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Effect of Confinement on Wetting and Drying between Opposing Boundaries.

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Abstract. – We study quasi-wetting transitions in confined systems in which capillary condensation is suppressed. In particular, we are concerned with adsorbates between opposing walls (one wall favours wetting, the other drying). We employ an Ising model and calculate the global phase diagram for a slab of width L and boundaries with opposite surface fields, in Landau theory. We find novel first-order, critical, and tricritical quasi-wetting transitions, which converge smoothly, for $L \to \infty$, to the familiar wetting transitions. We question the recently proposed novel mechanism for critical-point shifts in films.

While a semi-infinite system (*e.g.*, an adsorbate at a wall) can display a rich variety of first-order, critical, and tricritical wetting phase transitions [1, 2], a confined system (*e.g.*, an adsorbate between two closely spaced walls) is generally expected to be deprived of this wealth [3]. This expectation is based on essentially two observations: i) *true* wetting transitions are prevented by the finite wall separation L, and ii) wetting is pre-empted by the capillary condensation transition [4]. Although these observations are often pertinent, they must not be emphasized unduly. Indeed, i) neglects the possibility of *quasi*-wetting transitions. These are thermodynamically sharp phase transitions in which a wetting layer is formed, whose thickness is finite for finite L, but diverges for $L \to \infty$. (Note that this is different from prewetting. There, the layer thickness remains finite in that limit [1].) Furthermore, ii) ignores that in many systems (of fixed density or concentration, or with a certain symmetry) capillary condensation is suppressed, so that quasi-wetting can occur.

The existence and importance of quasi-wetting in confined systems has been established recently [5-8]. Furthermore, there is the intriguing possibility that quasi-wetting not only replaces true wetting, but replaces bulk phase transitions and bulk criticality as well! This conjecture [5, 8], however, is largely based on Landau theory or mean-field arguments, and caution is in order. The main objective of our contribution is to calculate and interpret the *global* phase diagram of quasi-wetting in Landau theory. Furthermore, we will also critically question its applicability *beyond* mean-field theory.

Which systems display capillary condensation and which show quasi-wetting? Capillary condensation prevails in confined systems with *like* walls (*e.g.*, favouring wetting), and quasi-wetting is abundant when there are *opposing* walls (*e.g.*, one wall wets, the other dries). In Ising model language walls can be represented by surface fields H_1 and H_2. $H_1 \approx H_2$ describes like walls, and $H_1 \approx -H_2$ opposing walls. Note that although capillary condensation is common for systems between two identical parallel walls or systems *enclosed* by a wall (*e.g.*, fluids in cylindrical or spherical pores), it can be easily suppressed by imposing conservation of particle number in a one-component adsorbate [9], or conservation of species in a mixture [10, 11].

Where should the experimentalist look for systems with opposing boundaries? Perhaps the most obvious example concerns magnetic multilayers with effective magnetic fields of alternating sign at successive interlayer interfaces. This and other examples were already suggested by Brochard and de Gennes [5]. In addition, in the spirit of experiments by Franck *et al.* [12], one could consider a liquid mixture with two phases (A and B) between plates of different surface chemical preparation, so that one plate preferentially adsorbs A, and the other B. Furthermore, especially relevant for us are the experiments by Laheurte *et al.* [6] on ^{3}He-^{4}He films bounded by a solid wall (bottom surface) and a liquid-vapour interface (top surface). The solid preferentially adsorbs the ^{4}He-rich phase, whereas the vapour favours ^{3}He. In these experiments a horizontal *stratification* of the phases is seen, along with a superfluidity phase transition. Precisely this stratification, implying the formation of a sharp liquid-liquid interface, exemplifies the quasi-wetting transition we are concerned with.

In computer simulations quasi-wetting between opposing boundaries has been studied in detail by Binder *et al.* [7]. Adsorption on stepped surfaces was simulated using a two-dimensional ($2d$) Ising lattice-gas model. The effect of surface steps was modelled by various types of boundary energies (surface fields) on the two parallel edges of a terrace of width L. For opposing boundaries (rounded) quasi-wetting transitions were observed which converge, for $L \to \infty$, to the wetting transitions of the $2d$ Ising model, calculated exactly by Abraham [13]. We now proceed to our theoretical results and will return to questions of general importance at the end.

