RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 36, NUMBER 13 1 NOVEMBER 1987

Critical-point dewetting

J. O. Indekeu
Katholieke Universiteit Leuven, Laboratorium voor Molekuulfysika,
Celestijnenlaan 200 D, B-3030 Leuven, Belgium

(Received 13 July 1987)

Already within Landau theory with short-ranged substrate-adsorbate forces, complete wetting is not necessary near critical points. Preferential adsorption, but only partial wetting all the way to the critical point, and even critical-point dewetting are possible. Physical systems displaying such behavior include uniaxial magnets with triplet surface fields, and special choices of adsorbed liquid-vapor systems, binary mixtures, liquid crystals, and critical-end-point systems.

When two coexisting phases α and β (e.g., a liquid and a vapor) are adsorbed at a phase γ (e.g., a substrate), and γ preferentially adsorbs α, then *complete wetting* of the β-γ interface by α is expected close to a α-β critical point. A macroscopic layer of α then intrudes between β and γ. If *partial wetting* occurs (when there is a three-phase contact line) the system is expected to display a phase transition to complete wetting as the critical point is approached. These expectations have become common since Cahn's theory of *critical-point wetting* and the discovery of the wetting phase transition in theory[1,2] and experiment.[3] Up to date several reviews have dealt with this topic.[4-9]

It has been found recently that critical-point wetting need not always occur in systems with long-range forces (with power-law decay), in theory[10-13] and experiment.[14] This is relevant for adsorbed fluids with van der Waals forces, for example. In systems with short-range forces (with exponential decay) between substrate and adsorbate, it is commonly believed that critical-point wetting is necessary and ubiquitous. Landau theory,[1,15] mean-field and density-functional theories,[7] and model calculations[5,16] provide firm grounds for this belief.

However, as this paper would like to emphasize, already in the Landau theory with short-range forces critical-point wetting need not always occur. Examples are given where preferential adsorption takes place, but only partial wetting is obtained up to the critical point. Moreover, *critical-point dewetting* is possible: The system makes a phase transition from complete to partial wetting as the critical point is approached. These findings contradict Cahn's scaling argument[1] but are consistent with scaling theory. The paradox is resolved by noting that from scaling theory alone critical-point wetting cannot be predicted.

The physical relevance of the following examples is probably limited because the choices of substrate-adsorbate energies are special.

Consider the Landau surface free-energy functional[1,6,15]

$$\gamma[m(z)] = \int_0^\infty \left[\frac{c^2}{4} \left(\frac{dm}{dz} \right)^2 + f(m(z)) \right] dz + \gamma_s(m_1) \ , \tag{1}$$

of the order-parameter profile $m(z)$, for $z \geq 0$. The substrate is at $z = 0$. The surface density of m at the substrate is denoted by m_1. For the bulk free-energy density the usual form

$$f(m(z)) = a_0 + a_2 m^2 + a_4 m^4 + \cdots \ , \tag{2}$$

is taken. For the substrate-adsorbate energy the form

$$\gamma_s(m_1) = -h_1 m_1 - \frac{g}{2} m_1^2 - \frac{h_3}{3} m_1^3 \tag{3}$$

is chosen. In addition to a surface field h_1 and a surface-coupling enhancement g, a "triplet" surface field h_3 is added. This new addition is pertinent, e.g., to model a three-spin coupling (or external triplet field) at the free surface of a uniaxial ferromagnet.

From now on attention will be restricted mainly to the special case $h_1 = 0$. An analysis of the profiles $m(z)$, which minimize γ, then yields critical-point wetting for $g > 0$ (enhancement), critical-point dewetting for $g < 0$ (dehancement), and temperature-independent contact angles for $g = 0$.

In calculations I have taken $a_n = 0$ for $n > 4$, $a_4 = 1$, $a_2 = 2(T - T_c)$, and a_0 such that $\min[f(m)] = 0$. Denoting by γ_+ and γ_- the surface free energies corresponding to bulk + and − phases at $z = \infty$, respectively, and by γ_{+-} the tension of a free + − interface, one obtains at coexistence ($T \leq T_c$), with $m_0^2 \equiv T_c - T$,

$$\begin{aligned} \gamma_- - \gamma_+ &= \tfrac{4}{3} c m_0^3 \{ \tfrac{1}{2} (Q_+^2 - Q_-^2) \phi^3 + \tfrac{3}{4} (Q_+ - Q_-) \phi + \tfrac{1}{2} [(\phi^2 Q_- + 1)^{3/2} Q_-^{1/2} - (\phi^2 Q_+ + 1)^{3/2} Q_+^{1/2}] \} \ , \\ \gamma_{+-} &= \tfrac{4}{3} c m_0^3 \ . \end{aligned} \tag{4}$$

Here, $Q_\pm = (1 \pm h_3/c)^{-1}$, and $\phi = -g(2cm_0)^{-1}$. The contact angle of the wetting problem is found via

$$\cos\theta \equiv (\gamma_- - \gamma_+)/\gamma_{+-} \ . \tag{5}$$

In this calculation, the physical domain is restricted to $0 \leq |h_3| < c$. For larger $|h_3|$ it is necessary to include a positive sixth-order term in $f(m)$.

