Structure and adsorption at gas–solid interfaces: Layering transitions from a continuum theory

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Packing effects in liquid-like films, adsorbed from bulk gas at the interface with an attractive solid substrate, may cause the fluid to adopt layer-like structure near the substrate. Such structure is inherent in the lattice gas model of adsorption where it is known to give rise to a sequence of layering transitions at low temperatures, provided the substrate (wall) is sufficiently attractive. We have used a nonlocal density functional theory to describe a continuum fluid near strongly attractive structureless walls. The theory yields oscillatory density profiles arising from packing effects. At low temperatures T (typically $0.5 \lesssim T/T_c \lesssim 0.6$, where T_c is the bulk critical temperature) the adsorption may increase with pressure in a series of discontinuous jumps, each corresponding to the appearance of a new dense layer in the adsorbed film. The transitions are first order, with very small metastable regions. As in the lattice gas model the transitions exhibit critical points; above the critical temperature of a given layer the adsorption increases smoothly with increasing pressure. However, we anticipate certain qualitative differences between the transitions we observe in the continuum theory and those of the lattice gas model, since the latter overemphasizes the role of hard-core repulsion. Layering transitions also occur for fluids confined in narrow pores. We find that in cylindrical pores the transitions are shifted to lower pressures. Moreover, capillary condensation (the first order transition to a "liquid" that fills the pore) competes with layering resulting in a rapid truncation of the sequence of layering transitions. The implications of our results for the interpretation of adsorption measurements performed near a bulk triple point are discussed and possible surface phase diagrams are suggested.

I. INTRODUCTION

The behavior of a fluid at the interface with a solid surface has been the subject of intense theoretical investigation in recent years. Attention has focused largely on two particular aspects of the interfacial problem, namely the way in which the structure of the fluid is influenced by the presence of the solid substrate,[1–3] and the variety of "surface phase transitions" which may be induced in the fluid close to that substrate.[4–9]

In addition to the effects of a single solid substrate or wall (i.e., systems which are semi-infinite normal to the wall) much work has been devoted to the study of fluids in confined systems,[10–14] where the fluid is confined by solid walls to a microscopic space which is finite in one or more dimensions. This is motivated by the desire to understand how fluid behavior is modified in narrow pores or capillaries. The thermodynamic and dynamic properties of fluids adsorbed in porous substrates is a topic of current relevance in many diverse fields of industrial importance.

A rich variety of surface transitions exists in both theory and experiments. Particularly well studied is the wetting transition.[5,6,8] Wetting phenomena may be described by a simple Landau-type[5,15] or crude density functional[16,17] theory without the need to include detailed structural information in the interfacial region. The microscopic fluid structure may play a crucial role in other transitions. For example, a dense adsorbed monolayer may exhibit a first order melting transition which is two dimensional in character.[7,9] Incommensurate–commensurate monolayer transitions[18] are a consequence of periodicity in the underlying solid substrate, which must therefore be incorporated in theoretical approaches[19] to this problem. Even in the absence of substrate periodicity, the density profile of an adsorbed film may be highly structured normal to the surface, exhibiting pronounced oscillatory behavior due to the packing of successive dense layers; this provides the possibility of discrete layering transitions whereby the adsorption jumps discontinuously due to the growth of a new layer as the pressure of adsorbate vapor is increased. In narrow capillaries similar oscillatory structures in dense fluid states could conceivably give rise to "packing transitions" by changing the capillary dimensions in and out of registry with the packing of the fluid.

Here we employ a density functional theory[20] to investigate the structure and phase equilibria of a fluid, gaseous in bulk, adsorbed at an attractive planar wall and in cylindrical capillaries. We asssume that the wall is smooth (structureless) so that the fluid is isotropic parallel to the surface; the implications of this assumption are discussed later. In order to obtain the oscillatory profiles due to packing effects we must incorporate in our theory a realistic description of short-ranged correlations arising from repulsive forces between molecules in the fluid. This is achieved via a smoothed density approximation[3,21–23] to $\mathscr{F}_{hs}[\rho]$, the Helmholtz free energy functional of an inhomogeneous hard sphere reference fluid. The basis of the smoothed density approximation (SDA) is that the hard sphere Helmholtz free energy density $f_{hs}(\mathbf{r})$ may be expressed as a function of a smoothed

density $\bar{\rho}(\mathbf{r})$ which is itself a nonlocal functional of the true density profile $\rho(\mathbf{r})$. Various prescriptions exist for the smoothed density $\bar{\rho}(\mathbf{r})$; here we use the version due to Tarazona,[23] who showed that it gives an excellent description of the density profiles of hard sphere liquids near hard walls. By treating attractive fluid–fluid forces in a mean field approximation it has also been shown[24] that this theory is able to reproduce accurately the density profiles, calculated from computer simulation,[25] for a fluid confined within narrow cylindrical capillaries.

We focus attention on layering transitions which have previously been studied only within the context of lattice models. The present theory predicts that a continuum fluid will exhibit a sequence of first order transitions, analogous to those calculated for lattice models, when the wall–fluid potential is strongly attractive and the temperature is well below the bulk critical temperature. The transitions are restricted to a narrow range of temperature; at higher temperatures the adsorption increases smoothly with pressure, although the density profiles still exhibit pronounced oscillatory structure.

The paper is arranged as follows: the nonlocal density functional theory is described in Sec. II. In Sec. III we present results for layering transitions observed at a single planar wall and in Sec. IV we describe how this transition may be modified by containing the fluid in narrow capillaries. We conclude in Sec. V with some speculations on the global characteristics of the model, and discuss how our results relate to adsorption experiments on real systems.

II. THEORY

We consider a fluid in an external potential $V(\mathbf{r})$ in contact with a reservoir at fixed μ and T. One constructs the grand potential functional $\Omega_v[\rho]$:

$$\Omega_v[\rho] = \mathscr{F}[\rho] + \int d\mathbf{r}[V(\mathbf{r}) - \mu]\rho(\mathbf{r}), \qquad (1)$$

where $\mathscr{F}[\rho]$ is the intrinsic Helmholtz free energy functional. The equilibrium density profile $\rho(\mathbf{r})$ is that which minimizes $\Omega_v[\rho]$, which is then equal to the grand potential Ω.

It is customary to divide $\mathscr{F}[\rho]$ into two terms, due to attractive and repulsive fluid–fluid interactions. Repulsive interactions are modeled by hard spheres, and attractive interactions are treated in mean field fashion:

$$\mathscr{F}[\rho] = \mathscr{F}_{hs}[\rho] + 1/2 \int\int d\mathbf{r}\, d\mathbf{r}'\rho(\mathbf{r})\rho(\mathbf{r}')\phi_{att}(|\mathbf{r} - \mathbf{r}'|), \qquad (2)$$

where $\phi_{att}(r)$ is the attractive part of the pairwise potential between two fluid molecules.