The microscopic model paradigm for our purposes is an Ising ferromagnetic slab of thickness L with bulk coupling J_B and surface coupling J_S. The bulk field is H and to the boundaries we apply surface fields H_1 and H_2. We first recall established results for $H_1 \approx H_2 (> 0)$ [3]. Bulk two-phase coexistence is shifted from $H = 0$ for $L = \infty$, to $H < 0$ for finite L. In particular, the bulk critical point $T_c(\infty)$ is shifted to $T_c(L)$, according to finite-size scaling,

$$T_c(L) - T_c(\infty) \propto Y(L^{\Delta_1/\nu} H_1) L^{-1/\nu}, \tag{1}$$

where the scaling function $Y(y)$ is nearly constant. Furthermore, wetting phenomena are largely suppressed, but not entirely. Prewetting transitions remain and can compete with capillary condensation, implying novel triple points [4, 14].

We now proceed to study the case $H_1 \approx -H_2$ in *Landau theory*, for obtaining the complete mean-field phenomenology in the neighbourhood of T_c. Two lengths are relevant, the «substrate» separation L and the bulk correlation length of the «adsorbate», ξ, which measures temperature relative to T_c. As expected, the ratio L/ξ is all-important. The substrate parameters are the surface fields h_1 and h_2 (simply related to H_1 and H_2) and the surface-coupling enhancements g_1 and g_2 (related to J_S/J_B). For clarity and simplicity we take $h_1 = -h_2$ and $g_1 = g_2 (= g)$. For fluids, $g < 0$, whereas for magnets both $g < 0$ and $g \geq 0$ are pertinent ($g > 0$ corresponds to surface ferromagnetism above T_c) [15]. When the surface fields are opposite, capillary condensation is suppressed by symmetry and it suffices to take the bulk field h equal to zero, in order to discuss the bulk phase equilibria and wetting phenomena (except for prewetting). For the more general case, $h_1 \approx -h_2$, $h \approx 0$, and $g_1 \approx g_2$, we expect the physics to be qualitatively the same.

From here on we will use *scaled variables* (like L/ξ), because they allow a more complete (but still compact) description from which the desired information in terms of L, T, h_1 and g can be extracted. The phase diagrams and order parameter profiles $m(z)$ have been obtained as usual [2, 3] by minimization of the Landau surface free-energy functional $\gamma[m]$,

$$\tilde{\gamma}[\tilde{m}] \equiv L^3 \gamma[m] = \int_0^1 \mathrm{d}\tilde{z} \left\{ \frac{c}{2} \left(\frac{\mathrm{d}\tilde{m}}{\mathrm{d}\tilde{z}} \right)^2 + (\tilde{m}^2 - (L/\xi)^2)^2 \right\} - \tilde{h}_1(\tilde{m}_1 - \tilde{m}_2) - \tilde{g}(\tilde{m}_1^2 + \tilde{m}_2^2)/2\,, \tag{2}$$

where c is a constant, $\tilde{z} \equiv z/L$, $\tilde{m} \equiv Lm$, $\tilde{h}_1 \equiv L^2 h_1$, and $\tilde{g} \equiv Lg$. Equation (2) is suitable when T is varied at fixed L, or when $T = T_c$. When L is varied at fixed $T (\neq T_c)$ we use different scaled variables, obtained by replacing L by ξ everywhere in eq. (2). (The upper limit of the integral, 1, is replaced by L/ξ.)