For $g > 0$, one obtains complete wetting for $h_3 > 0$ (or "drying" for $h_3 < 0$) provided $|h_3| \geq (\sqrt{3}/2)c$, and a first-order phase transition from partial to complete wetting when approaching the critical point for $|h_3| < (\sqrt{3}/2)c$. In this latter case, the phase boundary between partial and complete wetting in the critical region ($T \simeq T_c$) is described by (expressing $\cos\theta = \pm 1$),

$$h_3 g^3 \sim (T_c - T_W)^{3/2} , \tag{6}$$

where T_W is the wetting (or drying) transition temperature. For $g \leq 0$ one finds new behaviors. For $g = 0$, the wetting problem is independent of temperature and $\cos\theta$ depends only on h_3. The wetting phase boundary then reads (dashed lines in Fig. 1)

$$|h_3| = (\sqrt{3}/2)c . \tag{7}$$

For $g < 0$, partial wetting is found for all temperatures $T \leq T_c$ if $|h_3| \leq (\sqrt{3}/2)c$. For larger $|h_3|$ a phase transition from complete to partial wetting occurs as T_c is approached. The phase boundary represents *critical-point dewetting* and is shown in Fig. 1. It satisfies, for $|h_3| \gtrsim (\sqrt{3}/2)c$,

$$|h_3| - (\sqrt{3}/2)c \sim (-g)(T_c - T_W)^{-1/2} . \tag{8}$$

For the contact angle near criticality ($T \simeq T_c$), one finds

$$\cos\theta \sim h_3(-g)^{-3}(T_c - T)^{3/2} , \tag{9}$$

which implies the remarkably fast approach

$$\gamma_{-} - \gamma_{+} \sim (T_c - T)^3 ,$$

whereas

$$\gamma_{+-} \sim (T_c - T)^{3/2} .$$

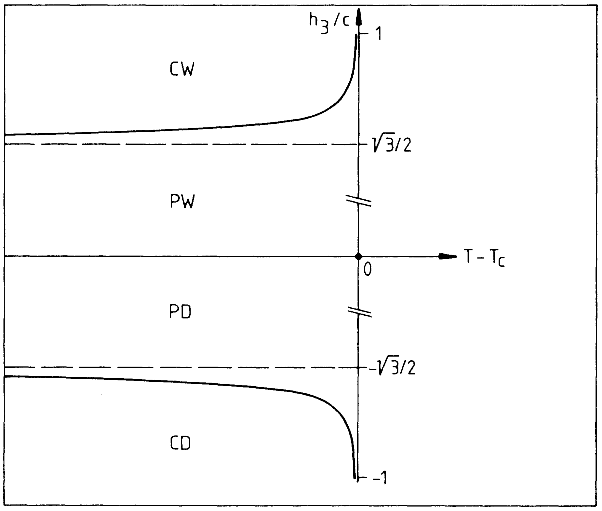

FIG. 1. Critical-point dewetting and dedrying phase boundaries (solid lines) in the plane of triplet field h_3 and temperature T, separating complete wetting (CW) from partial wetting (PW) at $h_3 > 0$, and complete drying (CD) from partial drying (PD) at $h_3 < 0$. The phase transitions are of first order.

In the previous example, a triplet field h_3 has been assumed. In the Landau theory with $h_3 = 0$ previous studies have shown that critical-point wetting is unavoidable in general.[15] However, even there exceptions can be constructed: systems with preferential adsorption but only partial wetting for all $T \leq T_c$.