There is no exact expression for $\mathscr{F}_{hs}[\rho]$ for a three-dimensional fluid. The simplest approximation assumes that the hard sphere Helmholtz free energy density $f_{hs}(\mathbf{r})$ is a local function of the density $\rho(\mathbf{r})$; this is the local density approximation (LDA)

$$\mathscr{F}_{hs}[\rho] = \int d\mathbf{r}\, f_{hs}(\rho(\mathbf{r})). \qquad (3)$$

The LDA is sufficient to describe certain features of the wall–fluid system—it incorporates the possibility of the wetting transitions that occur at bulk coexistence[16,17] and the associated prewetting (thick–thin) transition of adsorbed films out of bulk coexistence.[5,17] It gives a poor description, however, of the detailed fluid structure, since short-ranged correlations are treated very crudely.

A better treatment of short-ranged interactions is provided by theories in which $\mathscr{F}_{hs}[\rho]$ is a nonlocal functional of $\rho(\mathbf{r})$. As a means of incorporating nonlocal effects, the smoothed density approach[3,21,24] has proved particularly successful. Here one averages the true density $\rho(\mathbf{r})$ over a volume that reflects the range of interactions to obtain a smoothed density $\bar{\rho}(\mathbf{r})$. The pronounced peaks which may occur in the true (oscillatory) profile $\rho(\mathbf{r})$ are smoothed out in $\bar{\rho}(\mathbf{r})$ so that the free energy can then be calculated as a local function of $\bar{\rho}(\mathbf{r})$. We separate $\mathscr{F}_{hs}[\rho]$ into ideal gas and nonideal contributions; for the former, a LDA in terms of $\rho(\mathbf{r})$ is exact, whereas for the latter we use a LDA in $\bar{\rho}(\mathbf{r})$:

$$\mathscr{F}_{hs}[\rho] = \int d\mathbf{r}\, f_{id}(\rho(\mathbf{r})) + \int d\mathbf{r}\, \frac{\rho(\mathbf{r})}{\bar{\rho}(\mathbf{r})}$$
$$\times \{f_{hs}(\bar{\rho}(\mathbf{r})) - f_{id}(\bar{\rho}(\mathbf{r}))\}, \qquad (4)$$

where $f_{id}(\rho)$ is the free energy density of the ideal gas. The prescription for $\bar{\rho}(\mathbf{r})$, due to Tarazona,[23] is as follows. The smoothed density is given by an average of $\rho(\mathbf{r})$ weighted by a function W which may itself depend on $\bar{\rho}(\mathbf{r})$:

$$\bar{\rho}(\mathbf{r}) = \int d\mathbf{r}'\rho(\mathbf{r}')W[|\mathbf{r} - \mathbf{r}'|;\bar{\rho}(\mathbf{r})]. \qquad (5)$$

The weight function is specified by requiring that the direct correlation function of the uniform hard sphere fluid, $C_{hs}(r;\rho)$, obtained by functional differentiation of Eq. (4), be close to that obtained from the Percus–Yevick approximation. Details of the formula for W can be found in Ref. 23, and a summary is given in Ref. 12. For the nonideal term $[f_{hs}(\rho) - f_{id}(\rho)]/\rho$ in Eq. (4) we use the Carnahan and Starling result

$$\frac{f_{hs}(\rho) - f_{id}(\rho)}{\rho} = k_B T\eta\frac{(4 - 3\eta)}{(1 - \eta)^2},$$

where $\eta = \pi\rho\sigma^3/6$, with σ the hard sphere diameter. Differentiating Eq. (1) with respect to $\rho(\mathbf{r})$ yields an integral equation for the equilibrium profile which is solved by an iteration procedure.[23]

In the calculations for a single substrate the external potential $V(\mathbf{r})$ is taken to be that of a smooth planar wall, and depends only on the normal distance z from the wall. Then the density profile is one dimensional, $\rho(\mathbf{r}) \equiv \rho(z)$. We obtain $V(z)$ by integration of the wall molecule–fluid molecule pairwise potential $\phi_{wf}(r)$ over the transverse (x,y) directions, assuming a constant wall density n_w:

$$V(z) = n_w \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' \int_{-\infty}^{0} dz'$$
$$\times \phi_{wf}((x'^2 + y'^2 + |z - z'|^2)^{1/2}).$$

The form of $\phi_{wf}(r)$ is known to affect the wetting behavior.[5,17] We have investigated several types of substrate potential:

(a) Yukawa: Here $\phi_{wf}(r) = -C_w\sigma e^{-r/\sigma}/r$, $r > 0$.
This yields a wall potential

$$V(z) = \begin{cases} -\epsilon_w e^{-z/\sigma} & z > 0 \\ \infty & z < 0 \end{cases} ; \qquad (6)$$

(b) van der Waals: $\phi_{wf}(r) \propto -(\sigma/r)^6$, $r > \sigma$. Then

$$V(z) = \begin{cases} -2\epsilon_w(\sigma/z)^3 & z > \sigma \\ \infty & z < \sigma \end{cases} ; \qquad (7)$$

(c) Lennard-Jones $\phi_{wf}(r) = 4\epsilon_{wf}[(\sigma/r)^{1/2} - (\sigma/r)^6]$.
Then

$$V(z) = 2\epsilon_w\left[\frac{2}{15}\left(\frac{\sigma}{z}\right)^9 - \left(\frac{\sigma}{z}\right)^3\right]. \qquad (8)$$

The wall strength parameter ϵ_w is proportional to the density n_w and to the strength of ϕ_{wf} in each case. Equations (7) and (8) differ only at short distances from the wall.

For the attractive part of the fluid–fluid potential $\phi_{ff}(r) \equiv \phi_{att}(r)$ we use either a Yukawa or a Lennard-Jones (LJ) form with strength parameters chosen to give identical values of $\alpha = -\int dr\,\phi_{att}(r)$. This ensures that both fluids have identical equations of state; since the free energy density of the uniform fluid is, from Eq. (2),

$$f(\rho) = f_{hs}(\rho) - \alpha\rho^2/2.$$

The critical density ρ_c and temperature T_c of this generalized van der Waals model are well known[16]:

$$\rho_c\sigma^3 = 0.249; \quad 11.102k_BT_c\sigma^3 = \alpha.$$

III. LAYERING TRANSITIONS AT A SINGLE WALL

Experimental adsorption studies[27-31] of gases on solid surfaces conducted well below the bulk critical temperature T_c of the gas have revealed that as the pressure of the gas is increased from a low value towards the saturated vapor pressure p_{sat}, adsorption may increase in a series of abrupt steps.

