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Abstract. Adsorption phase transitions between distinct partial wetting states (or 'thin–thick' transitions at bulk two-phase coexistence) are studied systematically in the phenomenological Landau theory for Ising models, as well as in the Sullivan model, a more microscopic Van der Waals theory for fluids. In the Landau theory the previously proposed mechanism of competing surface fields is examined in detail and confirmed. In the generalized Sullivan model with combined exponential and square-well wall–fluid potentials, thin–thick transitions are found already if the potential is purely square-well. A mapping of the Van der Waals to the Landau theory suggests that the mechanism of competing surface fields can largely explain the new phase transitions.

1. Introduction

Wetting phenomena have been studied in great detail, experimentally, theoretically and in computer simulations, during the last 15 years. Several review articles have been devoted to wetting and related interfacial phenomena. Among the most recent are the reviews by Dietrich (1988), Evans (1990a,b), de Gennes (1990), Cazabat (1990), Schick (1990), Beysens (1990) and Forgács *et al* (1991). The wide range of possible wetting phenomena predicted by theory are not all observed in experiments. As a matter of fact, some of the theoretically allowed possibilities are very unlikely to be observable (for example, complete drying by vapour in a one-component fluid at a wall). The theoretically predicted phase diagrams are often complex. Even restricting ourselves to fluids at liquid–vapour coexistence adsorbed at a flat wall with only short-range substrate–adsorbate forces, a rich variety of surface and interfacial transitions and (multi-)critical phenomena can occur.

The Landau theory and the closely related continuum mean-field theory predict first- or second-order wetting phase transitions from partial to complete wetting, upon approach of the bulk critical point: critical-point wetting (Cahn 1977, Nakanishi and Fisher 1982). This is the generic behaviour for systems with short-range substrate–adsorbate forces. For a special (non-generic) choice of the interactions, the opposite phenomenon of critical-point dewetting is theoretically possible (Indekeu 1987).

In an alternative mean-field theory, the Van der Waals theory, Sullivan (1979) showed that, in the so-called zeroth-order approximation, the wetting transition is second-order, provided the attractive wall–fluid potential and the fluid–fluid potential

are decaying exponentially rapidly with distance and have the same range. Introducing different ranges for the potentials in this model, the wetting transition typically becomes first-order when the wall–fluid potential is longer ranged than the fluid–fluid potential, and remains second-order otherwise (Hauge and Schick 1983, Tarazona and Evans 1983, Teletzke *et al* 1983, Aukrust and Hauge 1985, Ding and Hauge 1987). For possible exceptions in closely related models, see, for example, Ding (1991).

If one theoretically allows for the presence of two independent surface fields, possibly competing with each other (one preferring liquid, and the other vapour), the wetting phase diagram becomes complex, but also very interesting. A new adsorption phase transition can occur, between two different states of partial wetting. It is commonly called a thin–thick transition, because the associated order-parameter profiles often (but not always!) resemble thin and thick wetting films. Perhaps the most important physical situation for this kind of transition to occur is in systems where short-range forces favouring, say, wetting, are in competition with weak but long-range forces favouring drying. This is the so-called antagonist case (de Gennes 1983) and has been dedicated much theoretical attention (Nightingale and Indekeu 1985, Ebner and Saam 1987) as well as experimental exploration (Durian and Franck 1987). The physics underlying this phenomenon is that a macroscopically thick wetting film is unstable in the presence of opposing long-range forces. The equilibrium wetting layer thickness is then finite rather than infinite.

Fairly surprisingly, similar thin–thick transitions were found in systems with strictly short-range surface fields, and at bulk two-phase coexistence (Aukrust 1987, Indekeu 1989). These transitions are, in our opinion, to be distinguished from prewetting phenomena that occur away from bulk phase coexistence (Cahn 1977, Nakanishi and Fisher 1982, Pandit *et al* 1982). Indeed, the presently considered thin–thick transitions can occur in the presence of macroscopic adsorbed drops with finite contact angles. Furthermore, the transitions have their own prewetting extensions and may interplay in interesting ways with the usual (finite–infinite) wetting transitions (see further).

As regards the relevance of these phenomena to realistic systems, one should note that wetting transitions in systems with short-range forces can be strongly influenced by those fluctuations which are not captured in the mean-field theories we apply. Indeed, at the upper critical dimension $d_{uc} = 3$ for critical wetting and complete wetting in the presence of short-range forces, important corrections to mean-field behaviour should be expected, as reviewed by Dietrich (1988). The situation is qualitatively different in systems with long-range forces. There $d_{uc} < 3$, and consequently mean-field behaviour should be observable in real systems in $d = 3$. An interesting example for our purposes is the thin–thick transition (e.g., a jump from 2 to 8 adsorbed layers) preceding a critical wetting transition, uncovered by Dietrich and Schick (1985) in a mean-field calculation for a lattice-gas model in which all potentials are long ranged. This result is quite likely to be applicable directly to real systems. Note that the accompanying sequence of single-layer transitions ('layering') is, in contrast, a consequence of the use of the lattice mean-field approximation (Dietrich and Schick 1985).

In the following two sections we discuss thin–thick transitions that precede wetting (or drying) transitions, within two theories in which only short-range substrate-adsorbate potentials are considered: the continuum mean-field theory (related to the Landau theory), in section 2, and the zeroth-order Van der Waals theory, in section 3. Finally, we will discuss to which extent there is a competition present between the substrate–adsorbate fields that are featured in these two theories, in section 4.

