Wetting Transitions at Fluid Interfaces and Related Topics

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Abstract

Wetting transitions, in which a fluid wets the interface between two fluid phases, are defined. There may be first, second, and higher order transitions. The line tension, an excess free energy per unit length of a three-phase contact line, and the boundary tension, another excess free energy associated with the boundary of two surface phases at the prewetting transition, are also defined. Mean-field density functional models of the fluid interfaces are introduced and their results on the wetting transitions, the line and boundary tensions, and the fluid structures in the three-phase contact region are presented.

1. Wetting transition

When three fluid phases coexist, they do so either in the two possible modes: (i) they meet at a common line of contact and the three interfaces make dihedral angles or (ii) one of them wets the interface of the other two, i.e., it occupies between the two phases as an infinitely thick layer. The transition between the two states is the wetting transition [1, 2]. There must be at least two components in a fluid system if the system exhibits a wetting transition, because otherwise the thermodynamic state of three-phase coexistence cannot be varied. The two modes are illustrated in Fig. 1, where α, β, γ are the three coexisting phases and the $\alpha\gamma$ interface is either not wet or wet by β. In the non-wet states, the surface tensions of the $\alpha\beta$, $\beta\gamma$, and $\alpha\gamma$ interfaces satisfy the inequality:

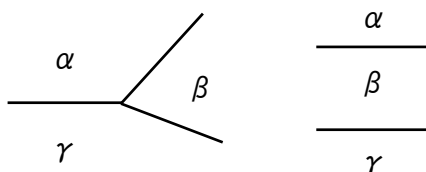$$\sigma_{\alpha\beta} + \sigma_{\beta\gamma} > \sigma_{\alpha\gamma} \qquad (1)$$

and the contact angle β is given by

$$\cos\beta = 1 - \frac{(\sigma_{\alpha\beta} + \sigma_{\beta\gamma} + \sigma_{\alpha\gamma})(\sigma_{\alpha\beta} + \sigma_{\beta\gamma} - \sigma_{\alpha\gamma})}{2\sigma_{\alpha\beta}\sigma_{\beta\gamma}}. \qquad (2)$$
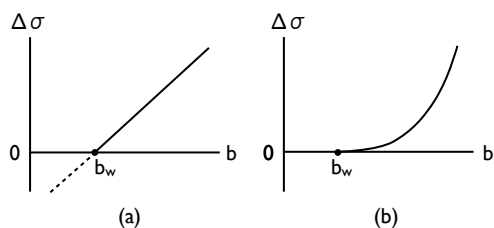
In the wet states, the $\alpha\gamma$ interface may be considered as a composite of the $\alpha\beta$ and $\beta\gamma$ interfaces. Then

$$\sigma_{\alpha\beta} + \sigma_{\beta\gamma} = \sigma_{\alpha\gamma} \qquad (3)$$

and the contact angle $\beta = 0$. The wetting transition may be viewed as a transition in the structure of the $\alpha\gamma$ interface, between one in which that interface does not, and one in which it does, consist of a layer of a macroscopic β phase.

Fig. 1. Two modes of three-phase equilibrium.

Fig. 2. (a) First-order wetting transition; (b) Second-order wetting transition.
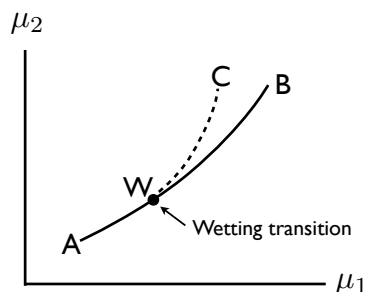
Let b be a thermodynamic field variable (temperature, pressure, or a chemical potential) that varies through the region of three-phase coexistence. The wetting transition occurs at $b = b_w$, with $b > b_w$ the regime in which $\alpha\gamma$ interface is not wet by the β phase and $b < b_w$ that in which it is. The order n of the wetting transition is the exponent in

$$\sigma_{\alpha\beta} + \sigma_{\beta\gamma} - \sigma_{\alpha\gamma} \sim (b - b_w)^n \qquad (4)$$

which shows $\Delta\sigma = \sigma_{\alpha\beta} + \sigma_{\beta\gamma} - \sigma_{\alpha\gamma}$ vanishes proportinally to the n-th power of $b - b_w$. Figure 2 shows the variation of $\Delta\sigma$ with b. In Fig. 2(a), $\Delta\sigma$ vanishes proportionally to $b - b_w$ and it has a metastable extension, indicated by the dashed line. This is the first-order wetting transition. In Fig. 2(b), on the other hand, $\Delta\sigma$ vanishes proportionally to $(b-b_w)^2$ and there is no metastable extension to $b < b_w$. From Eq. (2), the first-order and second-order wetting transitions may also be distinguished by the behavior of the contact angle β

$$\beta \sim (b - b_w)^{1/2} \quad \text{(first order)},$$
$$\beta \sim b - b_w \qquad \text{(second order)}. \qquad (5)$$

It is usually observed that the wetting transition at the liquid-vapor or liquid-liquid interface is of first order. The continuous wetting transition has long been studied in theoretical models but its experimental observations are scarce and controversial. One example is a wetting transition close to the critical point in methanol-alkane binary liquid mixtures [3].