The steps are most well defined when the adsorbent is smooth and homogeneous; graphite surfaces are particularly favored. It is generally accepted that the steps correspond to the condensation of an essentially complete monolayer on the adsorbed film. There is an abundance of experimental data outside of isotherm measurements to support this view.[32-38]

First order layering transitions have been observed for lattice models of adsorption, in mean field[6,39,40] and renormalization group calculations,[41] and in computer simulation.[42,43] Above the wetting temperature T_w of the wall–gas interface the film thickness diverges at p_{sat} (bulk coexistence of liquid and gas); in lattice models this divergence is manifest, for strongly attractive substrate potentials, as an infinite sequence of layering transitions which become increasingly closely spaced as $p \to p_{sat}^-$. Each first order transition has an associated critical point, with critical temperatures which we shall denote as T_{cj} for the jth transition. Generally speaking these T_{cj}'s are expected to increase with j.[44] If the lattice system exhibits a roughening transition of the free (liquid–gas) interface, at temperature T_R, then theories predict that $T_{cj} \to T_R$ as $j \to \infty$.[5,6] In a mean field theory there is no roughening transition, and the prediction becomes $T_{cj} \to T_c$, the bulk critical temperature, as $j \to \infty$. The lattice model predicts that for weaker substrate potentials these layering transitions merge into a single prewetting transition slightly out of coexistence at temperatures above but close to T_w.

While it is likely that the lattice model is adequate to determine some of the gross characteristics of systems which exhibit layering transitions, the discrete nature of the model tends to favor layer-like structure and thus to promote layering above any natural propensity of a more realistic fluid. Some consequences of this are unrealistic. For example, the particle-hole symmetry of a nearest-neighbor lattice model phase diagram means that layering transitions are also predicted for systems which undergo complete drying, i.e., the buildup of gas films between the wall and a liquid, as coexistence is approached from above, $p \to p_{sat}^+$, can occur in a series of distinct layering transitions. That this is an unrealistic artifact of the model was recognized by Pandit et al.[6] Furthermore, the lattice model imposes structure on a liquid–vapor interface even far from the wall, so that in both wetting and drying situations the sequence of transitions is infinite as the thickness of the film diverges. For a realistic (continuum) fluid the pronounced structure in a wetting film near the wall is gradually damped with increasing distance from the wall, so that the edge of a very thick film comes to resemble a structureless interface between bulk liquid and gas and there would appear to be no driving force for layering transitions. In mean field theories this interface is always smooth; in reality one anticipates that the interface is always rough, so that oscillatory structure, and hence layering transitions, are washed out rather sooner than mean field theory would suggest. The capillary wave-like fluctuations in the edge of the film should reduce the number of transitions.

We might expect a continuum theory for the fluid to cast more light on these aspects. For a density functional theory in which the local density approximation (3) is used, there is no evidence of layering transitions at any temperature. This is to be expected, since the density profiles which result are rather smooth, lacking in any pronounced structure. However, we can "induce" layering transitions in this model by adopting a coarse-grained approximation in which the density profile is parametrized as a series of slabs, each of uniform density and of thickness σ (the hard core molecular diameter)

$$\rho(z) = \rho_i, \quad i - 1 < z/\sigma < i.$$

By minimizing Ω_v with respect to $\{\rho_i\}$ the equilibrium profile and grand potential can be calculated for given (μ, T). While this model suffers from the same drawbacks as the lattice gas, i.e., that layer-like structure is artificially imposed, it does allow some insight into qualitative aspects of layering. Some results for adsorption isotherms are shown in Fig. 1. These refer to a model in which both fluid–fluid and wall–fluid attractive forces are of Yukawa form with equal range parameters $\lambda \equiv \sigma^{-1}$. The wall potential parameter $\epsilon_w = 10.0k_BT_c$. The adsorption Γ is defined as $\Gamma = \int_0^\infty dz[\rho(z) - \rho_b]$, where ρ_b is the density of the bulk fluid, and undersaturation is given in terms of the ratio of bulk (gas) density to the saturated vapor density, ρ_b/ρ_{sat}; at low temperatures this is essentially equivalent to the relative pressure p/p_{sat}. At low temperatures ($T \sim 0.4T_c$) layering transitions may be seen at sufficiently attractive walls [Fig.
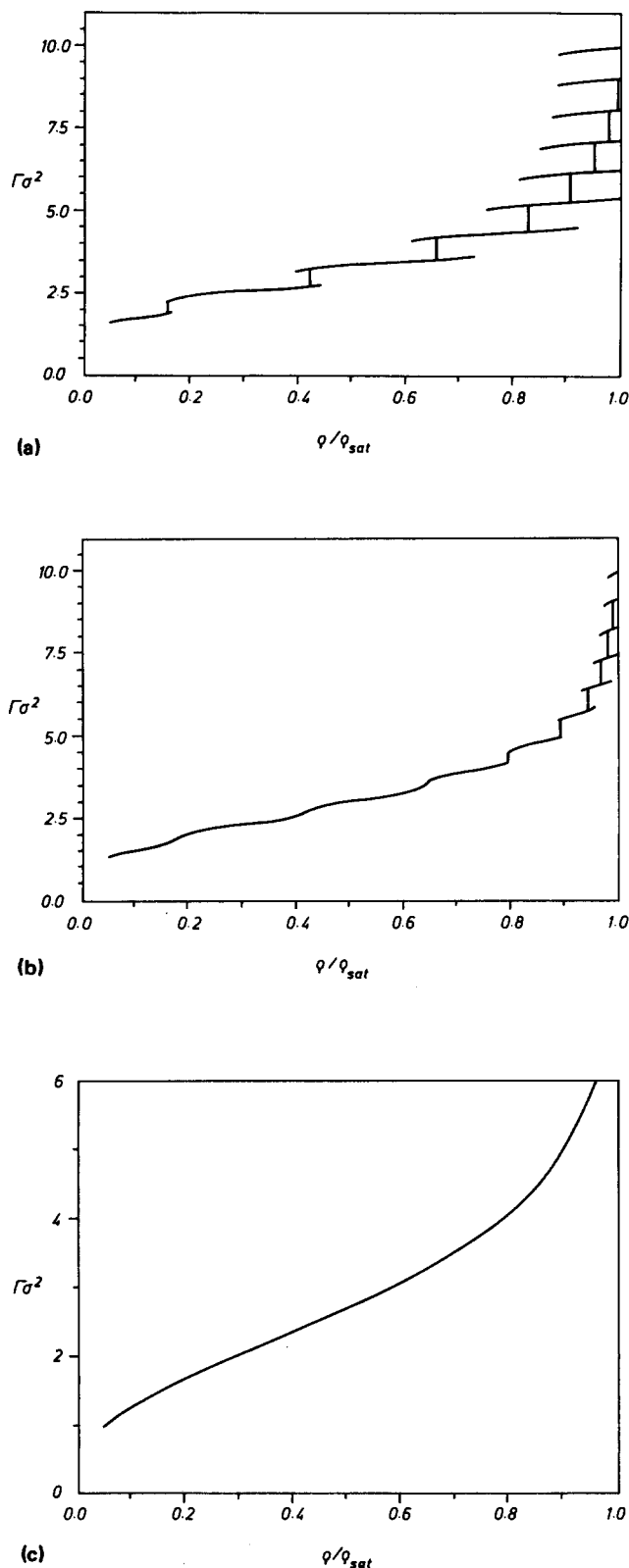
(a)

