Influence of Wetting on Phase Equilibria: A Novel Mechanism for Critical-Point Shifts in Films

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A fluid confined between two parallel walls that exert different (competitive) surface fields may exhibit phase equilibria strikingly different from those found for equal fields. Macroscopic arguments and an explicit mean-field analysis predict that if the fields are such that the fluid wets one wall and dries the other (above a certain critical wetting transition temperature T_w) coexistence of two phases can only occur, for finite wall separation L, when $T < T_{c,L}$, where the critical temperature $T_{c,L}$ lies *below* T_w. A scaling *Ansatz* suggests $T_w - T_{c,L} \sim L^{-1/\beta_s}$, where β_s is the exponent that describes the growth of the wetting layer.

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When a fluid, or an Ising magnet, is confined between parallel plates or walls, its phase behavior can be significantly different from that in bulk. The finite thickness, L, of the film and the presence of specific wall-fluid interactions modifies the bulk phase diagram. In particular, the location and the nature of critical points are different from those of the bulk fluid. For a film that is of infinite extent in $d-1$ dimensions, parallel to the walls, true criticality can occur provided $d-1 \gtrsim$ the lower critical dimension of the corresponding bulk system. The critical temperature $T_{c,L}$ will be removed from that in bulk, $T_{c,\infty}$, and criticality for finite L will lie in the universality class of the bulk $d-1$ system. Previous theoretical treatments[1,2] have usually focused on fluids confined between identical walls, which are assumed to exert a surface field h_1 on both surface layers. Finite-size scaling arguments, due to Fisher and Nakanishi,[1,2] predict a shift

$$\Delta T_c(L;h_1) \equiv T_{c,\infty} - T_{c,L} = T_{c,\infty} X_c(h_1 L^{\Delta_1/\nu}) L^{-1/\nu}, \tag{1}$$

where ν is the correlation-length exponent of the bulk d-dimensional fluid, $\xi_b \sim |T_{c,\infty} - T|^{-\nu}$, and Δ_1 is the surface (gap) exponent. $X_c(\omega)$ is a scaling function. Continuum Landau theory confirms (1), yielding $\Delta T_c \sim L^{-2}$ for $L \rightarrow \infty$; recall $\nu = \frac{1}{2}$ in mean-field theory. Moreover, the same theory indicates[2] that the extent of the shift is rather insensitive to h_1 since $\Delta T_c(L;\infty)/\Delta T_c(L;0) \approx 2.60$ for all thicknesses L. This result implies that critical-point shifts are not influenced strongly by wetting behavior; whether or not one phase wets the walls completely for $L = \infty$ does not appear to be of crucial importance[2,3] in determining the shift of the bulk critical point[4] for finite L.

Here we consider a fluid confined by walls that are not identical, $h_2 \neq h_1$, and enquire how the phase equilibria is altered from that in the symmetric case. By choosing to make the surface fields competitive [h_1 favors liquid (spin up) while h_2 favors gas (spin down)] we can ensure that above a certain critical wetting transition[5] temperature T_w ($< T_{c,\infty}$) wall 1 will be completely wet and wall 2 will be completely dry at bulk coexistence for $L = \infty$. On the basis of a mean-field calculation for a model of such a system we show that for finite L only one phase can exist for $T \gtrsim T_{c,L}$, where $T_{c,L}$ lies *below* T_w. Coexistence of two confined phases does occur for $T < T_{c,L}$ and the location of the appropriate critical point $T_{c,L}$ is accounted for by a scaling *Ansatz* which is of a very different character from (1). The wetting behavior induced by asymmetric wall fields has a profound effect on all aspects of the phase equilibria of the confined fluid.