Fig. 3. The triple-point line AB and the prewetting-transition locus CW projected onto the plane of two thermodynamic field variables.

2. Prewetting transition

A prewetting transition is a transition in the $\alpha\gamma$ interface in two-phase equilibrium, in which phase β is not present but comes to be anticipated by the sudden appearance of a β-like layer in the $\alpha\gamma$ interface. It is often associated with the first-order wetting transition in three-phase equilibrium.

Consider a two-component mixture which exhibits a wetting transition. The phase diagram is given in a three-dimensional space of thermodynamic field variables (e.g., temperature, pressure, and a chemical potential): regions of two-phase coexistence form surfaces and those of three-phase coexistence form lines in the 3-d thermodynamic space. Figure 3 shows a 'triple-point' line, AB, as projected onto the plane of two of the mixture's three thermodynamic field variables, called μ_1, μ_2 in the figure. The wetting transition occurs at W. The segment AW corresponds to the non-wet states and WB to the wet states. The prewetting line is CW. In the three-dimensional space the prewetting line lies in the $\alpha\gamma$ coexistence surface, where it is tangent to the triple-point line at W [4]. In states on the $\alpha\gamma$ coexistence surface far from the triple-point line AB the $\alpha\gamma$ interface is thin; but as the state of two-phase coexistence crosses the prewetting line, there is a discontinuous change in the structure of the $\alpha\gamma$ interface, to one that is thick with
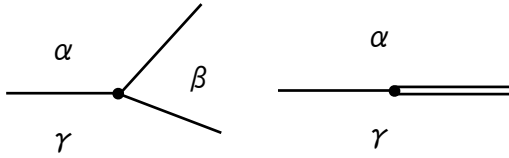
Fig. 4. (a) Three phases α, β, γ meeting at a line of common contact. The three-phase contact line, marked by a dot, and the interfaces are perpendicular to the plane of the figure. (b) Two distinct surface phases coexisting in the $\alpha\gamma$ interface. The boundary between the surface phases and the $\alpha\gamma$ interface are perpendicular to the plane of the figure.

the β-like layer. As the state further approaches the triple-point line, in the region between CW and WB in the figure, the β-like layer thickens and eventually becomes macroscopically thick when the triple-point line is reached.

3. Line and boundary tensions

The physical space occupied by the three equilibrium phases and that occupied by the two equilibrium phases are displayed schematically in Fig. 4. In Fig. 4(a), the three phases α, β, γ meet at a line of common contact. The contact line is perpendicular to the plane of the figure, as are the three interfaces. Of course, the contact "line" and surface "plane" have diffuse structures on a molecular scale. The structure and composition of the system vary only in the plane of the figure. There is an excess free energy per unit length of the contact line, which is the line tension τ. At prewetting, two distinct surface structures may coexist in the $\alpha\gamma$ interface with a boundary line separating them. This is shown in Fig. 4(b). Associated with the boundary between the surface phases is a different linear tension, which is the boundary tension τ_b. It may be viewed as an analog of the surface tension, σ, in two dimensions. The boundary tension τ_b is necessarily positive as the surface ten-

sion σ is; otherwise the linear boundary cannot be stable. However, the line tension τ may be of either sign, because the stability of the contact line is primarily determined by the surface tensions.

There has been long standing interest in how the line tension τ behaves as the wetting transition is approached along the three-phase line (AW in Fig. 3); and likewise in how the boundary tension τ_b behaves as the wetting transition is approached along the prewetting line (CW in Fig. 3).

As the wetting transition is approached along AW in Fig. 3, the contact angle β closes down to 0 and the $\alpha\beta$ and $\beta\gamma$ interfaces become parallel to each other and infinitely separated from each other by the β phase. As wetting is approached along the prewetting line, the β-like layer in one of the two surface structures becomes indefinitely thick. The two fluid structures, one having the contact line of the three phases and one having the boundary line of the two surface structures, becomes identical at the wetting transition. Therefore the line tension τ and the boundary tension τ_b should have the same limiting value τ_w at wetting. Since the boundary tension can never be negative, it follows that the line tension τ_w is necessarily nonnegative.