2. Landau theory and continuum mean-field theory

The Landau theory is based on a square-gradient approximation to the intrinsic free-energy functional. This phenomenological theory does not relate the properties of the non-uniform fluid to the interactions occurring on a molecular level, but provides good qualitative results in some vicinity of T_c (the critical temperature of the bulk fluid). In the magnetic language, the surface free-energy functional is written as

$$\gamma[m(z)] = \int_0^\infty \mathrm{d}z \left\{ \frac{c^2}{4} \left(\frac{\mathrm{d}m}{\mathrm{d}z} \right)^2 + f(m(z)) \right\} + \gamma_s(m_1). \tag{2.1}$$

The flat substrate is at $z = 0$, the fluid order parameter, or magnetization, $m(z)$, takes the value $m_1 \equiv m(z = 0)$ at the wall and varies between -1 and $+1$ for $z \geqslant 0$. The reduced bulk free-energy density $f(m)$ (divided by $k_B T_c$) is given by

$$f(m) = -\frac{m^2}{2} + \frac{T}{T_c} \int_0^m \tanh^{-1} m' \, \mathrm{d}m' + b_0 \tag{2.2}$$

where the constant b_0 is such that $\min[f(m)] = 0$. Concerning terminology, we note that $f(m)$ as given in (2.2) is the free-energy density appropriate to the continuum mean-field theory, whereas one usually speaks of the Landau theory if $f(m)$ is truncated and approximated by a fourth-order polynomial in m.

The substrate–adsorbate contribution to the surface free energy is modeled by a single term $\gamma_s(m_1)$, which depends only on the order parameter of the fluid at the wall. We assume the following form for $\gamma_s(m_1)$ (Diehl 1986, Indekeu 1987, Ciach and Diehl 1990)

$$\gamma_s(m_1) = -h_1 m_1 - g m_1^2/2 - h_3 m_1^3/3 \tag{2.3}$$

where h_1 and h_3 are two surface fields which act only on the first surface layer, and the surface-coupling enhancement g describes the modification of the fluid–fluid interaction near and parallel to the surface. For a derivation of (2.3), see, for example, Maritan *et al* (1991).

One can introduce competing fields in this theory by imposing $h_1 h_3 < 0$ (Langie and Indekeu 1989). To see how the competition arises, let us consider the effects of h_1 and h_3 separately. When one considers, e.g., a negative h_1-field (and $h_3 = 0$) the usual first- or second-order drying transitions are obtained, and complete drying is found sufficiently close to T_c (Nakanishi and Fisher 1982). A positive h_3-field (with $h_1 = 0$), on the other hand, results in first-order wetting or dewetting transitions (Indekeu 1987). Whether or not complete wetting is found close to T_c depends on the sign of g and the strength of h_3. When the two fields ($h_1 < 0$ and $h_3 > 0$) are combined, a new phase transition between two partial drying states can occur (Indekeu 1989). Intuitively, when T is raised towards T_c the system may display a transition between a thin and a thick drying layer, as a compromise between the drying tendency imposed by h_1 and the opposing wetting trend dictated by h_3. Sufficiently near T_c, however, the drying tendency dominates in such cases, and a genuine drying transition follows. (In a different region of the phase diagram, at larger h_3, the wetting trend wins and complete wetting is achieved.)
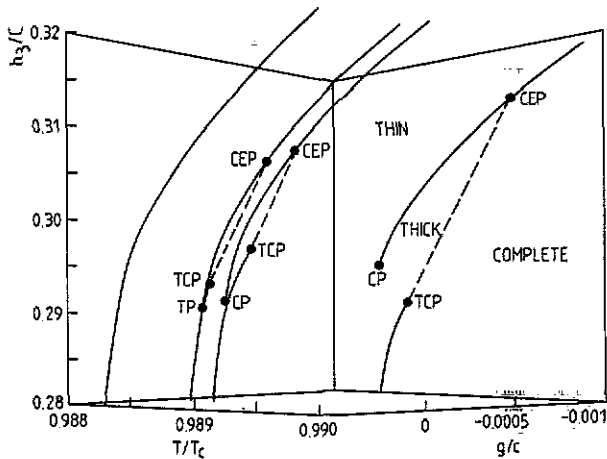
Figure 1. Sections through a three-dimensional drying phase diagram in the continuum mean-field theory for $h_1/c = -0.01$. First-order (solid lines) and second-order (dashed lines) partial-to-complete drying and thin–thick transitions, as well as critical points (CP), triple points (TP), critical endpoints (CEP) and tricritical points (TCP) are indicated for $g/c = -0.001, -0.0001, 0.00001$ and 0.0004. The first of these four sections lies entirely within the rear face (of which all four edges are drawn) of the displayed cubic frame, while the last lies within the front face (of which only two edges are drawn).

In figure 1 the influence of the surface-coupling enhancement g on the thin–thick transitions is visualized in a three-dimensional phase diagram for fixed $h_1/c = -0.01$. Note that reversing the signs of both h_1 and h_3 is of no consequence other than that 'drying' is to be replaced by 'wetting'. We have found that, in a narrow range of h_3-fields and for fixed $g/c < 4 \times 10^{-4}$, a first-order thin–thick transition precedes the first-order or second-order drying transition, as temperature is increased. For example, for $g/c = -1 \times 10^{-3}$, we distinguish a tricritical point (TCP), where the order of the drying transition changes, a surface critical point (CP), where the thin–thick phase boundary terminates, and a critical endpoint (CEP), where the critical drying phase boundary meets the first-order phase boundaries of thin–thick transitions or drying transitions. It is seen that, at that point, the state of critical drying coexists with the (non-critical) thin-layer phase, justifying the denomination of critical endpoint.