(b)

(c)

FIG. 1. Adsorption isotherms for the LDA histogram model. Fluid–fluid and wall–fluid attractive interactions are Yukawa; $\epsilon_w = 10.0 k_B T_c$. (a) $T = 0.4 T_c$. A finite number of first order layering transitions are seen as p is increased up to p_{sat}. Equilibrium transitions are indicated by vertical lines. Note the extensive metastable regions. (b) $T = 0.5 T_c$. The sequence of layering transitions remains finite, i.e., $T < T_w$. However, the first few transitions are now supercritical and the metastable regions close to p_{sat} have shrunk considerably. (c) $T = 0.7 T_c$. The adsorption increases smoothly, and diverges at p_{sat}, i.e., $T > T_w$.

1(a)]. These transitions become rounded as T is increased [Fig. 1(b)], and all traces of the transitions have vanished at a temperature that lies substantially below T_c [Fig. 1(c)]. The system can be regarded as a series of "capillary slits"[10] of width σ, coupled together by fluid–fluid interactions. The layering transitions are equivalent to capillary condensation in each slit; the T_{cj}'s are then identified with capillary critical points, so that their low values (typically ~ 0.5 to $0.6 T_c$) can be ascribed to the narrowness of the slits. A crude approximation which decouples the slits at the transition points gives the result[10] $T_{cj} \approx e^{-1} T_c = 0.368 T_c$ for all j, for Yukawa attractive fluid–fluid forces. Furthermore, we find that when wall–fluid interactions are longer ranged than fluid–fluid interactions the chemical potential at which layering occurs μ_j is determined at large j by the form of the wall potential[45]

$$\mu_j - \mu_{sat} \sim V(j\sigma). \tag{9}$$

This result was obtained for the mean-field lattice model by Pandit et al.[6] When the two types of forces are of equal range, there is generally a fluid–fluid contribution to Eq. (9).

As μ, and hence j, becomes large the density profile of this "histogram" model attains a constant shape which is essentially that of the free liquid–gas interface (Fig. 2). For the parameters of Fig. 2 there is partial wetting of the wall–gas interface by the dense fluid phase; hence there is a finite number of transitions up to p_{sat}; the sequence continues into the region of supersaturated (metastable) vapor. By increasing the strength of the wall potential we can pass to a complete wetting situation, in which case the sequence of transitions becomes apparently infinite at coexistence.

The LDA histogram models retain all the failings of the lattice model. For a better description of layering one requires an approach in which structuring of the fluid arises naturally rather than being imposed from the outset. Such is the case in the SDA theory, for which the layer-like packing of a dense fluid near a wall is simply a consequence of the accurate treatment of short-ranged correlations. Previous work[46] using this model has tended to focus on either weakly attractive walls or relatively high temperatures, both of which are inappropriate conditions under which to look for layering transitions. We have performed calculations for strong walls at low temperatures and have found that under such conditions layering transitions in adsorbed films appear to be a quite general phenomenon, i.e., they are found for a variety of wall–fluid and fluid–fluid intermolecular potentials.

Figure 3 shows the adsorption isotherm of a Yukawa fluid at a Yukawa wall with potential parameter $\epsilon_w = 4.0 k_B T_c$; the reduced temperature T/T_c is 0.5. In the LDA the wetting temperature of this model is $0.661 T_c$, and the transition is second order. However, it is known[12] that wetting temperatures are generally considerably lower for the SDA than for the corresponding LDA; moreover, under certain circumstances the transition may become first order. We have not determined the SDA wetting temperature explicitly, but on the basis of Fig. 1 of Ref. 12 and the form of the calculated isotherm above we are confident that T_w for the SDA is below $0.5 T_c$. Furthermore, the transition is prob-
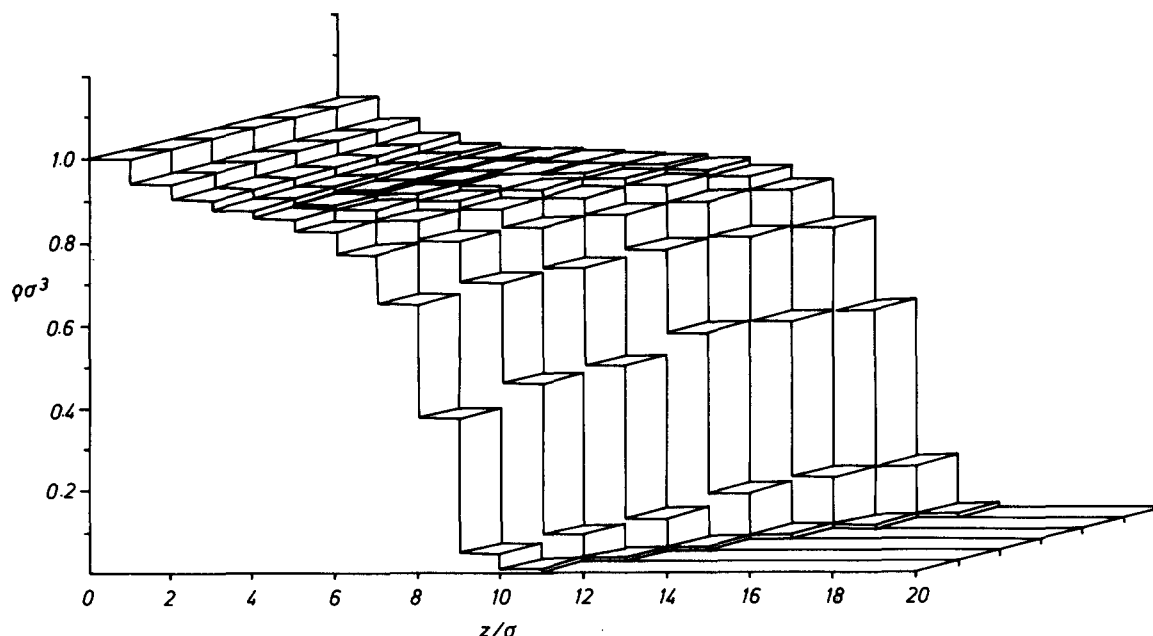
FIG. 2. Density profiles of successive layering states for the higher order transitions in Fig. 1(b). $\epsilon_w = 10.0k_BT_c$, $T = 0.5T_c$. As the adsorbed film grows, the edge of the profile attains a constant shape which moves outwards by a distance σ at each transition.

ably first order. This implies the possibility of a prewetting transition. We find no evidence for this, and suggest that for strong walls at low temperatures layer-by-layer film growth might be preferred over a single thick–thin transition.