4. Theoretical Approaches

4.1 Density-Functional Models

Van der Waals published in 1893 a paper entitled *The thermodynamic theory of capillarity under the hypothesis of a continuous variation of density* [5]. This may be considered the origin of molecular theory of capillarity, for it presented the basic idea of the mean-field density-functional theory of inhomogeneous fluids and succeeded in determining the shape of the density profile $\rho(z)$ and the surface tension σ of a liquid-vapor interface. The mean-field theory remains to be an indispensable tool for studying inhomogeneous fluids [6–9].

The mean-field density-functional theory of wetting [1, 6–9] assumes that the free-energy density Ψ is defined at any point of an inhomogeneous system. It is *not* a function of densities but a functional of them and in general is of the form

$$\Psi = e[\{\rho_i(\mathbf{r})\}] - \sum_i \mu_i \rho_i(\mathbf{r}) + p(\{\mu_i\}) + K,$$
$$= F(\{\rho_i\}) + K \qquad (6)$$

where e is a mean-field energy density and a function of $\{\rho_i\}$ alone, p is a mean-field pressure and a function of $\{\mu_i\}$ alone, and K is a non-local functional of $\{\rho_i(\mathbf{r})\}$ and independent of μ_i. The $F(\{\rho_i\})$ denotes all the terms except K in the first line of Eq. (6). In three phase equilibrium the function F has a common minimum value of 0 when $\{\rho_i\}$ are the densities of the three coexisting phases α, β, and γ far from the interfaces and the contact line. The tensions of the three interfaces are obtained by minimizing the functional

$$\sigma = \int_{-\infty}^{\infty} \Psi dz \qquad (7)$$

with respect to variations in $\{\rho_i(z)\}$, subject to the boundary conditions at $z \pm \infty$. Here z is the direction perpendicular to an assumed planar interface; $\{\rho_i\}$ vary only in the direction and approach the values of the bulk phases as z goes to $\pm\infty$. The F is also a function of thermodynamic field variables which change the thermodynamic state of three phase equilibrium. One can study the nature of a wetting transition by calculating the three surface tensions as functions of the field variables and examining the behavior of $\sigma_{\alpha\beta} + \sigma_{\beta\gamma} - \sigma_{\alpha\gamma}$ as in Eq. (4).

To calculate the line tension τ [6, 7], choose a point in the plane of Fig. 4(a) to be the normal location of the contact line, and construct around that point a triangle (Neumann triangle) with sides perpendicular to the three interfaces and distant $R_{\alpha\beta}$, $R_{\beta\gamma}$, $R_{\alpha\gamma}$ from the chosen point. The size of the triangle is taken to be sufficiently large so that the densities along the sides are ef-

fectively identical with what they are in the interfaces infinitely far from the contact line. Then

$$\tau = \lim_{R_{\alpha\beta} \to \infty, \text{ etc.}} [\min \int \Psi da$$
$$- (\sigma_{\alpha\beta} R_{\alpha\beta} + \sigma_{\beta\gamma} R_{\beta\gamma} + \sigma_{\alpha\gamma} R_{\alpha\gamma})], \quad (8)$$

where the integration is through the area A of the triangle with da an element of area. The variational minimization is now over the densities $\{\rho_i(\mathbf{r})\}$ with the boundary conditions that $\{\rho_i(\mathbf{r})\}$ on the sides of the triangle be the respective interfacial profile $\{\rho_i(z)\}$. Numerical calculation of the line tension τ is much more difficult than that of the surface tension σ, for it requires the minimization in two dimensions instead of in one dimension [7].

For the boundary tension τ_b, the spacial structure is like that in Fig. 4(b). If we define an x, z coordinate system in the plane of the figure, with origin at the boundary between the surface phases, and with the x axis parallel to the plane of the $\alpha\gamma$ interface and the z axis perpendicular to it. Then

$$\tau_b = \min_{\{\rho_i\}} \int_{-\infty}^{\infty} \left(\int_{-\infty}^{\infty} \Psi dz - \sigma_{\alpha\gamma}^* \right) \qquad (9)$$

with $\sigma_{\alpha\gamma}^*$ now the common value of the surface tensions for the two surface phases [7].

