

First- and second-order wetting transitions at liquid–vapor interfaces

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Wetting transitions, in which one liquid wets, or spreads at, the interface between a second liquid and their common vapor, are defined and first- and second-order transitions are distinguished. The mean-field density-functional models of fluid interfaces are recalled. A criterion is noted for determining when the wetting transitions in those models are required to be of first order or may be of second order. It is seen how two examples of such density-functional models that have been treated in the past, one leading to a first-order and the other to a second-order wetting transition, provide examples of the application of the criterion.

1. Introduction

We consider two liquid phases (called phases 2 and 3) in equilibrium with their common vapor (phase 1). The three phases may meet at a line of common contact with three non-vanishing contact angles, or alternatively one of the phases, say 2, may “wet” (spread at) the interface between 1 and 3. Let the three interfacial tensions be denoted σ_{12} , σ_{23} , and σ_{13} , and suppose the liquid–vapor tension σ_{13} to be the greatest of the three. Then the condition for the three phases to meet at a line of common contact (“non-wetting”) is the triangle inequality

$$\sigma_{13} < \sigma_{12} + \sigma_{23} \text{ (non-wetting)}. \quad (1)$$

The alternative (“wetting”) is that phase 2 spreads as a macroscopically thick film at the 1,3 interface, with

$$\sigma_{13} = \sigma_{12} + \sigma_{23} \text{ (wetting)}. \quad (2)$$

A transition between these two modes of three-phase contact is termed a wetting transition.

Such a transition might occur as the temperature or a chemical potential varies, leading to two continuous ranges of three-phase states (triple points), with (1) holding over one range and (2) over the other. Between those two ranges of triple points there would then be a boundary at which (1) goes over continuously to (2) or the reverse. According to the phase rule, to have a continuum of three-phase states instead of just isolated triple points requires that the system be a mixture of at least two components. In a one-component system there are only isolated triple

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points, where either one of the phases wets the interface between the other two, or not. There is no transition between those two circumstances because no field variable can then vary without one or two of the three phases disappearing.

For simplicity we consider here systems with the minimum number, two, of components. By the phase rule, the system of three phases and two components then has one degree of freedom; *i.e.*, there is then a one-dimensional manifold of triple points parameterized by a single field variable, which we henceforth call b , and which we may think of as some function of the temperature and the two chemical potentials. The wetting transition between (1) and (2) occurs when b takes some value b_w . We shall take $b > b_w$ to be the range of non-wet states, where (1) is then satisfied, and $b < b_w$ to be the range of states where the 1,3 interface is wet by 2, so that (2) holds.

In reality, many such liquid–liquid–vapor three-phase equilibria occur in systems of $c > 2$ components. To model such systems and still have the simplicity of having only one variable field we would imagine holding fixed $c - 2$ of the system's $c + 1$ field variables. Then with the two phase-equilibrium constraints we would still be considering only a one-dimensional manifold of triple points, parameterized by a single varying field.

The distinction between first- and second-order wetting transitions is illustrated in Fig. 1, where $\sigma_{12} + \sigma_{23} - \sigma_{13}$, which we call $\Delta\sigma$, is shown schematically as a function of b . In the first-order transition $\Delta\sigma$ vanishes linearly with $b - b_w$, and has a metastable extension, shown by the dashed line in Fig. 1(a), in which the non-wet interface for $b < b_w$ is at a local but not global minimum of the free energy. At the global minimum, $\Delta\sigma = 0$ over the range $b < b_w$. At a classical second-order wetting transition (in the sense of the Ehrenfest classification), $\Delta\sigma$ vanishes proportionally to $(b - b_w)^2$ as b approaches b_w from above [Fig. 1(b)], and does not have a metastable extension to states with $b < b_w$. A wetting transition may be very weakly first order, when the curve of $\Delta\sigma$ in Fig. 1(a) crosses the b -axis at $b = b_w$ so shallowly that it may be difficult to locate b_w or to distinguish the slope of the curve at b_w from 0.¹

2. Mean-field density-functional theories recalled

In each of the three interfaces, the densities ρ_1 and ρ_2 of the two components vary in the direction z perpendicular to that interface. We define an excess free energy of inhomogeneity $\Psi[\rho_1(z), \rho_2(z); b]$, which is a functional of the two spatially varying densities and depends on the single field variable b . We take it to be of the classical square-gradient form

$$\Psi = F[\rho_1(z), \rho_2(z); b] + \frac{1}{2} [\rho_1'(z)^2 + \rho_2'(z)^2] \quad (3)$$