Increasing g, the surface critical point (CP) moves towards the first-order drying phase boundary, and touches it, at some g-value in the interval $-1 \times 10^{-4} < g/c < -1 \times 10^{-5}$. If g is increased further, a triple point (TP) is found where the thin-layer phase, the thick-layer phase and the complete-drying phase coexist. In other words, in this three-dimensional phase diagram, a line of surface critical points and a line of triple points meet in a distinct critical endpoint (CEP*). At this (unique) point, a critical partial drying phase coexists with a non-critical complete drying phase.

Increasing g further, the triple point (TP) and the formerly discussed critical endpoint (CEP) move closer to one another and finally coincide at a g-value in the interval $3 \times 10^{-4} < g/c < 4 \times 10^{-4}$. This results in the disappearance of the thick-layer phase and of the thin–thick transitions. Thus, they are absent for $g/c \geqslant 4 \times 10^{-4}$.

In summary, in this continuum mean-field theory, the thin–thick transition is found in the regime where the two surface fields, h_1 and h_3, have opposite sign. These competing local fields play a subtle role because their competition is not persistent

enough (as a function of temperature) to suppress transitions to complete wetting (or drying). In contrast, in the case of competing long-range and short-range surface fields, thin–thick transitions replace true wetting transitions (Nightingale and Indekeu 1985, Ebner and Saam 1987). In the following section we will investigate if the thin–thick transitions that appear in an alternative density functional theory can also be interpreted in terms of competing wetting and drying tendencies.

3. Van der Waals theory

3.1. Model

The preceding continuum mean-field theory is highly phenomenological and not specific, in the sense that it applies not only to one-component fluids, but to a whole class of systems with an Ising-type order parameter (uniaxial magnets, ...). In contrast, the Van der Waals (VDW) theory for non-uniform fluids, an alternative theory of mean-field type, is specific and is based on a microscopic description of the intermolecular forces. We will examine only its simplest, zeroth-order, realization. The intermolecular pair potentials are considered as consisting of two separate additive parts, a short-range repulsive part and a weak long-range attractive part. We take the following form for the surface excess free-energy density functional $\gamma[\rho(x)]$ of an inhomogeneous single-component fluid in the presence of an external field (Evans 1979)

$$\gamma[\rho(x)] = \int_0^\infty dx \left\{ f_h(\rho(x)) - (\mu - \phi(x))\rho(x) \right. $$
$$\left. + p + \frac{1}{2} \int_0^\infty dx' \chi(|x - x'|)\rho(x)\rho(x') \right\} \tag{3.1}$$

for a fluid with density profile $\rho(x)$, which is a function of the distance x from a structureless wall at $x = 0$. (We assume a uniform density in all other directions.) The first term in the integral is the Helmholtz free-energy density $f_h(\rho(x))$ of a uniform hard-sphere reference fluid in the local density approximation, μ is the chemical potential of the system, ϕ is an external potential (in this case the wall–fluid potential), p is the bulk pressure and $\chi(|x - x'|)$ is the attractive fluid–fluid pair potential (integrated over lateral dimensions). The properties of the hard-sphere fluid are regarded as known. We choose the ideal lattice gas-model for the hard core system. That is,

$$\mu_h \equiv \partial f_h / \partial \rho = k_B T \ln(\rho/(1 - \rho)). \tag{3.2}$$

The following forms for the substrate–adsorbate potential $\phi(x)$ and the fluid–fluid potential $\chi(x)$ are taken (Piasecki and Hauge 1987)

$$\phi(x) = -\epsilon e^{-x} - \epsilon_0 \theta(x_0 - x) \tag{3.3}$$

$$\chi(|x - x'|) = -(\alpha/2)e^{-|x - x'|}. \tag{3.4}$$

Following previous works, we assume short-range (essentially exponentially decaying) interparticle potentials. This restricts the physical applications but provides substantial technical advantages, allowing a thorough analysis of various important physical mechanisms described by the theory. The wall–fluid potential contains two parts: an

exponential part (as in Sullivan's model) and a square-well part (with range x_0). Note that the range (i.e., the characteristic decay length) of the two exponential potentials is the same and we define it as our unit of length. Also note that the short-range oscillations in the density, due to the presence of a hard wall, are neglected in this theory. Thus, since only slowly varying density profiles are featured, the theory is primarily applicable in some vicinity of the bulk critical point (located at $k_B T_c = \alpha/4$, in the mean-field approximation). In this respect, the zeroth-order VDW theory is similar in scope to the Landau theory.

Functional differentiation of $\gamma[\rho(x)]$ with respect to $\rho(x)$ gives the following integral equation for $\rho(x)$,

$$\mu = \mu_h(\rho(x)) + \phi(x) + \int_0^\infty \mathrm{d}x' \chi(|x - x'|)\rho(x') \tag{3.5}$$

as the equilibrium condition, with the boundary conditions $\rho(x < 0) = 0$ and $\rho(x \to \infty) = \rho_{\text{vapour}}$ (which is the proper set-up for investigating wetting phenomena if there is preferential adsorption of liquid) or $\rho(x \to \infty) = \rho_{\text{liquid}}$ (in case of preferential adsorption of vapour). Integral equation (3.5) can be reduced to a second-order differential equation for μ_h, so that the free-energy minimalization problem can be solved making use of the mechanical analogy of a particle moving in an external potential (Sullivan 1979, Piasecki and Hauge 1987).