The first example deals with systems without intrinsic order-parameter inversion symmetry ($m \leftrightarrow -m$), such as liquid-vapor systems, binary mixtures, liquid crystals, etc. Let η denote a generalized density (particle density or concentration . . .). In the Landau theory for critical phenomena one assumes an expansion of the bulk free-energy density in powers of the order parameter $x \equiv \eta - \eta_c$ of the form

$$f(p,T,x) = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + a_4 x^4 + \cdots . \tag{10}$$

Here, p and T denote, e.g., pressure and temperature. At the critical point (p_c, T_c):$a_k = 0$, $k = 1, \ldots, 3$, and $a_4 > 0$. The bulk phase boundary is a curve in the (p,T) plane

$$a_k(p,T) = a_k(x_0^2), \; k = 1, \ldots, 3 , \tag{11}$$

parametrized by a variable x_0^2 ($x_0^2 \sim T_c - T$ or $p_c - p$). There is no *a priori* reason why $a_1(x_0^2)$ and $a_3(x_0^2)$ should vanish, unless there is a physical symmetry as in the case of a uniaxial ferromagnet in zero field h ($p \leftrightarrow h$). However, the order parameter can always be redefined to obtain a symmetric f up to the fourth-order terms. Physically this redefinition transforms an asymmetric coexistence curve into a symmetric one in the (x,T) plane.

Consider now a Landau theory as given by Eq. (1) with $f(x(z))$ of the general form of Eq. (10) and the special choice

$$\gamma_s(x_1) = -\frac{g}{2} x_1^2. \tag{12}$$

For concreteness, consider a one-parameter family of functions f_a of the form

$$f_a(x) = (x - x_0)^2 (x + a x_0)^2 , \tag{13}$$

with $a \geq 1$, to describe the coexistence region ($x_0^2 = T_c - T \geq 0$). The coexistence curve is asymmetric for $a \neq 1$. Alternatively, one can symmetrize the model and work with

$$f_{\text{sym}}(y) = (y^2 - y_0^2)^2 , \tag{14}$$

with $y_0 = [(1+a)/2]x_0$. This brings f back to the form of Eq. (2) but transforms γ_s to

$$\gamma_s(y_1) = \frac{a-1}{a+1} g y_0 y_1 - \frac{g}{2} y_1^2 , \tag{15}$$

corresponding to the presence of a *temperature-dependent* surface field h_1. The presence of h_1 induces preferential adsorption and, therefore, the wetting problem is well posed. One obtains

$$\cos\theta = -3\frac{\alpha-1}{\alpha+1}\phi^2+\frac{1}{2}\left[\left(1+\phi^2+2\frac{\alpha-1}{\alpha+1}\phi\right)^{3/2}-\left(1+\phi^2-2\frac{\alpha-1}{\alpha+1}\phi\right)^{3/2}\right] , \tag{16}$$

where $\phi=-g(2cy_0)^{-1}$. In the case $g>0$ (enhancement) one finds critical-point wetting by the phase with $y=-y_0$ (since $h_1<0$). The wetting phase boundary in the (g,T) plane close to criticality takes the form

$$g\sim(T_c-T_W)^{1/2} . \tag{17}$$

For $g<0$ (dehancement) novel behavior occurs. The contact angle then satisfies $0<\cos\theta<1$ for all $T\le T_c$, signifying persistent partial wetting by the phase with $y=y_0$. In particular, as $T\to T_c^-$,

$$\cos\theta\to\frac{1}{2}\left(\frac{\alpha-1}{\alpha+1}\right)\left[3-\left(\frac{\alpha-1}{\alpha+1}\right)^2\right] . \tag{18}$$

In closing this example it is worthwhile pointing out how the discussion is translated in the liquid-crystal language. The Landau–de Gennes theory for the nematic-isotropic transition features a quadrupolar order-parameter tensor Q which reduces to a scalar q in the case of a uniaxial bulk nematic phase which homeotropically aligns at a substrate.[8,17] The bulk free-energy density $f(q)$ then takes the form of Eq. (10) with $a_k=a_k(h,T)$, for $k=0,\ldots,3$. Here, an external magnetic field h is included. Because $a_1(0,T)=0$ but $a_3(0,T)\neq 0$ the isotropic-nematic transition is necessarily of first order in zero field. In the (h,T) plane the phase boundary terminates at a critical point at (h_c,T_c). There a "paranematic" and a nematic phase become identical, at $q=q_c$. Once more, there is no *a priori* reason why the function f should have a symmetric expansion in $x\equiv q-q_c$ in the vicinity of the critical point. [If one assumes a_3 in $f(q)$ to be a constant, independent of h and T, a symmetric expansion results.] In the theory where f is not symmetric in x (up to fourth order) and where γ_s is taken of the form

$$\gamma_s(q_1)=-h_1q_1-\frac{g}{2}q_1^2 , \tag{19}$$

one obtains preferential adsorption but only partial wetting for all $T\le T_c$, provided $g<0$ and