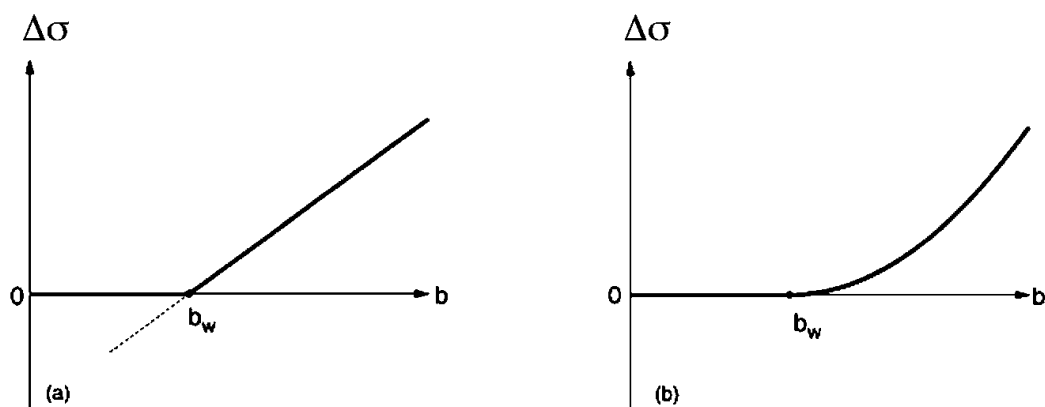


Fig. 1 (a) First-order transition; (b) second-order transition.

where $F(\rho_1, \rho_2; b)$ is such that it, along with $\partial F/\partial\rho_1$ and $\partial F/\partial\rho_2$, vanish when, for the given b , the densities ρ_1 and ρ_2 are those of any of the three coexisting bulk phases; while $F > 0$ otherwise. The tension σ of each of the three interfaces is then

$$\sigma = \min_{\rho_1(z), \rho_2(z)} \int_{-\infty}^{\infty} \Psi dz \quad (4)$$

i.e., the variational minimum of the integrated free-energy density, minimized with respect to the densities $\rho_1(z)$, $\rho_2(z)$ subject to their taking their respective bulk-phase values at $z = \pm \infty$. The minimizing $\rho_1(z)$ and $\rho_2(z)$ satisfy the Euler–Lagrange equations

$$\frac{\partial F}{\partial\rho_1} = \frac{d^2\rho_1}{dz^2}, \quad \frac{\partial F}{\partial\rho_2} = \frac{d^2\rho_2}{dz^2} \quad (5)$$

These are to be solved subject to the boundary conditions at $z = \pm \infty$ noted above.

When z is eliminated between $\rho_1(z)$ and $\rho_2(z)$ for any of the interfaces the result is a trajectory in the ρ_1, ρ_2 plane that describes how ρ_1 and ρ_2 vary with each other through that interface. There are three such trajectories, one for each of the three interfaces, as shown schematically in Fig. 2. The density variables are taken to have the values $\rho_1 = -1, \rho_2 = 0$ in phase 1; $\rho_1 = 0, \rho_2 = b$ in phase 2; and $\rho_1 = 1, \rho_2 = 0$ in phase 3. Here ρ_1 and ρ_2 are not to be taken literally as densities but rather as two independent functions of the physical densities, chosen to make the notation and the representation in Fig. 2 simple.

The curve in Fig. 2 extending from $-1, 0$ to $0, b$ is the 1,2 interfacial trajectory; that from $0, b$ to $1, 0$ is the 2,3 interfacial trajectory; that from $-1, 0$ to $1, 0$ that does not go *via* $0, b$ is that of a 1,3 interface that is not wet by phase 2; while the composite trajectory that does go from $-1, 0$ to $1, 0$ *via* $0, b$ is that of a 1,3 interface that is wet by phase 2.

Each trajectory corresponds to a solution $\rho_1(z), \rho_2(z)$ of the Euler–Lagrange eqns (5) with the appropriate boundary conditions. When these are substituted in the integrand on the right-hand side of (4) the result is the tension σ of the corresponding interface. The three tensions are functions of b .