The global phase diagram we calculated is shown in fig. 1. It focusses on the immediate vicinity of bulk criticality (L/ξ small) (1). From here we can go smoothly to the opposite regime $L/\xi \gg 1$. The limit $L \to \infty$ corresponds to moving out from the origin in fig. 1 along straight lines, and the result is the phase diagram for wetting in semi-infinite geometry [2] (fig. 2). Thus, our first conclusion is that the quasi-wetting transitions between opposing boundaries can be understood as *shifted wetting transitions*, for $L/\xi \gg 1$. This is true not only for the location of the transitions (in T, h_1, and g), but also for their order (first-order, critical, or tricritical), as well as for the profiles $m(z)$. Note, however, that the character (*e.g.*, universality class) of the shifted wetting transition *beyond* Landau theory is qualitatively different from that of the wetting transition itself (because, to begin with, the dimensionality d is changed) [8]. As far as typical profiles $m(z)$ are concerned, some representative ones have been sketched [5], or calculated and shown in earlier works [7, 8]. (Note that we use «wetting» as a general term to denote wetting and/or drying, depending on which reference phase is assumed in bulk.)

Our second conclusion is that the full variety of phase transitions persists near bulk criticality ($L/\xi \lesssim 1$). We find first-order, critical, and tricritical transitions (even for $T > T_c$, provided $g > 0$), in addition to an important region without transitions, for $T < T_c$ and $g < 0$ (fig. 1). A first step towards more comprehensible phase diagrams is to take sections through fig. 1 or 2. Figure 3 shows a «temperature» scan through fig. 1, for $Lg/c = -1$. The phase boundary represents transitions from a «bulklike» two-phase coexistence region (with profiles $m_-(z)$ and $m_+(z) = -m_-(L-z)$) to an «interface-like» one-phase region ($m(z) = -m(L-z)$), as h_1 or ξ are increased at fixed L. *Finite-size effects* overwhelm when the natural decay length ξ of the profile becomes as large as the separation L, causing the absence of phase transitions for $L/\xi \lesssim 1$, unless $g > 0$. Another selected phase diagram is shown in fig. 4 (for $\xi g/c = -0.5$), illustrating the transitions when L is varied at fixed T. Note the possibility of *re-entrance* of the interface-like phase.

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(1) As usual, the Landau theory applies well when both L and ξ are much larger than molecular lengths. This imposes no restrictions on the *ratio* L/ξ. Clearly, the regime $L/\xi \lesssim 1$ describes the vicinity of the bulk critical point. Critical adsorption (with $m(z) \propto z^{-1}$ in Landau theory), and the algebraic decay of the finite-size interaction between boundaries at bulk criticality (with $\gamma(L) - \gamma(\infty) \propto L^{-3}$ in Landau theory) naturally obtain for $L/\xi \to 0$. On these topics and their relevance for wetting, see [16, 4].

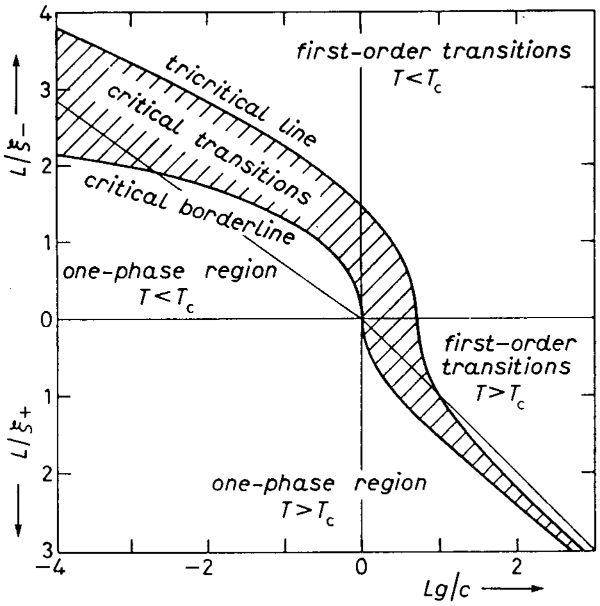

Fig. 1.