To illustrate several kinds of the wetting transitions in the density-functional models, consider the three-phase equilibrium of a two-component system. The function F in Eq. (6) is taken to be $F(\rho_1, \rho_2; a, b)$ a function of two densities ρ_1, ρ_2 and two field parameters a, b [9]. As mentioned earlier the function F has a common minimum value of 0 when ρ_1, ρ_2 are the densities of the three coexisting phases α, β, and γ:

$$\alpha : \rho_1 = -1, \ \rho_2 = 0;$$
$$\beta : \rho_1 = 0, \ \rho_2 = b; \qquad (10)$$
$$\gamma : \rho_1 = 1, \ \rho_2 = 0;$$

The parameter b is a thermodynamic field parameter that induces wetting; a is an anisotropy parameter that, as we will see, determines the
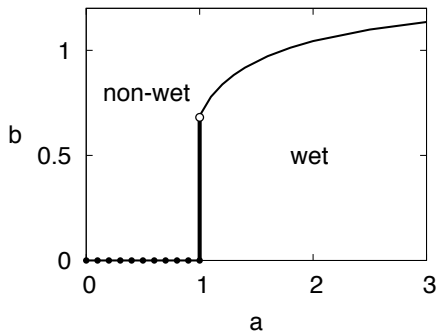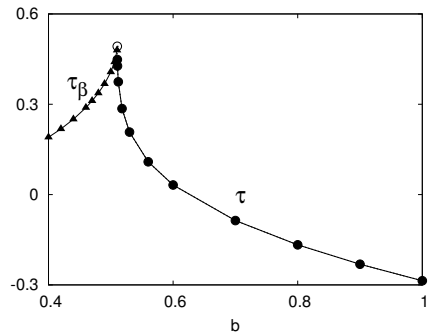
Fig. 5. Global phase diagram of wetting transitions in the plane of two thermodynamic field variables a, b.

Fig. 6. Line tension τ and boundary tension τ_b as functions of b.

character of the wetting transition. It is the ratio a_1/a_2 of two axes, parallel to the ρ_1 and ρ_2 axes, of elliptical contours of constant F in the ρ_1, ρ_2 plane in the neighborhood of the bulk β phase.

4.2. Order of Wetting Transitions

From the numerical calculation, one can determine the locus of wetting-transition points in the a, b plane, as shown in Fig. 5. In states a, b above and to the left of the transition locus, the $\alpha\gamma$ interface is not wet by β; in states a, b below and to the right, the $\alpha\gamma$ interface is wet by β. The character of the wetting transition observed as decreasing b with a fixed depends on the fixed value of a. The wetting transition is of first order, as in Fig. 2(a), when $a > 1$. It is, however, of second order, as in Fig. 2(b), when $a = 1$. The transition point $b_w(a)$ is positive and a continuous function of a in the range $a \geq 1$. But when $a < 1$, the locus $b_w(a)$ becomes identical to 0, the transitions are nonuniversal critical wetting transitions, and the critical exponents are found to be $2/(1 - a)$. That is, in the range $a < 1$, the exponents varies with a and becomes infinite as $a \to 1$ from below. At $a = 1$, there is a vertical segment of the transition locus. When any point of the vertical segment is approached by changing a with fixed b, then $\sigma_{\alpha\beta} + \sigma_{\beta\gamma} - \sigma_{\alpha\gamma}$ vanishes proportionally to $\exp[-c/(1 - a)]$ with a posi-

tive constant c, so the wetting transitions are all of infinite order.

4.3 Behavior of Line Tension

In an earlier study [7,8] the fluid structure near the contact line of the three coexisting phases and the line tension associated with the contact line have been calculated for the density-functional model with two different F's: F_1 and F_2. The $F_1(\rho_1, \rho_2; b, \epsilon)$ is a function of two field variables b and ϵ. This is always positive except at the composition of α and γ phases, where it is 0. When $\epsilon \neq 0$, these are the only phases that may coexist. When $\epsilon = 0$ the β phase may coexist with α and γ, and $F_1 = 0$ there also. It is confirmed that this model with $\epsilon = 0$ exhibits the first-order wetting transition when $b = b_w$ and that it also exhibits the prewetting transitions on a line $b = b(\epsilon)$ in the two-phase coexistence region. The model with F_2 is the spacial case ($a = 1$) of the earlier models $F(\rho_1, \rho_2; a, b)$. This exhibits the second-order wetting transition.