Considering the specific choice (3.3) and (3.4) for the attractive potentials, Piasecki and Hauge (1987) mentioned the possibility that not only a second-order or first-order wetting transition was possible, but also a first-order 'thin–thick' transition between partial wetting states, followed by a continuous wetting transition. Aukrust (1987) showed the existence of such a thin–thick transition in a restricted region of the parameter space $(x_0, \epsilon_0, \epsilon)$. In his calculations, Aukrust employed the iteration scheme of Tarazona and Evans (1983).

3.2. Thin–thick adsorption phase transitions

Because of the presence of the square-well wall potential, the model can be viewed as a combination of two Sullivan models. For $x > x_0$ it reduces to the original Sullivan model, at two-phase coexistence, with $\mu/k_B T_c = -2$. For $x < x_0$, it reduces to the Sullivan model out of two-phase coexistence, with an effective chemical potential $\mu_{\text{eff}} \boxminus \mu + \epsilon_0$. From now on we work with the scaled variables $m = \mu/k_B T_c$, $A = \alpha/k_B T_c = 4$, $E = \epsilon/k_B T_c$, $E_0 = \epsilon_0/k_B T_c$, and $\xi = \mu_h/k_B T_c$. These definitions are almost identical to those used by Piasecki and Hauge (1987).

Our numerical procedure for obtaining the profiles that extremize the free energy is as follows. An arbitrary value of $\xi(x_0^+)$ is chosen. The matching condition at x_0 (Piasecki and Hauge 1987) then implies $\xi(x_0^-) = \xi(x_0^+) + E_0$. From this value of $\xi(x_0^-)$ follows the precise form of the 'potential' $V^-(\xi)$ that determines the trajectory in the phase portrait, for $0 \leqslant x < x_0$. The boundary condition at the wall then selects the appropriate initial value $\xi(0)$. From the knowledge of $\xi(0)$ and $\xi(x_0^-)$, simple integration along the trajectory in the phase portrait gives x_0. In sum, a (multi-valued) function $x_0(\xi(x_0^-))$ is obtained. The extrema of the free energy for a given x_0 are finally obtained as the intersections of this multi-valued function with a straight line at the given value of x_0.

The equilibrium solution, with the lowest free energy, can be obtained by computing the surface excess free energy of the extremal solutions, using an analogue of

Sullivan's geometric interpretation of the surface tension (Sullivan 1981, Piasecki and Hauge 1987). Following this procedure we have computed surface phase diagrams corresponding to various regions of the parameter space (x_0, E_0, E). We have also developed an alternative procedure, which amounts to minimizing a one-variable free-energy function $\gamma(\xi(0))$. This refinement has proven to be very useful for mapping the VDW theory onto a Landau theory, and will be discussed in some detail further on.

Figure 2 represents a phase diagram computed for fixed values of x_0 and E_0, chosen within a region where the thin–thick transitions should be expected according to Aukrust's preliminary calculations. The square-well wall potential has a width $x_0 = 4.5$ and a depth $E_0 = 0.04$. The amplitude of the exponential wall potential, E, and the scaled temperature, T/T_c, are the variables of the phase diagram. Firstly, along the dashed-dotted line there is no preferential adsorption (the surface excess free energy for liquid in bulk is the same as for vapour in bulk; in other words, Young's contact angle equals 90°). This line ends at $T = T_c$ and $E \approx 0.706$. Below this line, the vapour phase preferentially adsorbs on the wall and a drying transition appears, which is first-order for low temperatures and changes to second-order at a tricritical point TCP (at $E \approx 0.076$ and $T/T_c \approx 0.893$). On the wetting side (above the dashed-dotted line), a phase boundary of first-order thin–thick transitions is found (solid line), preceding a phase boundary of second-order wetting transitions (dashed line). The two phase boundaries are very close to each other. The thin–thick phase boundary ends at a surface critical point CP (at $E \approx 1.209, T/T_c \approx 0.876$). The wetting phase boundary near T_c behaves as

$$E(T_w) - E(T_c) \propto (T_c - T_w)^{0.5} \tag{3.6}$$

where T_w is a wetting temperature, and the uncertainty on the numerically determined exponent is 0.03. We note that the same exponent $1/2$ is obtained in the Landau theory with surface-coupling dehancement $(g < 0)$ (Nakanishi and Fisher 1982). It is known that the present VDW theory corresponds to $g < 0$ in the Landau theory (Sullivan 1979, 1981; see also our next section). Physically, dehancement of the surface coupling corresponds to the reduction of the fluid–fluid interaction near a wall, due to the reduction of the number of nearest-neighbour pairs.