A first indication that asymmetric confinement can lead to new features comes from consideration of capillary condensation,[3] i.e., the shift of the bulk first-order transition. For a system with Ising symmetry, bulk coexistence, between states + and − with magnetizations m_+ and m_- ($= -m_+$), occurs at bulk field $h = 0$. In the limit $L \rightarrow \infty$ macroscopic arguments[3] predict coexistence at a shifted bulk field

$$-h_{co} = 2\sigma_{+-} \cos\theta / L(m_+ - m_-), \tag{2}$$

for the symmetric film $h_2 = h_1$. The contact angle θ is given by Young's equation $\sigma_{w-} = \sigma_{w+} + \sigma_{+-} \cos\theta$, where the interfacial tensions refer to $h = 0$; σ_{+-} is the tension of the (free) +− interface and w refers to a single, isolated wall. If the wall favors + phase, $\cos\theta > 0$. When h_1 is sufficiently large, so that $\theta = 0$, wetting layers develop at each wall and (2) should be modified by replacing L by $L - 2l$, where l is the thickness of a wetting layer.[3] Explicit calculations[3,4] show that the effects of wetting layers are of quantitative rather than qualitative importance for capillary condensation in the symmetric case.

The analog of (2) for asymmetric confinement replaces $2\cos\theta$ by $\cos\theta_1 + \cos\theta_2$, where θ_1 is the contact angle at wall 1, determined by the surface field h_1, and θ_2 is the corresponding quantity for wall 2. In the perfectly asymmetric case $h_2 = -h_1$, $\cos\theta_2 = -\cos\theta_1$, and the Kelvin equation predicts $h_{co} = 0$. Clearly this result is consistent with symmetry considerations; any coexistence must occur at bulk field $h = 0$. For small h_1 we expect partial wetting, $\theta_1 \neq 0$, and there are no difficulties in envisaging coexistence of two distinct confined phases with different magnetization profiles (see Fig. 2). This situation is akin to the symmetric case with $h_1 = 0$; then $\theta = \pi/2$ for all T but coexistence, and its accompanying criticality, certainly occur.[1-3] The novel situation, which has no direct counterpart in the symmetric case, arises for larger h_1 when complete wetting occurs so that $\theta_1 = 0$ and $\theta_2 = \pi$, the latter corresponding to complete wetting of the wall-+ interface by the − phase, i.e., complete drying. In this case it is difficult to imagine what phases might coexist for finite L and the status of the Kelvin prediction becomes uncertain. Indeed, it is straightforward to show that any macroscopic approach[6] that goes beyond Kelvin, by including the effects of the wetting and drying layers, predicts no coexistence.

We can investigate the possible phase equilibria using the same continuum Landau theory used earlier[2] for the symmetric case. The magnetization profile $m(z)$ is obtained by minimizing the free-energy functional

$$\begin{aligned}\mathcal{F}[m] = \int_0^L dz\left[\tfrac{1}{2}b(dm/dz)^2 + f(m(z))\right] \\ + b\left[\tfrac{1}{2}cm^2(0) - h_1 m(0)\right] \\ + b\left[\tfrac{1}{2}cm^2(L) - h_2 m(L)\right],\end{aligned} \tag{3}$$

where b is a constant and c is the surface enhancement parameter. The bulk free-energy density is taken to be

$$f(m) = \tfrac{1}{2}a\tilde{t}m^2 + \tfrac{1}{3}am^4 - hm, \tag{4}$$

with $\tilde{t} \equiv (T - T_{c,\infty})/T_{c,\infty}$ and a a constant. This functional has been studied extensively for semi-infinite ($L = \infty$) geometry and the global phase diagram is well known.[5] Provided $c > \xi_b^{-1}(T_w)$ continuous (critical) wetting and drying transitions occur[7] at a temperature T_w which is given by $m_+(T_w) = h_1/c$. On increasing T at fixed h_1 (or h_1 at fixed T) a layer of positive magnetization develops at the wall when the bulk phase, far from the wall, has magnetization $m_-(T)$; $h = 0^-$. The thickness of the layer diverges continuously at $T \to T_w^-$ [or as $h_1 \to h_{1w}^- \equiv cm_+(T)$, the critical value]. The fields $\delta T \equiv (T_w - T)/T_w$ and $\delta h_1 \equiv (h_{1w} - h_1)/h_{1w}$ are equivalent for this transition and the critical exponents describing the singular contribution to the interfacial tension, the divergence of the film thickness l, and the transverse correlation length $\xi_\parallel$ are the same for both thermodynamic paths:

$$\sigma_{w-}^{\text{sing}} \sim |\delta T|^{2-\alpha_s}, \quad l \sim |\delta T|^{-\beta_s},$$

$$\xi_\parallel \sim |\delta T|^{-\nu_\parallel} \quad (L = \infty).$$

Within the present mean-field treatment[5] $\alpha_s = 0$, $\beta_s = 0$ (logarithmic growth), and $\nu_\parallel = 1$; all forces are short ranged. For $T \geq T_w$ and $h = 0^-$ the wall is wet completely by + spin, $l = \infty$, and $\theta = 0$. The drying transition occurs as a layer of negative magnetization develops when the bulk phase has magnetization $m_+(T)$; $h = 0^+$. In this case $\theta = \pi$ for $T \geq T_w$ and $h = 0^+$.

For finite L minimization of (3) yields an Euler-Lagrange equation that can be investigated using a graphical construction similar to that described in earlier[3,8] work. The equilibrium excess free energy per unit area $\sigma \equiv \mathcal{F} - Lf(m_b)$. If more than one solution exists, the stable phase(s) corresponds to the profile with the lowest value of σ, for given (T, h_1, h, L). Specializing now to $h = 0$ and $h_2 = -h_1$ we find that for $T > T_w$ only one solution, satisfying the boundary conditions, can exist for any finite L and the profiles are always monotonic in this single-phase regime.[9] Note that T_w can be made arbitrarily small, by increasing h_1, so that coexistence can be suppressed until arbitrarily far below the bulk critical point.

At first sight it may seem surprising that coexistence should disappear for arbitrarily large L and $h_1 \neq 0$. However, unlike the infinite system, where each wall can accommodate a macroscopic layer of the phase different from the bulk, the finite system is frustrated by lack of bulk and the competitive effects of the walls. The compromise is a single phase with a monotonic profile exhibiting a + − interface[9] at $z = L/2$. This does not mean that critical points close to $T_{c,\infty}$ never exist. By decreasing h_1, T_w can be made arbitrarily close to $T_{c,\infty}$; see Fig. 1, which illustrates a section of the global phase diagram, plotted in terms of the variables (T, h_1, L^{-1}).

Figure 1 indicates that T_w does not constitute the critical temperature for any finite L. Inspection of the graphical construction for $T < T_w$ reveals a rather complex structure. For small L ($< L_c$) there is a single monotonic solution whereas for large L multiple solutions exist. If $L > L_m$, two distinct nonmonotonic solutions exist with identical L and σ—see the insets to Fig. 2. If $L_c < L < L_m$, three solutions exist, all of which are monotonic. Only two of them correspond to the same L

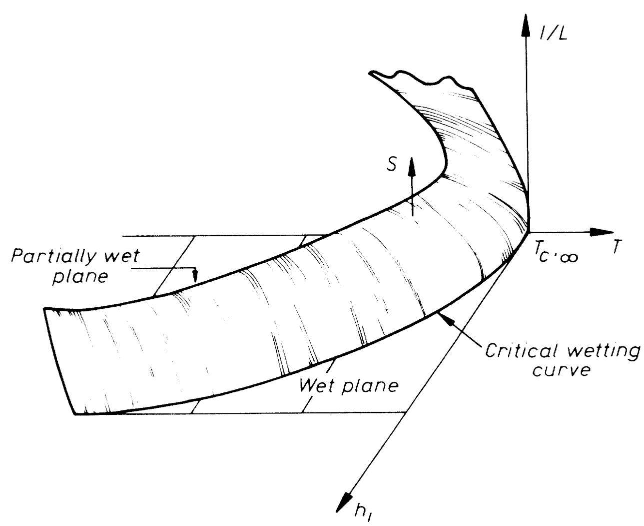

FIG. 1. Sketch of the surface S of critical points. The critical wetting curve $T_w(h_1; h = 0)$ lies in the plane $1/L = 0$.