A series of first order transitions is observed, corresponding to discontinuous jumps in adsorption Γ. The density profiles (Fig. 4) reveal that each jump corresponds to the addition of roughly one dense layer to the adsorbed film, while in each case the rest of the profile remains relatively unchanged. The magnitude of the jumps increases steadily:
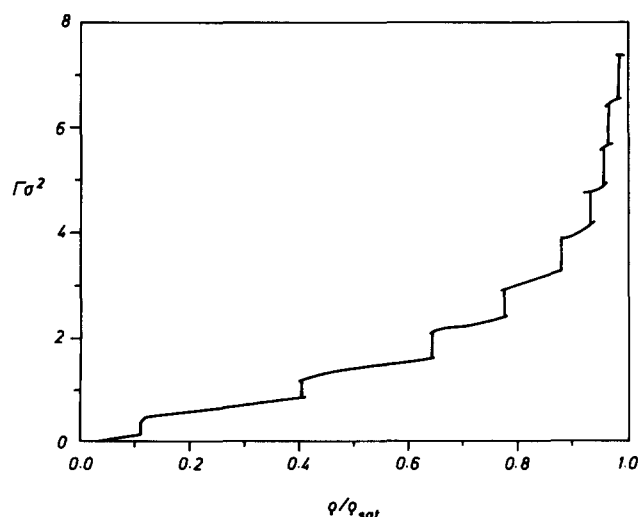

FIG. 3. Adsorption isotherm for a Yukawa fluid at a Yukawa wall in the SDA. $\epsilon_w = 4.0k_BT_c$, $T = 0.5T_c$. This temperature is above T_w, so that Γ diverges at p_{sat}. We have not extended the calculation beyond the ninth layering transition. Note that the jumps in Γ become successively larger, and that the metastable regions are always very small.

the reason for this is clear from the density profiles. The first few peaks are very sharp, so that while the maxima may be large the amount of fluid in each of these layers is relatively small. As oscillations die away the peaks broaden and the integrated density over each "layer" (i.e., the adsorption corresponding to each layer) increases. Moreover, there are then also significant increases in the peak densities of at least two of the previous layers when the transition occurs.

The transitions cluster together more closely as saturation is approached, and it becomes increasingly difficult to distinguish individual transitions. The iteration procedure used to obtain the equilibrium density profiles converges increasingly slowly, making accurate calculation still more problematic. We have not continued our calculation beyond the ninth layering transition, although the film thickness (and hence Γ) diverges at saturation.

The density at wall contact ($z = 0$) becomes very large ($\rho\sigma^3 \sim 8$). This is a consequence of the hard wall repulsion—the fluid sits in a very deep potential well at wall contact. As a result one might speculate as to whether the fluid in the first layer is still truly liquid-like, or whether instead it may crystallize. Within the framework of this theory there is no way of telling; one would have to allow for structure in the density profile parallel to the wall and to then examine the profile for signs of solid-like ordering. This approach has been applied to the SDA model in order to investigate the bulk freezing transition,[22,23,47] but a comparable approach for adsorbed films has been used only to study monolayer transitions.[48] Whether or not we choose to allow the underlying substrate any structure becomes important for the freezing of adsorbed layers. Evidence from computer simulations suggests that freezing of the first layer is only observed if the wall itself has some transverse structure,[1,49] and that even then such ordering does not extend beyond the first
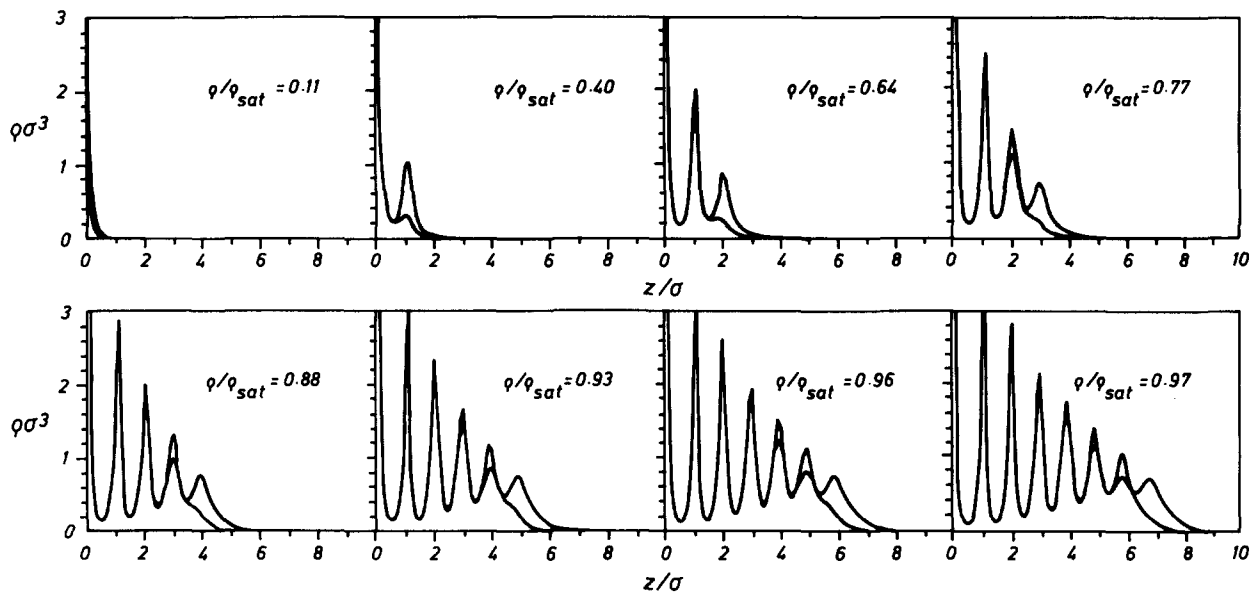
FIG. 4. Coexisting density profiles in the SDA at the first eight layering transitions in Fig. 3. The undersaturation (relative density) is given for each transition. A new peak, corresponding to an adsorbed layer, develops at each transition. Note the similar shape of the edge of the film for the last three transitions.

adsorbed layer. However, any propensity of the fluid to exhibit transverse crystalline order should depend on the strength of the wall potential and, in a realistic model which incorporates a solid bulk phase, on how close the system is to the bulk triple point. Note that the triple point temperature of the Yukawa fluid used in Fig. 3 has been estimated,[12,22] via an appropriate parametrization of the SDA density profile to be $\approx 0.47 T_c$.