Probably our most important new result is that the thin–thick transition occurs already in a simpler model in which only the square-well wall-fluid potential is featured (i.e., $E = 0$). We have computed phase diagrams in the variables E_0 and T/T_c for several values of x_0. The phase diagrams for $x_0 = 2$ and $x_0 = 3$ are qualitatively similar to the one of figure 2, with a thin–thick phase boundary well separated from the wetting phase boundary. (For these phase diagrams, the interested reader is referred to unpublished work (Langie 1991).) When the range of the square well, x_0, is increased, the distance between the wetting phase boundary and the thin–thick phase boundary decreases. At some x_0 between 3 and 4.5 the two phase boundaries meet, and partly coincide when x_0 is increased further. This is illustrated in the phase diagram of figure 3, for $x_0 = 4.5$. The two critical endpoints (CEP) represent the coexistence of the critical wetting transition with the (non-critical) thin-layer phase. In between these CEPs, the wetting transition is first-order. On the drying side it is seen that the drying phase boundary approaches $E_0 = 0$, in the limit of low temperatures. This is consistent with the known fact that a hard wall ($E_0 = 0$) is always completely dry (Henderson and Van Swol 1984). If x_0 is further increased the segment of the thin–thick transitions on the high-temperature side (from CEP to
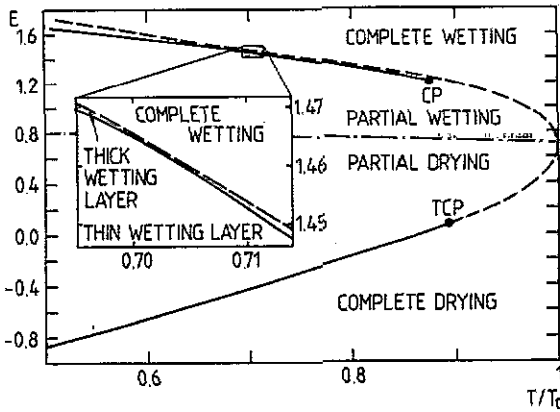
Figure 2. Wetting (and drying) phase diagram in the Van der Waals theory for $E_0 = 0.04$ and $x_0 = 4.5$. Solid lines represent first-order phase boundaries and dashed lines second-order ones. The inset shows that the thin–thick transition is separated, for all temperatures, from the wetting transition.

CP) shrinks away, and what is left is a tricritical point (TCP) on the wetting phase boundary. For example, for $x_0 = 10$, $T_{TCP}/T_c \approx 0.989$ and $E_{0,TCP} \approx 0.034$. For $x_0 = 10$ also the wetting phase diagram has been computed (Langie 1991).
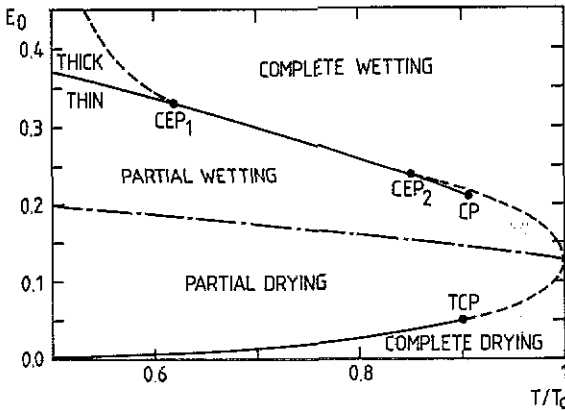

Figure 3. Wetting (and drying) phase diagram in the Van der Waals theory for $x_0 = 4.5$ and $E = 0$. Solid lines: first-order transitions; dashed lines: second-order ones.

Furthermore, we have also studied prewetting phenomena (away from bulk coexistence) for the model with the square-well wall–fluid potential ($E = 0$), for $x_0 = 4.5$, and for various values of E_0 (see figure 4). The scaled bulk field H is defined as $H \equiv m + 2$. The prewetting phase boundaries as well as the extensions of the thin–thick transitions into the bulk one-phase region terminate in surface critical points (CP) which converge, with decreasing E_0, to the surface critical point of the thin–thick transitions at bulk coexistence. Note that all critical points are qualitatively similar. Provided they still exist beyond mean-field theory, they are expected, for Ising-like fluids, to belong to the two-dimensional Ising universality class.
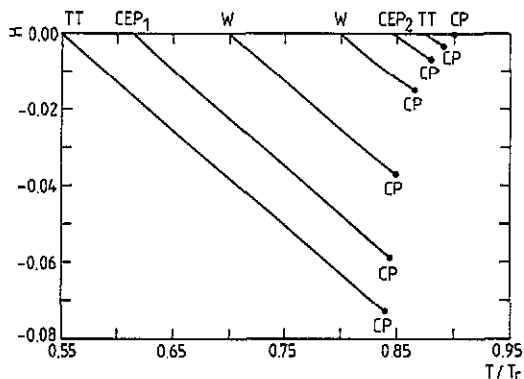
Figure 4. Prewetting phase diagram in the Van der Waals theory out of bulk two-phase coexistence (H is the bulk field), for $x_0 = 4.5$ and $E = 0$. The prewetting lines as well as the extensions of the thin–thick transitions are drawn for various values of E_0 (from left to right, $E_0 = 0.355, 0.333, 0.300, 0.259, 0.238, 0.225, 0.211$). They originate, at bulk coexistence ($H = 0$), respectively, at a thin–thick transition TT, the critical endpoint CEP_1, the wetting transitions W, the critical endpoint CEP_2, and a thin–thick transition TT. CP is a surface critical point at bulk coexistence. Prewetting lines meet the line $H = 0$ horizontally (not visible on this scale!), at W and CEP, whereas the extensions of the thin–thick transitions approach TT with non-zero slope.

4. Discussion

The first part of this discussion is devoted to some novel implications of the phase diagrams, and the second part deals in detail with the mechanism of competing surface fields.