and σ; the other is a metastable state. All three solutions become identical as $L \to L_c^+$, so that the nature of the bifurcation is of interest in its own right (see Fig. 2). For $L > L_c$ two distinct phases of equal σ coexist, whereas for $L \leq L_c$ only one phase exists. The quantity $(\partial^2\sigma/\partial L^2)_{h,T}$ is zero for $L \to L_c^-$ but is negative for $L \to L_c^+$ so that on the *stable* branches $(\partial^2\sigma/\partial L^2)_{h,T}$ is discontinuous at the critical value L_c.

As $T \to T_w(h_1)$, $L_c(T,h_1) \to \infty$ and analysis shows that

$$T_w - T_{c,L} = \text{const} \times \exp(-L/2\xi_b), \quad L \to \infty, \tag{5}$$

which is the main result of the calculation. This is clearly of a totally different character from the mean-field version of (1). Figure 1 shows that the surface of critical points merges into the bulk critical point as $h_1 \to 0$.

Two points of immediate interest are the following:

(i) The nature of the critical point.—There are three routes by which the critical point can be reached from the two-phase region: $L \to L_c^+$ at fixed T,h_1, $h_1 \to h_{1c}^-$ at fixed L,T, and $T \to T_{c,L}^-$ at fixed h_1,L. It is straightforward to show that the three scaling fields $\delta L \equiv (L_c - L)/L_c$, $\delta h_1 \equiv (h_{1c} - h_1)/h_{1c}$, and $\delta T \equiv (T_{c,L} - T)/T_{c,L}$ are equivalent within mean-field theory. Consequently, the discontinuity in the second derivative of σ with respect to L corresponds to a discontinuity in the heat capacity. Moreover, it is possible to show that the order parameter $\Delta\Gamma \equiv |\int_0^L dz[m_1(z) - m_2(z)]|$, measuring the difference between the adsorptions for the coexisting profiles, vanishes as $\Delta\Gamma \sim \delta\epsilon^{1/2}$, where $\delta\epsilon$ represents any of the three scaling fields. The transverse correlation length $\xi_\parallel$ diverges in the standard mean-field fashion $\xi_\parallel \sim \delta\epsilon^{-1/2}$, and *not* in the (capillary-wave-induced) fashion of the critical wetting transition. The latter can only occur in the semi-infinite ($L = \infty$) system. We conclude that criticality in the asymmetric case is of the same nature[10] as that in the symmetric ($h_2 = h_1$); both are standard second-order transitions within mean-field theory. Furthermore, we conjecture that, in reality, criticality corresponds to that of the $(d-1)$-dimensional bulk system for both cases.

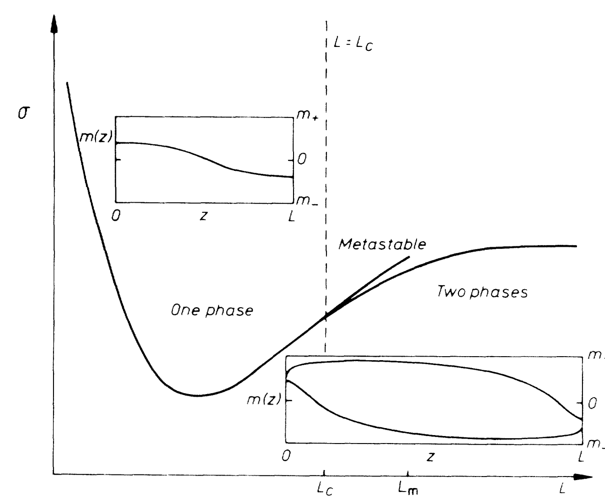

FIG. 2. The excess free energy per unit area $\sigma(L)$ for $T < T_w$; $h_2 = -h_1$ and $h = 0$. For $L > L_c$ the lower branch is associated with two stable coexisting phases, while the upper branch corresponds to a metastable state. The magnetization profiles are nonmonotonic for $L > L_m$, the end of the metastable branch (see inset). For $L < L_c$ only one phase exists and this has the monotonic profile shown in the other inset.