Figure 6 shows the line tension τ and the boundary tension τ_b as functions of b. In this model, for $b > b_w$ (and $\epsilon = 0$) the three phases coexist and the $\alpha\gamma$ interface is not wet by β, so there is a contact line with the line tension τ. In the range $b < b_w$ there is a prewetting line $b = b(\epsilon)$ which corresponds to the line CW in Fig. 3 and there may be a surface boundary with

the boundary tension τ_b. When b approaches b_w, the line tension τ changes its sign from negative to positive values, as remarked earlier, and approaches a positive value τ_w. When $b(\epsilon)$ goes to b_w as $\epsilon \rightarrow 0$, the boundary tension τ_b increases and approaches τ_w. Both τ and τ_b increases rapidly as the wetting transition is approached as seen in the figure as a cusp. In fact, the approach of τ to τ_w is found to follow

$$\tau \sim \tau_w - c_1 \sqrt{b - b_w} \ln[1/(b - b_w)] \qquad (11)$$

the analytical result derived by Indekeu for an interface-potential model of short-range forces [10, 11]. Also the behavior of τ_b near the wetting transition agrees with

$$\tau_b \sim \tau_w - c_4 \sqrt{\frac{b_w - b}{\ln\left[\frac{1}{b_w - b}\right]}} \qquad (12)$$

which follows from the result of Hauge and Schick [4] and that of Indekeu [10].

Indekeu had shown from the interface-displacement model that with short-range forces in mean-field approximation, on approach to a second-order wetting transition, τ vanishes through a range of negative values proportionally to the first power of the contact angle β, or,

$$\tau \sim -k(b - b_w), \qquad (13)$$

with a positive constant k [10]. In the mean-field density-functional model with F_2, the numerical calculation of τ demonstrates that Eq. (13) indeed holds for the second-order wetting [8].

The different behaviors of τ near the first-order and second-order wetting transitions are related to different structures of the fluid in the neighborhood of the contact line near the wetting transition. Figure 7 shows as contour plots the spacial variations of ρ_1 near the first-order and second-order wetting transitions. The distinction between the two cases is clear. The contours of constant ρ_1 in a state close to the first-order wetting have a fork-like shape. It is similar to those

(a)

(b)
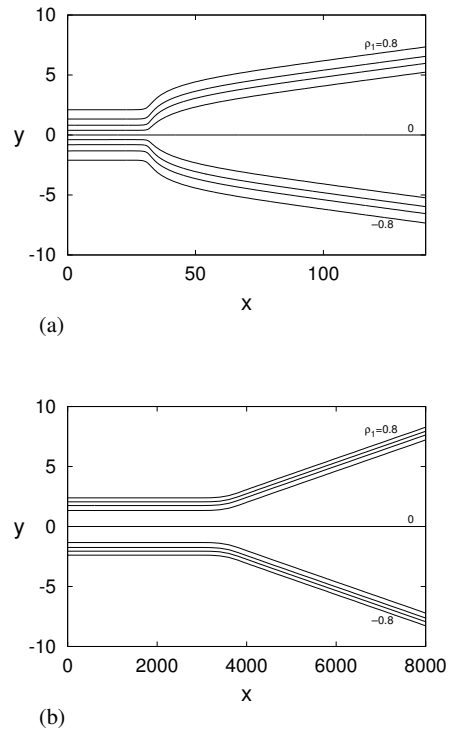
Fig. 7. Spatial variations of ρ_1 in the neighborhood of the contact line near the wetting transition: (a) Contour plots for the model of the first-order wetting; (b) Plots for the model of the second-order wetting.

of constant ρ_1 in the neighborhood of the boundary between two surface phases in the $\alpha\gamma$ plane at the prewetting transition. Both structures ultimately become identical in the limit of the wetting transition where τ and τ_b have a common value τ_w. On the other hand, the contours in a state close to the second-order wetting are gently curved in the three-phase contact region. These are in accord with the analogous picture found in the interface-displacement model [10, 11].

5. Summary

The wetting transition in the three-phase (α, β, γ) coexisting system is reviewed. The transition between states in which the β phase does and does not wet the $\alpha\gamma$ interface is associated with the transition between two conditions

$\sigma_{\alpha\gamma} = \sigma_{\alpha\beta} + \sigma_{\beta\gamma}$ and $\sigma_{\alpha\gamma} < \sigma_{\alpha\beta} + \sigma_{\beta\gamma}$, respectively. The transition may be of first, second, or higher-than-second order. Density-functional models of wetting are recalled which exhibit those different kinds of wetting transition. In the class of models, the character of wetting is determined by an anisotropy parameter a. This parameter reflects the ratio of characteristic physical length scales of the problem. They appear in the form of decay lengths of ρ_1 and ρ_2 to their values of the bulk β phase.

The line tension τ is associated with a three-phase contact region and the boundary tension τ_b is associated with a surface-phase boundary at the prewetting transition. The behavior of the line tension and the boundary tension near the first-order wetting transition as obtained from the density-functional models is presented. It was remarked that the different behaviors of the line tension near the first-order and second-order wetting transitions reflect the different fluid structures near the three-phase contact region in the two cases.

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