The equilibrium 1,3 interface is or is not wet by phase 2 according to whether the tension σ_{13} that corresponds to the direct 1,3 trajectory is respectively greater or less than the sum $\sigma_{12} + \sigma_{23}$, which is the tension of the wet 1,3 interface. The wetting transition occurs at that $b(=b_w)$ for which σ_{13} of the non-wet interface equals $\sigma_{12} + \sigma_{23}$. If the transition is of second order, there is no solution of the Euler–Lagrange equations corresponding to a non-wet 1,3 interface when $b < b_w$ [*cf.* Fig. 1(b)], hence no direct 1,3 trajectory in the ρ_1, ρ_2 plane, only the indirect trajectory *via* $0, b$. The latter is always present because it is a composite of the 1,2 and 2,3 interfacial

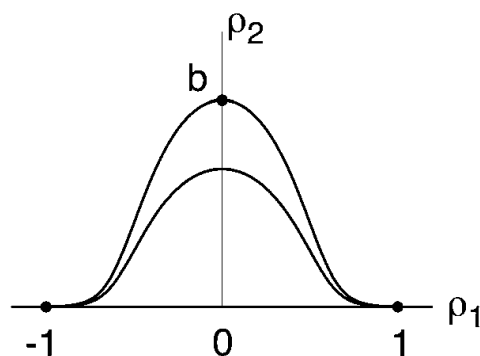


Fig. 2 Wetting and non-wetting trajectories in the ρ_1, ρ_2 plane. The bulk-phase densities are $\rho_1 = -1, \rho_2 = 0$ (phase 1); $\rho_1 = 0, \rho_2 = b$ (phase 2); $\rho_1 = 1, \rho_2 = 0$ (phase 3).

trajectories, and those interfaces are present irrespective of whether phase 2 wets the 1,3 interface or not.

3. First- and second-order transitions

Wetting transitions, which here are transitions in the structure of the 1,3 interface, are in many ways analogous to the transitions between bulk phases in three dimensions. For the latter, while the free energy is necessarily continuous at the transition, its first derivatives with respect to the thermodynamic fields, *viz.*, the energy, entropy, and mass densities and the chemical composition, are discontinuous for first-order transitions (except for accidental azeotropies), but are still continuous at transitions of higher order. Discontinuity in the thermodynamic densities reflects discontinuity in the structures of the phases; at higher-order transitions the structures are continuous.

The relevant free energy in the wetting transitions is $\Delta\sigma$. Its derivative with respect to the field variable b is discontinuous at $b = b_w$ for the first-order transition in Fig. 1(a) but continuous for the second-order transition in Fig. 1(b). In our mean-field density-functional models the “structures” of the two alternative 1,3 surface phases are the alternative chemical composition profiles $\rho_1(z)$, $\rho_2(z)$ of the wet and non-wet 1,3 interfaces. These correspond to the two alternative 1,3 trajectories in the ρ_1, ρ_2 plane of Fig. 2, one going directly from $-1,0$ to $1,0$ (non-wet) and the other indirectly, *via* $0, b$ (wet). If the transition is of first order the structure is discontinuous; *i.e.*, the two alternative trajectories are still distinct at $b = b_w$. If it is of second order the two trajectories coincide at the transition, where there is then only the one, which goes *via* $0, b_w$.

As noted earlier, the function $F(\rho_1, \rho_2; b)$ in (3) and its derivatives $\partial F/\partial\rho_1$ and $\partial F/\partial\rho_2$ are 0 at the points ρ_1, ρ_2 in Fig. 2 representing the compositions of the bulk phases, while $F > 0$ everywhere else. Near those points contours of constant F are ellipses. For simplicity we suppose $F(\rho_1, \rho_2; b)$ to be an even function of ρ_1 , so the trajectories are symmetric in ρ_1 , as in the example in Fig. 2. Then in the immediate neighborhood of the phase-2 point at $0, b$ we will have

$$F(\rho_1, \rho_2; b) \sim \left(\frac{\rho_1}{a_1}\right)^2 + \left(\frac{b - \rho_2}{a_2}\right)^2 \quad (6)$$

where $a_1\sqrt{F}$ and $a_2\sqrt{F}$ are the semi-axes of the elliptical contours of constant F in the directions of the ρ_1 and ρ_2 axes, respectively, with a_1 and a_2 , in general, functions of b . In related work² it is shown from the Euler–Lagrange eqns (5) and their first integral, and from (6), that when the wetting transition is of higher than first order, $d^2\rho_2/d\rho_1^2$ evaluated at the maximum on the non-wetting 1,3 trajectory in Fig. 2 must diverge at the wetting transition, while $d^2\rho_2/d\rho_1^2$ on the wetting trajectory near $0, b$ diverges or remains finite as $b \rightarrow b_w$ according to whether, at $b = b_w$, $a_1/a_2 < 2$ or $a_1/a_2 \geq 2$, respectively. Then since the wetting and non-wetting trajectories coincide at a higher-order wetting transition, a necessary condition for the transition to be of higher order is that $a_1/a_2 < 2$ at $b = b_w$, and then a sufficient condition that it be of first order is that $a_1/a_2 \geq 2$.