(ii) Heuristic scaling argument for the critical-point shift.—Here we put forward a simple interpretation of the result (5). This is analogous to the well-known interpretation of (1) that states that the growth of droplets within the film is determined by bulklike fluctuations until, at the shifted critical point $T_{c,L}$, the droplet size is comparable with the smallest film dimension, i.e., $L \sim \xi_b \sim |T_{c,\infty} - T_{c,L}|^{-\nu}$. Note that the extent of the shift does not depend on any transverse length scale. In the asymmetric case the magnetization profile, for $T > T_w$ and large L, resembles that for a free interface located near $L/2$. Alternatively we may regard such a profile as that due to a wetting layer of thickness $l = L/2$, developed at wall 1. But the growth of wetting layers is associated with the exponent β_s so it follows that $L/2 \sim l \sim |T_w - T_{c,L}|^{-\beta_s}$ and we deduce that

$$T_w - T_{c,L} = \text{const} \times (L/2)^{-1/\beta_s} \tag{6}$$

should be the general result for the critical-point shift in the asymmetric case. In mean-field theory $\beta_s = 0$ and (6) is consistent with the explicit result (5). We can place (6) in a more formal context by means of a finite-size scaling *Ansatz*. We recall that for the symmetric case (1) follows directly from a scaling hypothesis[1,2] for the singular part of the excess free energy. For the asymmetric case we propose

$$\sigma^{\text{sing}} \approx (\delta T)^{2-\alpha_s}\Omega(L^{1/\beta_s}\delta T), \tag{7}$$

with $\delta T \equiv (T_w - T)/T_w$. Such an *Ansatz* is consistent with (6). It also predicts $\sigma^{\text{sing}} \sim L^{-(2-\alpha_s)/\beta_s}$ when we *sit at* a shifted critical point. The critical exponents for critical wetting satisfy the relations $2 - \alpha_s = (d-1)\nu_\parallel$ and $\beta_s = (3-d)\nu_\parallel/2$ for $d < 3$ (and for $d = 3$, outside the strong fluctuation regime). Thus $\sigma^{\text{sing}} \sim L^{-\tau}$ for $d < 3$, where $\tau = 2(d-1)/(3-d)$ is the exponent introduced by Lipowsky and Fisher[11] to account phenomenologically for fluctuation effects at wetting transitions. In the weak- and intermediate-fluctuation regimes in $d = 3$, $\beta_s = 0$ and we expect $\sigma^{\text{sing}} \sim \exp(-L)$, the mean-field result. Notice that for $d = 2$ the scaling arguments predict $\sigma^{\text{sing}} \sim L^{-2}$. Of course, in this dimension the singular contribution to the excess free energy should be evaluated at a *pseudo* critical point, since no true phase transition can occur.[12]

We have also investigated the applicability of (6) for the situation where both wall-fluid and fluid-fluid forces are long ranged. Within the framework of density-functional theory and "slab" approximations[5(b),6] to the density (magnetization) profiles we can show that if critical wetting occurs ($L=\infty$) within such models then there is a shifted critical point at finite L with $T_{c,L}$ given by (6) and $\beta_s=1$ when both types of force are of van der Waals form.[5] Moreover, the same kind of analysis can be applied in the weak-fluctuation regime of critical wetting. Again we recover (6) and rederive the result $\sigma_{\rm sing} \sim L^{-\tau}$.