In Fig. 3 the first layering transition (at $\rho/\rho_{\text{sat}} = 0.11$) is very close to (just below) a critical point. It seems a general feature of all models of layering that T_{c1} is significantly lower than the critical temperatures of the higher j transitions [see, e.g., Fig. 1(a)], and that furthermore the latter are rather close together.[39,43] This is borne out in Fig. 5, which shows an isotherm for the same system as Fig. 3 but now at $T/T_c = 0.6$. Only a few "bumps" remain as evidence of the layering transitions which occur at the lower temperature.

Figure 6(a) shows part of the adsorption isotherm for a Lennard-Jones gas against a Lennard-Jones wall. Here the wall strength parameter ϵ_w, as defined in Eq. (8), is $4.0 k_B T_c$. For the fluid–fluid pairwise potential we use[24] a cutoff and shifted (WCA) LJ potential with cutoff $r_c = 2.5\sigma$. The reduced temperature T/T_c is 0.5. Again there is clear indication of layering which is supported by the shape of the density profiles shown in Fig. 6(b). Although the walls are of comparable strength, the soft repulsion of the LJ wall results in somewhat smaller peaks in $\rho(z)$ than those for the Yukawa wall.

With the aim of investigating more easily the global systematics of layering in the SDA we have attempted to develop realistic simpler models. At the lower order layering transitions of Fig. 3 the peaks in the density profiles are quite sharp, with rather low densities between them. In this case

the profiles can be approximated by a set of Gaussians superimposed on a uniform bulk gas "background" density

$$\rho_n(z) = \rho_b + \sum_{i=1}^{n} h_i \exp\left\{\left[\frac{z}{\sigma} - (i-1)\right]^2 / \Delta_i\right\}, \quad (10)$$

where $\rho_n(z)$ denotes the density profile of a film with n layers, and h_i and Δ_i are the Gaussian heights and widths, respectively. It is a good approximation to assume that all Δ_i are equal (typically ~ 0.22). Layering equilibria are then determined in terms of a small number of order parameters

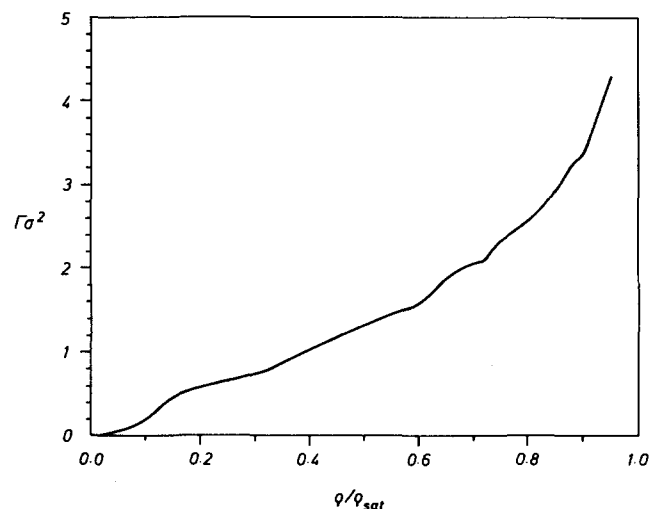FIG. 5. Adsorption isotherm in the SDA for the same model as Fig. 3 but at the higher temperature $T = 0.6 T_c$. Although the density profiles are still highly structured, all first order transitions have disappeared; only slight bumps in $\Gamma(p)$ remain. This implies that the critical temperatures of (at least) the first nine transitions all lie within the range $0.5 T_c < T_{cj} < 0.6 T_c$.
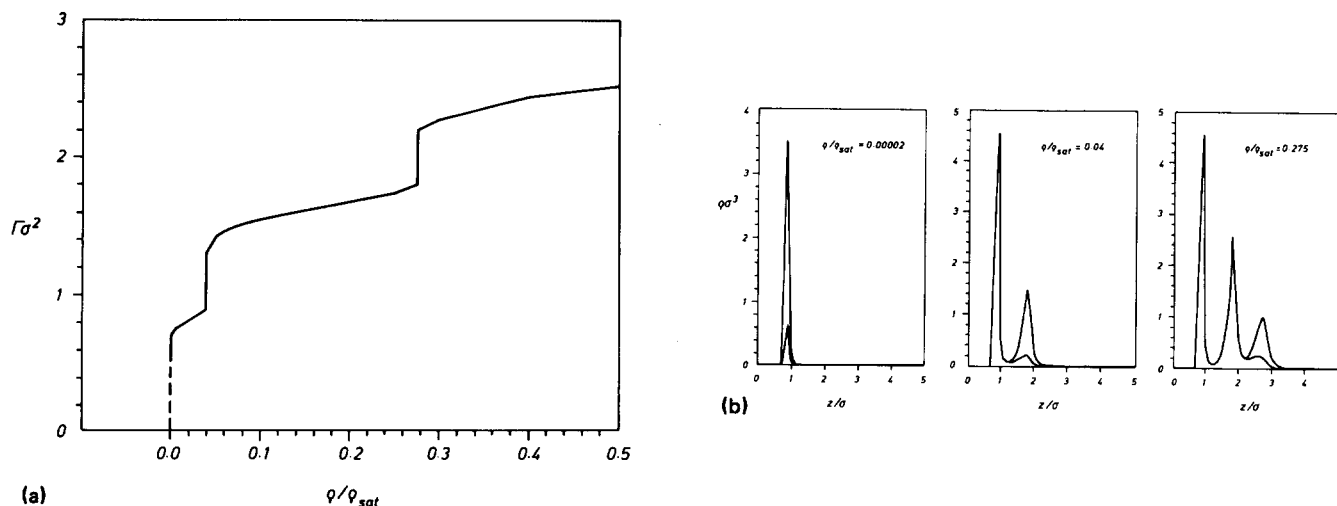
FIG. 6. (a) Adsorption isotherm in the SDA for a Lennard-Jones fluid at a Lennard-Jones wall. $\epsilon_w = 4.0 k_B T_c$, $T = 0.5 T_c$. (b) Coexisting density profiles at the layering transitions.