$$h_1+gq_c=0 . \tag{20}$$

The second example features a system at a critical end point near a tricritical point.[18] In this case

$$f(x)=(x+x_0)^4(x-x_0)^2 , \tag{21}$$

representing a critical phase at $x=-x_0$ coexisting with a noncritical phase at $x=x_0$. The tricritical temperature is T_{tc} and $x_0^2=T_{tc}-T$. Furthermore, consider the choice

$$\gamma_s(x_1)=-\frac{g}{2}x_1^2 . \tag{22}$$

Although no surface fields are present there is preferential adsorption because f is now intrinsically asymmetric with respect to interchange of x_0 and $-x_0$, reflecting the physical distinction between the bulk phases.

In this model one finds $\gamma_{+-}=\frac{4}{3}cx_0^4$ and, for $g<0$, partial wetting by the critical phase is obtained all the way to the tricritical point. In fact, as $T\to T_{tc}^-$,

$$\cos\theta\to-\tfrac{3}{8} . \tag{23}$$

All the examples presented so far have the following features in common. The substrate-adsorbate energy $\gamma_s(x_1)$ has a minimum at (or near) the critical value of the bulk order parameter $x=0$. In any case, as $T\to T_c$, the minimum moves to $x_1=0$ at least as fast as $x_0\sim(T_c-T)^{1/2}$. Secondly, γ_s or the bulk function f should have some asymmetry in the order parameter in order to guarantee preferential adsorption.

Scaling theory[5,15] predicts that the cosine of the contact angle is a scaling function of the form

$$\cos\theta=X(h_1t^{-\Delta_1}, gt^{-\phi_1}, h_3t^{-\Delta_3}) , \tag{24}$$

where $t=(T_c-T)/T_c\ll 1$. Many physical scenarios are compatible with this relationship. One checks that the behaviors outlined in this paper can be cast in this form and the corresponding values of Δ_1, ϕ_1, or Δ_3 can be easily read off. Cahn's argument[1] goes further by assuming that, e.g.,

$$\cos\theta\sim h_1t^{-\Delta_1} \tag{25}$$

in the entire partial-wetting regime. From this would necessarily follow critical-point wetting (given $\Delta_1>0$). However, Eq. (25) presents only one possibility compatible with scaling theory, and is in fact contradicted by most of the present examples.

A subject of further research will be the effect of long-range forces on persistent partial wetting and critical-point dewetting.

This research was supported by the National Fund for Scientific Research in Belgium.

---

[1] J. W. Cahn, J. Chem. Phys. **66**, 3667 (1977).

[2] C. Ebner and W. F. Saam, Phys. Rev. Lett. **38**, 1486 (1977).

[3] M. R. Moldover and J. W. Cahn, Science **207**, 1073 (1980).

[4] M. R. Moldover and J. W. Schmidt, Physica D **12**, 351 (1984).

[5] R. Pandit, M. Schick, and M. Wortis, Phys. Rev. B **26**, 5112 (1982).

[6] P.-G. de Gennes, Rev. Mod. Phys. **57**, 827 (1985).

[7] D. E. Sullivan and M. M. Telo da Gama, in *Fluid Interfacial Phenomena*, edited by C. A. Croxton (Wiley, Chichester, 1986), Chap. 2.

[8] T. J. Sluckin and A. Poniewierski, in Ref. 7, Chap. 5.

[9] S. Dietrich, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, in press), Vol. 12.

[10]P.-G. de Gennes, C. R. Acad. Sci. Ser. B **297**, 9 (1983).

[11]V. Privman, J. Chem. Phys. **81**, 2463 (1984).

[12]M. P. Nightingale and J. O. Indekeu, Phys. Rev. B **32**, 3364 (1985).

[13]C. Ebner and W. F. Saam, Phys. Rev. B **35**, 1822 (1987).

[14]K. Abeysuriya, X.-l. Wu, and C. Franck, Phys. Rev. B **35**, 6771 (1987); D. J. Durian and C. Franck, Phys. Rev. Lett. **59**, 555 (1987).

[15]H. Nakanishi and M. E. Fisher, Phys. Rev. Lett. **49**, 1565 (1982).

[16]J. Fröhlich and C.-E. Pfister, Europhys. Lett. **3**, 845 (1987).

[17]A. K. Sen and D. E. Sullivan, Phys. Rev. A **35**, 1391 (1987).

[18]R. Lipowsky and U. Seifert, Phys. Rev. B **31**, 4701 (1985).