Concerning the phase diagrams, in particular figures 1, 3, and 4, we would like to point out the following feature. When a first-order wetting transition changes into a continuous one, this is commonly expected to occur via a tricritical point. At this point a line of prewetting critical points merges with bulk two-phase coexistence. In other words, at tricritical wetting as well as at critical wetting there is no prewetting line (Nakanishi and Fisher 1982). This scenario applies, of course, to the tricritical wetting transitions labelled with TCP in our phase diagrams. However, a qualitatively very different and in our opinion novel scenario is seen at the critical endpoints CEP. There, first-order wetting changes to critical wetting, but at the point where this change occurs there is a genuine prewetting line (as demonstrated in figure 4). Furthermore, beyond this point, i.e., at critical wetting, the prewetting line is absent (as should be expected), but it is perhaps meaningful to say that, at CEP, it disconnects from the wetting transition and shifts towards lower temperatures. Thus, the prewetting line appears to be replaced by the line that extends the thin–thick transition into the bulk one-phase region.

Figure 4 naturally raises the interesting question of how the prewetting lines and the lines of off-coexistence thin–thick transitions approach the bulk phase boundary (i.e., the horizontal line at $H = 0$). As is well known, Hauge and Schick (1983) made definite predictions in this regard and argued that the prewetting line approaches the bulk phase boundary tangentially, asymptotically as $dH/dT \propto (\ln H)^{-1}$ for short-range forces, and as $dH/dT \propto H^{1/x}$ for wall–fluid potentials decaying as z^{-x}. For the mean-field theories we have employed, the result for short-range forces applies, implying that the slope of the prewetting line approaches zero extremely slowly as

$H \rightarrow 0$. We have checked this numerically, e.g., for the prewetting line starting at the first-order wetting transition W at $T/T_c \approx 0.80$ in figure 4. The data are consistent with the inverse logarithm, but, as one might have expected, this behaviour is not visible on a normal scale and this tangential approach is therefore not evident from figure 4. Next, what about the lines starting at thin–thick transitions (TT in figure 4)? Examining Hauge and Schick's argument again, it is clear that the tangential approach is a consequence of the fact that the jump in layer thickness at prewetting diverges as $H \rightarrow 0$. Since, in contrast, this jump remains finite (and usually small) when TT is approached as $H \rightarrow 0$, we conclude that, in general, the approach will be at a non-zero angle. We have checked numerically that, e.g., for the line starting at the thin–thick transition at $T/T_c \approx 0.87$, the asymptotic behaviour for small H is consistent with $dH/dT \approx$ constant. Finally, at the critical endpoints CEP the argument of Hauge and Schick applies, because the jump in layer thickness diverges for $H \rightarrow 0$, and one should thus expect a tangential approach as for prewetting, but possibly with a different algebraic form. We have not done detailed calculations for this special case.

Our second topic concerns the mechanism of competing surface fields. In the Landau theory (or, more precisely, the continuum mean-field theory) discussed in section 2, it is evident how to introduce a competition between the two surface fields h_1 and h_3. It suffices to take them to be of opposite sign so that, when they are considered separately, they prefer opposite phases. Our results so far indicate, in agreement with what was inferred in a preliminary work (Indekeu 1989), that competing surface fields appear necessary (but not sufficient) for a thin–thick transition to occur. This consequently suggests that the mechanism for the thin–thick transition is the competition of the surface fields.

Can we attribute the thin–thick transition that is found in the Van der Waals theory of the generalized Sullivan model (section 3) to a similar competition mechanism? At first sight it looks as if this question should be answerable in terms of a possible competition between the two wall–fluid potentials (exponential well and square well). However, it is not obvious how to define a competition at the level of these potentials, because the effect of their sum need not be a simple combination of the effects of each of them, considered separately. For example, it is quite possible that the two potentials are both too weak to be able to attract the liquid phase, but that their sum is strong enough. This happens, e.g., at $E = 0.9$, $x_0 = 4.5$ and $E_0 = 0.04$. For these parameter values there is preferential adsorption of liquid (see figure 2), although both the exponential and square-well potentials prefer vapour, when considered separately. Indeed, if only the exponential wall–fluid potential is present, as in the Sullivan model, one easily shows that there is preferential adsorption of liquid provided $E > 1$. (Note that in Sullivan's calculations (1981) the threshold value is actually a little higher, $E = 1.38$, because the Carnahan–Starling expression for the hard-sphere chemical potential is used.) On the other hand, when only the square-well wall–fluid potential is present, e.g., with the choice $x_0 = 4.5$, preferential adsorption of liquid occurs provided $E_0 > 0.129$ (see figure 3). (Note that a hard wall $(E_0 = 0)$ is completely dry at all temperatures, so that the introduction of an attractive square-well wall potential does not change the preferred phase as long as E_0 is sufficiently small.)

Similarly, if in some region of parameter space the two wall–fluid potentials prefer opposite phases, when considered separately, that information alone is not sufficient to conclude that there is a competition of any meaningful kind. Furthermore, the

location of the thin–thick transitions is not systematically related to the effects of the two separate potentials. We have found thin–thick transitions, for example, for $E > 1.209$, with $x_0 = 4.5$ and $E_0 = 0.04$. Incidentally, this is in the regime where the two wall potentials prefer opposite phases. However, we have also found thin–thick transitions in the purely square-well case, i.e., with only one potential present ($E = 0$). In conclusion, the clear-cut competition of surface fields in the Landau theory cannot be immediately translated in terms of a competition of wall–fluid potentials in the Van der Waals theory.