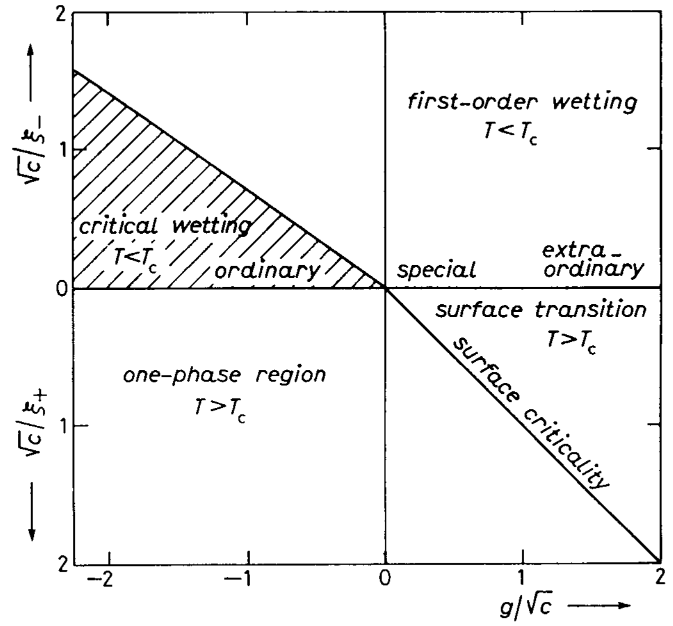

Fig. 2.

Fig. 1. – Global phase diagram near bulk criticality, projected in the plane of scaled variables Lg/c and L/ξ ($\xi_- \equiv \xi(T<T_c)$ and $\xi_+ \equiv \xi(T>T_c)$). This diagram is suitable for (vertical) temperature scans at fixed g and L. A third axis perpendicular to this plane can serve for the scaled surface field $L^2|h_1|/c^{3/2}$ (h_1 and $-h_1$ are equivalent). The phase transitions (first-order, tricritical, and critical) occur at $h_1 \neq 0$ and lie on a sheet which comes down to intersect the $h_1 = 0$ plane at the (analytically calculated) critical borderline. This line approaches a horizontal asymptote for $gL/c \to -\infty$, at $L/\xi_- = \pi$. The tricritical line approaches a straight line with slope $-2^{-1/2}$, parallel to the thin line in the figure, for $Lg/c \to -\infty$. For $Lg/c \to +\infty$, both the critical borderline and the tricritical line approach a similar straight line with slope -1.

Fig. 2. – Global phase diagram for wetting in a semi-infinite geometry, projected in the plane of $c^{1/2}/\xi$ and $g/c^{1/2}$. A third axis perpendicular to this plane can serve for the surface field $|h_1|/c^{1/2}$. The wetting transitions (first-order, tricritical and critical) occur at $h_1 \neq 0$ ($h_1 > 0$ for wetting and $h_1 < 0$ for drying), and form a sheet which meets the $h_1 = 0$ plane at bulk criticality ($c^{1/2}/\xi = 0$). There, the ordinary ($g<0$), special ($g=0$), and extraordinary ($g>0$) transitions are indicated [15]. For $T>T_c$ and $g>0$, there is a region of surface phase transitions at $h_1 = 0$, ending at the line of surface criticality. This phase diagram smoothly emerges from fig. 1 in the limit $L \to \infty$, and thus also gives the location of the quasi-wetting transitions for $L \gg \xi$.

Using our scaled variables, but invoking true critical exponents instead of the mean-field ones, our results suggest that the location $T_w(L)$ of the quasi-wetting transitions for, fixed g and $L \to \infty$, is compatible with the finite-size scaling form

$$T_c(\infty) - T_w(L) \propto X(L^{\Delta_1/\nu} h_1)\, L^{-1/\nu}. \tag{3}$$

We have $X(x) \to \text{const}$, for $x \to 0$ (see fig. 3). This limit is well known: for $h_1 = 0$, $T_w(L) = T_c(L)$ and eq. (3) gives the familiar *bulk critical-point shift*, as a particular case of eq. (1). We also have $X(x) \to x^{1/\Delta_1}$, for $x \to \infty$, because we recover the *wetting phase boundary* for $L \to \infty$. Indeed, for $h_1 = -h_2 \neq 0$, $T_w(L) \to T_w(\infty)$, with

$$T_c(\infty) - T_w(\infty) \propto h_1^{1/\Delta_1}. \tag{4}$$

In Landau theory eqs. (3) and (4) are obeyed with $\nu = 1/2$, $\Delta_1/\nu = 1$, 2, or 3, for $g<0$, $g=0$, or $g>0$, respectively. Furthermore, when we write $T_c(\infty) - T_w(L) = (T_c(\infty) - T_w(\infty)) -$