$\{h_i\}$. In particular, the first transition is described simply by the function $\Omega_v (h_1)$ and the second by $\Omega_v (h_1, h_2)$. By using the parametrized profile (10) in the SDA functional we can examine the grand potential surface $\Omega_v [\{h_i\}]$ and thus obtain a graphical understanding of this function in the vicinity of the transition. Figure 7 shows $\Omega_v (h_1, h_2)$ close to the second layering transition, using the same parameters as in the full calculation of Fig. 3. Ω_v has double minima—one or other of these minima disappears very rapidly as we either increase or decrease the pressure, i.e., the spinodals are very narrow. Notice that the jump in h_2 is accompanied by a small jump in h_1—the layers are not entirely independent of one another. Considering the crudeness of the approximation,
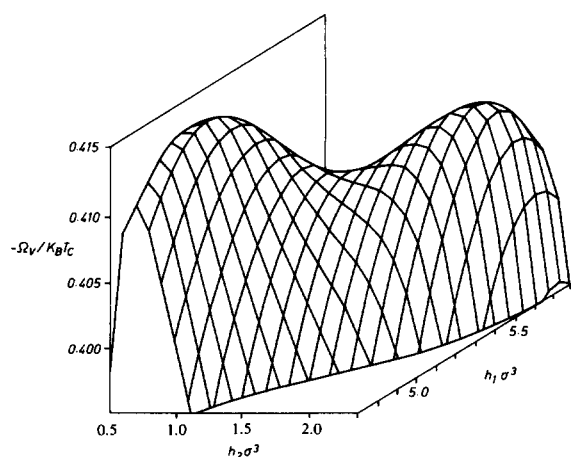
the relative pressure p/p_{sat} at the transition (0.472) is remarkably close to that in the full calculation (0.40). At the higher temperature of $0.6 T_c$ the double minima in $\Omega_v (h_1, h_2)$ have coalesced to a single minimum so that h_1 and h_2 increase monotonically with pressure, i.e., we are now above the critical temperature of the transition. Although we have not studied this parametrized model in detail it would seem to provide a promising means of determining the global characteristics of the SDA layering phase equilibria.

When comparing and contrasting our results with those of lattice models it is important to recognize that the SDA is a mean-field treatment of a continuum fluid. Thus, in the first instance we should compare with mean-field results for the lattice models. Earlier we alluded to the unphysical layering in the drying region of the phase diagram for a lattice model. The approach to complete drying has been investigated using the SDA[3,12]; one finds that the density profiles close to coexistence (as $p \to p_{sat}^+$) are similar to those for the corresponding LDA, being rather smooth. As the gas "film" thickens the profile becomes that of a free liquid–gas interface, which gradually unbinds from the wall. Since packing considerations are not important there is no layer-like structure, and consequently one expects no layering transitions. Further from coexistence (i.e., moving into the bulk liquid region) the picture is less clear, since liquid density profiles in the SDA are then oscillatory near the wall. Whether erosion of these oscillations, as $p \to p_{sat}^+$, is gradual or sharp is then open to question, but nevertheless we feel that discrete transitions are unlikely—there is a fundamental asymmetry in the nature of liquid and gas phases.

Second, we suggested that the infinite sequence of layering transitions in the lattice model (above T_w) may be a consequence of the discrete structure imposed on the density profile. Structure is only pronounced close to the wall for a wetting film in the SDA; as the thickness increases the oscillations die away (Fig. 4) and the profile becomes rather flat, ultimately resembling the liquid–gas interface at the edge of

FIG. 7. Grand potential surface $\Omega_v (h_1, h_2)$ (inverted for clarity), as a function of peak heights h_1 and h_2 in the Gaussian SDA model. The two minima of Ω_v correspond to the two states in the vicinity of the 1 → 2 layer transition. These minima are very shallow, and disappear rapidly either side of the transition.

the film. One might expect that layering will then disappear, possibly via criticality of the last few transitions, and the film would grow continuously. If such was the case we might find, within a certain temperature range, criticality or super-critical behavior with respect to both the first and the last few transitions, while still observing first order transitions for the intermediate layers.[50] At present our calculations are unable to confirm this, and it must be said that there is no evidence for "weakening" of the first order transitions in Fig. 3, even when the oscillations in the profile have become rather weak, layering remains clearly first order, with well-defined metastable regions. However, we have not been able to extend the calculation close enough to saturation for the liquid film to exhibit a truly flat bulk-like region (as eventually it must), and it is not until such a region develops that our argument holds. If the sequence were to be infinite then the SDA results would be reflecting the fact that the liquid–gas interface is smooth in this mean-field theory, and in this respect the situation would be the same as that which pertains in the mean-field treatment of the lattice gas. It would then be interesting to ask what happens as the strength of the wall–fluid attraction is reduced. We know that for weaker walls there is continuous film growth, or a single prewetting transition, although the liquid–gas interface is, of course, still smooth.

Beyond mean field we expect a somewhat simpler picture to emerge. Since the liquid–gas interface is rough the layering transitions in the continuum fluid will be washed out rather sooner and the overall pattern should be similar to that for the lattice gas above its roughening temperature. Experimentally up to eight well defined transitions have been seen in liquid-like films but we will return to this in Sec. V. We should note that criticality of layering transitions, whether in the lattice or in the continuum model, should correspond to that of the *two-dimensional* Ising universality class; the phases have finite extent normal to the substrate and the correlation length can only diverge in directions parallel to the substrate.

IV. LAYERING IN NARROW CAPILLARIES

The phenomenon of layering in the SDA theory came to our attention while using the theory for studies motivated by a somewhat different objective, namely the investigation of capillary condensation in narrow pores. Both surface and bulk behavior are known to be modified when a fluid is confined within a finite geometry, and in particular surface transitions "compete" with the shifted bulk liquid–gas transition (capillary condensation).[13,26] Moreover, confinement within dimensions of the order of a few molecular diameters (e.g., within micropores and small mesopores) may have a profound effect on the fluid structure.[14,24,25,12]

Previous work[13,26] on the prewetting transition has revealed that it is relatively unaffected by confinement. Since prewetting occurs close to coexistence, fairly large pores are required in order that the stable equilibrium transition be seen at all, and the influence of confinement is consequently rather small. However, one cannot necessarily expect this to be a general property of surface transitions.

We have studied the effect on layering of confining fluids within cylindrical pores of radius R_c and infinite length. We chose a system which was expected to show strong layering transitions for a single planar wall: the wall fluid potential was of van der Waals form (7). Hard repulsion and the deep potential well at $z = \sigma$ results in pronounced oscillations in $\rho(z)$. The potential parameter $\epsilon_w = 4.0k_B T_c$. In previous work it was assumed that it is meaningful to compare different forms of wall potential via the integrated strength, defined as $\int_0^\infty dz\, V(z)$. The potential parameter ϵ_w used here was chosen such that the integrated strength is the same as that of the Yukawa wall used in Fig. 3—see Eqs. (6) and (7). Thus, a comparison of the single wall isotherms in the two cases gives an indication of the influence of the form of the potential on layering (fluid–fluid forces are of Yukawa form in both cases).