Our point of view is that, in order to examine the mechanism for the new transition in the Van der Waals theory, it is useful to derive an explicit correspondence with the Landau theory. In the following we assume that the adsorbate is at bulk two-phase coexistence. We have worked out the surface excess free energy γ, given in (3.1), with use of the second-order differential equation for μ_{h} (Piasecki and Hauge 1987), but without imposing the boundary condition at the wall, and obtain γ as a (multi-valued) function of $\xi(0)$,

$$
\gamma(\xi(0)) = \frac{1}{4}\left\{ \int_{\xi(0)}^{\xi(x_0^-)} \dot{\xi}\,\mathrm{d}\xi + \int_{\xi(x_0^-)-E_0}^{\pm\varphi} \dot{\xi}\,\mathrm{d}\xi - E^2 - \frac{1}{2}E_0 x_0(4 - E_0) \right.
$$
$$
+ W(\xi(x_0^-))x_0 + \tfrac{1}{2}\dot{\xi}^2(0) + \tfrac{1}{4}(\dot{\xi}(0) - \xi(0) - 2 + 2E + E_0)^2
$$
$$
\left. - (\dot{\xi}(0) - \xi(0) - 2 + 2E + E_0)\dot{\xi}(0) \right\} \tag{4.1}
$$

where $\pm\varphi$ is the bulk order parameter. (For the meaning of $W(\xi(x_0^-))$, see further.) Note that this expression reduces to that derived by Piasecki and Hauge (1987) as soon as the boundary condition at the wall is imposed. This condition reads

$$
\dot{\xi}(0) = \xi(0) + 2 - 2E - E_0. \tag{4.2}
$$

A number of remarks are in order concerning the expression (4.1). Firstly, in spite of appearances, it depends only on the variable $\xi(0)$. Indeed, the auxiliary variable $\dot{\xi}(0)$, for example, is nothing more than a compact notation for the (multi-valued) function of $\xi(0)$ that is given by the so-called energy-conservation relation applied at the wall (Piasecki and Hauge 1987). Secondly, (4.1) has the interesting property that minimization of it (with respect to $\xi(0)$) gives the equilibrium density profile. Indeed, we have checked that extremalization of (4.1) implies the boundary condition (4.2). In other words, the minimization of (3.1), which amounts to solving the integral equation (3.5), can alternatively be done in two steps. The second-order differential equation implied by (3.5) is implemented first, before imposing the wall-boundary condition also implied by (3.5). A significant advantage of this stategy is that, in the first step, a free energy expression is obtained that is numerically equal to the original expression (3.1) for all profiles that obey the second-order differential equation (the Euler–Lagrange equation) with arbitrary $\xi(0)$. In contrast, the related expressions derived by Piasecki and Hauge, and originally by Sullivan, reproduce the actual free energy values only in the extremal solutions.

The mapping of the Van der Waals theory onto an equivalent Landau theory is now almost accomplished. We split the free energy function into two parts (using $-\mathrm{d}V^+/\mathrm{d}\xi \equiv \ddot{\xi}$, for $x > x_0$):

$$
\gamma^{\mathrm{I}}(\xi(0)) = \frac{1}{4}\int_0^{x_0}\left\{ \frac{\dot{\xi}^2(x)}{2} - V^+(\xi(x)) - E_0\xi(x) - W(\xi(x_0^-)) \right\}\,\mathrm{d}x
$$

$$+ W(\xi(x_0^-))x_0/4 + \cdots \tag{4.3}$$

$$\gamma^{II}(\xi(x_0^+)) = \frac{1}{4}\int_{x_0}^{\infty}\left\{\frac{\dot{\xi}^2(x)}{2} - V^+(\xi(x))\right\}\,\mathrm{d}x \tag{4.4}$$

where the dots in (4.3) stand for all the remaining (boundary) terms of (4.1).

The first part γ^I is now recognized as the Landau excess free energy for a fluid confined between two parallel walls, a distance x_0 apart. $V^+(\xi)$ is the bulk free-energy density (identical, apart from factors T/T_c, to that given by Piasecki and Hauge 1987), and E_0 corresponds to an effective bulk field $H = E_0$, present in the interval between the two walls. The second part γ^{II} is seen to correspond simply to the Landau excess free energy for a semi-infinite system with a wall at $x = x_0$. The two Landau problems are coupled in a non-trivial way, through two matching conditions imposed by the equilibrium condition (3.5). These conditions are $\dot{\xi}(x_0^-) = \dot{\xi}(x_0^+)$ and $\xi(x_0^+) = \xi(x_0^-) - E_0$, and determine the value of the integration constant $W(\xi(x_0^-))$ that must be included in the energy-conservation relation for part I. Note that this constant is trivially canceled in (4.3), but the notation used clarifies the connection with (4.1).