In conclusion, we have described a model system where the location of the critical point is determined by the (critical) wetting properties of the confining walls rather than the bulk critical properties. Although we have specialized to perfect asymmetry ($h_2=-h_1$), it is fairly straightforward to show that our results are not restricted to this special case. Provided one wall wets completely and the other dries completely above some wetting or drying temperature, the same *type* of phase equilibria will result.[13]

M. P. Allen, J. R. Henderson, C. J. Howls, D. Nicolaides, P. Tarazona, and C. J. Walden listened patiently during our formulation of these ideas. The research was supported by the Science and Engineering Research Council, United Kingdom.

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[1]For example, M. E. Fisher and H. Nakanishi, J. Chem. Phys. **75**, 5857 (1981), and references therein.

[2]H. Nakanishi and M. E. Fisher, J. Chem. Phys. **78**, 3279 (1983).

[3]R. Evans, U. Marini Bettolo Marconi, and P. Tarazona, J. Chem. Phys. **84**, 2376 (1986). This work and Ref. 2 show that, in a complete wetting situation, critical points of the confined fluid occur outside the bulk spinodal. This implies thick wetting films do not exist at such points.

[4]Wetting *does* have an important effect on other aspects of the phase equilibria; see Ref. 3 and R. Evans and U. Marini Bettolo Marconi, Phys. Rev. A **32**, 3817 (1985); E. Bruno, U. Marini Bettolo Marconi, and R. Evans, Physica (Amsterdam) **141A**, 187 (1987); D. Nicolaides and R. Evans, Phys. Rev. B **39**, 9336 (1989).

[5]For reviews, see (a) D. E. Sullivan and M. M. Telo da Gama, in *Fluid Interfacial Phenomena,* edited by C. A. Croxton (Wiley, New York, 1986), p. 45; (b) S. Dietrich, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Lebowitz (Academic, New York, 1988), Vol. 12, p. 1.

[6]That is, of the type described in Secs. II and IV of Ref. 3.

[7]Here we deliberately avoid the complication of first-order wetting transitions and the accompanying prewetting transitions that occur out of bulk coexistence; see Ref. 4.

[8]U. Marini Bettolo Marconi, Phys. Rev. A **38**, 6267 (1988).

[9]An explicit mean-field calculation of the susceptibility shows that the transverse correlation length $\xi_\parallel \sim \exp(L/4\xi_b)$ for $T_{c,\infty}>T>T_w$. A simple scaling analysis predicts $\xi_\parallel \sim (L/2)^{2/(3-d)}$ in the same regime. This result implies that the interface is wandering wildly.

[10]However, when $h_2=h_1$ criticality is associated with the vanishing of loops in $\Delta p(L)$, see Ref. 3, which is not the case for $h_2 \neq h_1$.

[11]For example, R. Lipowsky and M. E. Fisher, Phys. Rev. Lett. **56**, 472 (1986); **57**, 2411 (1986).

[12]We have since learnt that E. V. Albano, K. Binder, D. W. Heermann, and W. Paul [Surf. Sci. (to be published)] have performed Monte Carlo simulations for a $d=2$ asymmetric Ising strip. They find pseudo coexistence below $T_{c,L}$ with $T_w - T_{c,L} \sim L^{-1}$ in agreement with our prediction (6); $\beta_s=1$ for critical wetting in $d=2$. Above $T_{c,L}$ they observe one phase with the interface wandering wildly. V. Privman and N. M. Svrakic, Phys. Rev. B **37**, 3713 (1988), have studied $\xi_\parallel$ for a restricted solid-on-solid model in strip geometry. Their results are consistent with (6) and, for $T>T_w$, with the prediction in Ref. 9, i.e., $\xi_\parallel \sim L^2$.

[13]Some of the features we describe were discussed by F. Brochard-Wyart and P. G. de Gennes, C. R. Seances Acad. Sci. Ser. 2 **297**, 223 (1983). They suggested, without detailed calculation, that T_w should play a central role for phase equilibria in an asymmetric system.