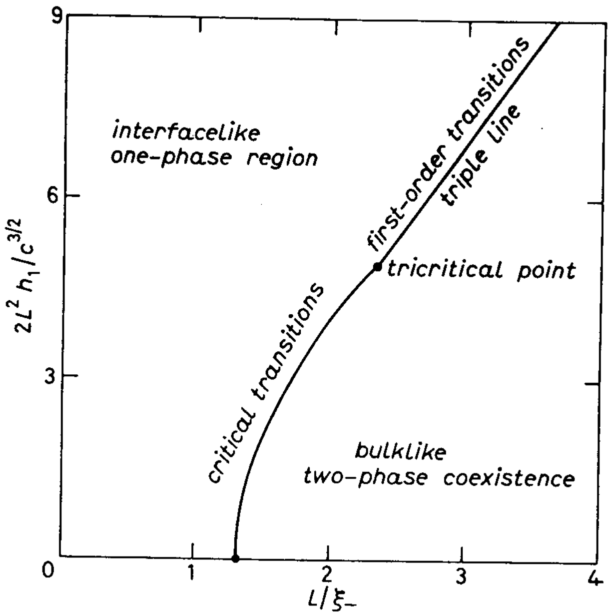

Fig. 3.

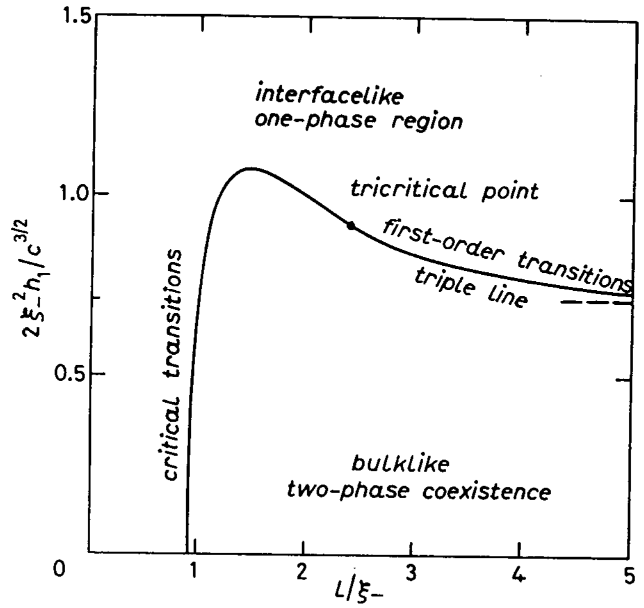

Fig. 4.

Fig. 3. – Selected phase diagram corresponding to a temperature scan at $Lg/c = -1$ in fig. 1, for $T < T_c$. The bottom point on the phase boundary describes the shift of the bulk critical point. Useful paths are (horizontal) temperature scans at fixed L and h_1, or (vertical) surface-field scans at fixed L and T.

Fig. 4. – Selected phase diagram corresponding to a separation (L) scan at $\xi g/c = -0.5$, for fixed $T < T_c$. Useful paths are (horizontal) separation scans at fixed T and h_1, or (vertical) surface-field scans at fixed T and L. The value of $\xi g/c$ (< 0) is chosen to give a first-order wetting transition for $L = \infty$ (cf. fig. 2). The dashed line gives the asymptote of the phase boundary for $L \to \infty$ (cf. eq. (5)). Note that for finite L the transition can change order and become tricritical or critical.