In order to pursue the analogy with the Landau theory further, we identify explicitly the effective surface fields and enhancements at the two 'walls' at $x = 0$ and $x = x_0$. From the boundary condition (4.2) it is seen that, at the 'first wall', the surface field is $h_1 = 2E + E_0 - 2$, and the enhancement is $g = -1$. The boundary condition at the 'second wall' at x_0 reads

$$\dot{\xi}(x_0^-) = \pm\sqrt{-2V^+(\xi(x_0^-) - E_0)}. \tag{4.5}$$

In principle, both signs must be considered. In the actual calculations, it turns out that only the minus sign is important for wetting phenomena and only the plus sign for drying phenomena. It is instructive to expand this last expression as a series in $\xi(x_0^-)$,

$$\dot{\xi}(x_0^-) = -h_1 - g\xi(x_0^-) - h_3\xi^2(x_0^-) - g_4\xi^3(x_0^-) - h_5\xi^4(x_0^-) - \cdots \tag{4.6}$$

where the effective surface fields and enhancements h_1, g, h_3, etc., are functions of temperature (T/T_c), the depth of the square-well wall–fluid potential (E_0) and the order parameter in bulk $(\pm\varphi)$. They do not depend on the amplitude of the exponential wall–fluid potential. The effective surface field h_1 is positive or negative if the sign in (4.5) is negative or positive, respectively. Explicit calculation gives, for the leading three terms, $-h_1 = \pm\sqrt{-2V^+(E_0)}$ as is seen immediately from (4.5),

$$g = [2\tanh(E_0 T_c/2T) - E_0]/h_1 \tag{4.8}$$

$$h_3 = [(1 - g^2)T/T_c - 1 + \tanh^2(E_0 T_c/2T)]/(2h_1 T/T_c). \tag{4.9}$$

In the pertinent regions of parameter space (near the thin–thick transitions on the wetting side of the phase diagrams) we find $h_1 > 0$, $g > 0$, and $h_3 < 0$. Note that $h_1 h_3 < 0$.

We conclude that the profiles that extremize the free energy are fully determined by solving the equivalent Landau theory of a fluid confined between parallel walls, with the boundary conditions derived above. In particular, in order to see if thin–thick

transitions are possible, it suffices to estimate the number of solutions of the Landau theory for the slab ($x < x_0$). To do this, the following qualitative considerations are helpful. The confined system features the following fields: (i) a bulk field $H = E_0 > 0$, which favours the liquid phase; (ii) at $x = 0$, a surface field h_1 and a surface coupling enhancement g (e.g., $h_1 > 0$ for $E > 0.98$ (with $E_0 = 0.04$), and $h_1 < 0$ for $E_0 < 2$ (with $E = 0$)—furthermore, $g = -1$); (iii) at $x = x_0$, competing surface fields h_1 and h_3 ($h_1 h_3 < 0$). Higher-order fields $h_5, h_7,$ etc., are also present, but a numerical analysis indicates that their magnitude decreases rapidly with increasing order. Similar results apply for the surface coupling enhancements. For example, for $x_0 = 4.5$, $T/T_c = 0.87$, and $E_0 = 0.04$, we obtain $h_1 = 0.314$, $h_3 = -0.238$, $h_5 = 0.011$, $h_7 = -0.001, \ldots$, $g = 0.019$, $g_4 = -0.002$, $g_6 = 0.0002, \ldots$.

In view of the presence of these various effective fields, a number of known mechanisms for phase transitions in confined systems apply. Firstly, there is the mechanism of capillary condensation (possibly coexisting with prewetting), which is most effective when the two surface fields, h_1 at $x = 0$ and h_1 at $x = x_0$, are (nearly) equal, and opposite in sign to the bulk field H (Evans 1990b, Nakanishi and Fisher 1983). Secondly, so-called quasi-wetting transitions may occur, in which a nearly uniform profile changes to an interface-shaped profile. This mechanism is strongest when the two surface fields h_1 are (nearly) opposite, and when the bulk field is small (Parry and Evans 1990, Swift *et al* 1991). Thirdly, the competition of the surface fields h_1 and h_3, at $x = x_0$, which can lead to thin–thick transitions (with prewetting-like extensions for $H \neq 0$) in semi-infinite geometry (see section 2), should be expected to give rise to similar phenomena in a confined system. In summary, even when neglecting possible complications of higher than third-order surface fields, there are not less than three distinct mechanisms at work, each of which is capable of inducing a phase transition in the slab, and thereby causing a transition between distinct partial wetting states, or an ordinary wetting transition, in the full profile of the Van der Waals theory.

For concreteness we briefly discuss two typical cases. Let both the exponential and the square well be present, and consider the thin–thick transition at $E > 1.209$ (see figure 2). We obtain, in the region where the thin–thick transitions occur, $h_1 > 0$ at $x = 0$, $h_1 > 0$ at $x = x_0$, and $H > 0$. In this case the only mechanism that is pronounced is the competition of surface fields at $x = x_0$ ($h_1 h_3 < 0$). The second example concerns the purely square-well wall potential ($E = 0$; see figure 3). We obtain $h_1 < 0$ at $x = 0$, $h_1 > 0$ at $x = x_0$, and $H > 0$. This case permits the interplay of the quasi-wetting transition mechanism and the mechanism of competition of the surface fields (as in the previous case).

Our final conclusion is that in the Van der Waals theory the occurrence of thin–thick transitions at bulk coexistence can be attributed to a number of mechanisms which govern phase transitions in confined and semi-infinite systems in Landau theory. Through an explicit mapping of the former theory on the latter these mechanisms can be pointed out in terms of effective bulk and surface fields. In all cases investigated, the mechanism of competing surface fields h_1 and h_3 was seen to be active, which suggests that among the mechanisms we distinguished, it is the prominent one.

Acknowledgments

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