beta_1}$ for small t) above T_w. According to mean field theory [18] the surface tension above and below T_w is determined by $\sigma_{\alpha v}\sim\int[\partial\psi(z)/\partial z]^2 dz$, where $\psi(z)$ is the order parameter profile at the liquid/vapor surface. Below T_w, $\psi(z)$ is described by critical adsorption; we have shown [4] that the metastable state $\psi_{\mathrm{meta}}(z)$ above T_w is also described by critical adsorption. Therefore $\psi(z)$ and $\psi_{\mathrm{meta}}(z)$ exhibit the same temperature dependence and hence $\sigma_{\alpha v}$(equil) and $\sigma_{\alpha v}$(meta) will also exhibit the same temperature dependence above and below T_w.

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