We shall now recall two wetting-transition models that have been treated in the past,^{1,3} in one of which the transition is of first order and in the other of which it is of second order, and we shall see how the stated criterion is satisfied.

In the first,¹

$$F(\rho_1, \rho_2; b) = 16\rho_2^2(\rho_2 - b)^2 + [(\rho_2 - b\rho_1)^2 - b^2]^2 + [(\rho_2 + b\rho_1)^2 - b^2]^2 \quad (7)$$

The coexisting phases are again of compositions $(-1,0)$, $(0, b)$, and $(1,0)$, as in Fig. 2. In the immediate neighborhood of $0, b$ this F is again of the form (6), now with $a_1/a_2 = \sqrt{3}/b$. There is a first-order wetting transition at $b = b_w \approx 0.51$,¹ where

then $a_1/a_2 \approx 3.4$. Thus, the wetting transition in this model had to be of first order, as it is. Indeed, the non-wetting trajectory in this model just runs along the ρ_1 axis itself, from $-1,0$ to $1,0$, nowhere near the wetting trajectory, which passes through $0, b$.

In the second of the two earlier models,³

$$F(\rho_1, \rho_2; b) = [(\rho_1 + 1)^2 + \rho_2^2][(\rho_1 - 1)^2 + \rho_2^2][\rho_1^2 + (\rho_2 - b)^2] \quad (8)$$

This, too, is of the form (6) near $0, b$, now with $a_1/a_2 = 1$. It thus satisfies the necessary condition for its wetting transition to be of higher order, and indeed what is found is a classical second-order transition as in Fig. 1(b). (In this case the diverging second derivative $d^2\rho_2/d\rho_1^2$ at $b = b_w$ is manifested as a discontinuous first derivative: $b - \rho_2 \sim |\rho_1|$.)

From (6) it is apparent that the ratio a_1/a_2 plays the role of an asymmetry, or anisotropy parameter, $a_1/a_2 = 1$ corresponding to the symmetric (isotropic) model. In general, the thermodynamic singularities at wetting are expected to be non-universal with respect to this ratio, in the sense that the critical exponents associated with higher than first-order wetting transitions vary continuously with a_1/a_2 . Indeed, in earlier work on models of wall wetting with a two-component order parameter⁴ or anisotropic vector order parameter⁵ this non-universality was demonstrated.

Particularly interesting cases arise when the ratio a_1/a_2 reflects the ratio of characteristic physical length scales of the problem. These two lengths can already appear in a single-component order parameter model, in the form of decay lengths of the wall-fluid and the fluid-fluid potential, respectively.⁶ In this model, the non-universality of the critical exponents at wetting, found at the classical (van der Waals theory) level, was found to be robust when thermal fluctuations are taken into account using functional renormalization group calculations.⁷

In the entirely different physical system of a type-I superconductor, in which a “wetting” or interface delocalization transition was uncovered theoretically⁸ and verified experimentally,⁹ these two lengths are the superconducting coherence length ξ and the magnetic penetration depth λ . For the case in which the theoretically predicted interface delocalization transition is critical, the critical exponent of the surface excess free energy was shown¹⁰ to vary continuously with the Ginzburg-Landau parameter κ , which is the ratio of λ to ξ .

Now, returning to our model defined through (3) and (6), higher than first-order wetting transitions are found in the entire interval $0 < a_1/a_2 < 1$.² This is again consistent with the criterion we exposed. Moreover, for these transitions, too, the critical exponents of the surface free energy at wetting are found to be non-universal and vary continuously with the asymmetry or anisotropy parameter a_1/a_2 (ref. 2). It is of interest that the order of the wetting transition in mean-field density-functional models with excess free-energy density Ψ of the form (3), with two spatially varying densities $\rho_1(z)$ and $\rho_2(z)$, depends on the structure of the function F only in the immediate neighborhood of the composition ρ_1, ρ_2 of the wetting phase.

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