$-(T_w(L) - T_w(\infty))$ we see that the *next-to-leading* term of $X(x)$, for $x \to \infty$, gives the *wetting transition shift* $T_w(L) - T_w(\infty)$. We find that the wetting transition shifts are typically *exponentially* small in L/ξ, in Landau theory. This generalizes an earlier result of Parry and Evans for the shift of critical wetting [8]. We have found analogous results for the wetting transition shifts when h_1 is allowed to vary at constant T. For example, when the transition for $L \to \infty$ is first-order wetting (as for fig. 4), numerical computation indicates

$$h_1(L) - h_1(\infty) \propto A \exp[-2^{-1/2} L/\xi]/\xi^2 \tag{5}$$

with $A > 0$. For critical wetting, $A < 0$. Parry and Evans proposed scaling laws, beyond mean-field theory, for the shift of critical wetting [8], and could explain quantitatively the simulations by Binder *et al.* in $d = 2$ [7].

The final step towards realistic phase diagrams is to deconvolute the scaled variables and to draw 3-dimensional phase diagrams in $(1/L, T, h_1)$-space, for a particular g. Parry and Evans have sketched one for when the transition for $L \to \infty$ is critical wetting [8].

A very important question arises. Where is $T_c(L)$? Parry and Evans interpreted $T_w(L)$ as $T_c(L)$! Brochard and de Gennes did this too [5]. However, this interpretation appears rather problematic for the following reasons. Let the dimension d be large enough to allow bulk phase transitions in the confined system, that is $d > 2$. For clarity, let $d = 3$. Then, the Landau theory predicts that the quasi-wetting transition, at $T_w(L)$, is at the same time the *terminus* of *bulk* two-phase coexistence (see, *e.g.*, fig. 3). Indeed, the interfacelike profile, which lives at $T > T_w(L)$, apparently constitutes a single and unique phase. This mean-field picture has led to the conjecture that the bulk critical point $T_c(\infty)$ shifts, or rather *leaps*, for finite L, all the way to the quasi-wetting point $T_w(L)$ [5, 8]. Note that $T_w(L)$ can lie anywhere between $T_c(\infty)$ and $T=0$, depending on the strength of the surface fields.

A first problem is that finite-size scaling is not compatible with the proposal that $T_c(L)=T_w(L)$, because $T_c(\infty)\neq T_w(\infty)$ unless $h_1=0$ (see eq. (4)). Next, there is the obvious possibility that the Landau theory *misses* the true bulk critical point $T_c(L)$ altogether, because the pertinent transverse fluctuations, in x and y directions parallel to the interface, are neglected (see eq. (2)). Note that the Landau theory makes a one-to-one correspondence between *phase* and *profile*. This can be misleading. For example, we know that the interfacial profile remains single and unique in the limit $L\to\infty$, but definitely represents two $3d$ bulk phases... What happens to these two phases for finite L? Do they remain distinct as quasi-$2d$ phases separated by an interface that runs parallel to the walls (assuming we are above the wetting point)? Or do they suddenly become part of a single thermodynamic phase? Furthermore, the answer to this question may depend on whether one is above or below the roughening transition. Clearly, further research beyond Landau theory is needed. We have begun to carry out pertinent computer simulations.

In conclusion, our study indicates that the quasi-wetting transitions between opposing walls can be unambiguously understood as shifted *wetting* transitions. Our results do not support the alternative interpretation in terms of novel critical-point leaps.

In summary, the original predictions coming out of our calculations are, firstly, the novel global phase diagram of wetting between opposing walls, which reveals first-order, critical, and tricritical quasi-wetting transitions. (Previous work was restricted to qualitative considerations [5], or to the critical transitions alone [8].) Secondly, our calculation and interpretation of quasi-wetting in terms of a shifted wetting transition leaves open the possibility that the quasi-wetting point be different from the shifted bulk critical point. Our predictions (in particular, the phase diagrams fig. 1, 3 and 4) can be tested most straightforwardly in computer simulations of $3d$ Ising slabs, along the lines of previous simulations of first-order, critical, and tricritical wetting by Binder *et al.* [17]. To this end, it would suffice to replace, in these simulations, the identical walls ($H_1=H_2$) by opposing ones ($H_1=-H_2$).

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