In cylindrical capillaries the external potential is obtained by integrating ϕ_{wf} over the axial (z) direction of the capillary. $V(\mathbf{r})$ then becomes a function only of the radial distance R from the pore center. In Figs. 8(a) to 8(d) we illustrate the adsorption isotherms calculated for $T = 0.5T_c$ at a single planar wall and in capillaries of decreasing radii. For the capillaries we also indicate the capillary condensation transition from a low density state to a dense liquid-like state; the latter are highly structured.[14,24,25,51]

We see that even in a relatively large pore ($R_c = 15\sigma$) layering transitions may be shifted to significantly lower pressures relative to the single wall system. This shift becomes increasingly pronounced as R_c decreases. On the scale of Fig. 8 the $0 \rightarrow 1$ layer transition occurs at such low pressures in each case that the shift as a function of R_c cannot be seen. All transitions other than the first two become preempted at fairly large radii by capillary condensation, and triple points may occur at which two gas-like phases coexist with "liquid." For $R_c = 15\sigma$ the third layering transition lies very close to such a triple point. The mechanism for these triple points is essentially the same as for those discussed previously[26] in connection with prewetting, but whereas in that case there was only a single thick–thin transition on the "gas" branch, here we find a series of triple points associated with the series of layering transitions.

Figure 8 shows that layering transitions persist for pressures greater than that corresponding to capillary condensation but such transitions now occur between metastable "gaseous" states, since the liquid has the lowest grand potential. Similar behavior was observed in mean-field calculations for confined lattice gases.[13] As the radius R_c is reduced the sequence of metastable layering transitions is truncated at increasingly lower pressures. This behavior is consistent with the adsorption isotherms calculated[10,11] at higher temperatures, i.e., above any layering critical temperatures. Then the capillary spinodal on the (single) gas branch shifts to lower pressures and the loop in Γ shrinks as R_c is reduced. At these lower temperatures the metastable layering transitions are taking place within a gas branch whose extent, in pressure or ρ/ρ_{sat}, is decreasing with decreasing R_c. We note also that the spinodals of the individual layering transitions are always very narrow. This contrasts with the rather extensive metastable regions calculated for lattice models[13,43] and
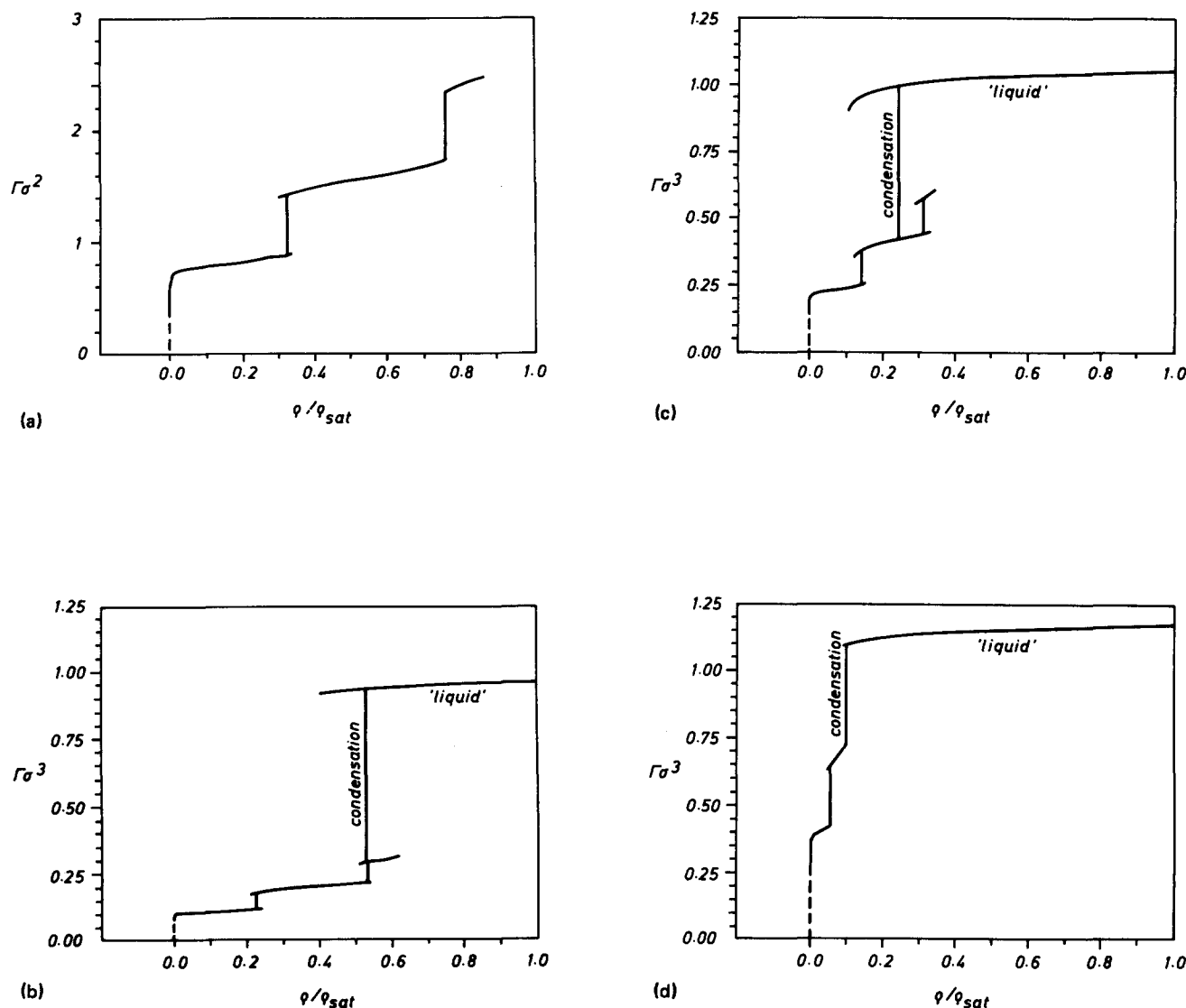
FIG. 8. Adsorption isotherms in the SDA for a Yukawa fluid confined within cylindrical capillaries. The walls have hard repulsion and van der Waals attractive forces, exerting a potential $V(z) = 2\epsilon_w \sigma^3 z^{-3}$ in the planar limit. $\epsilon_w = 4.0 k_B T_c$; $T = 0.5 T_c$. In cylindrical capillaries the adsorption Γ is defined as $\Gamma = 2/R_c^2 \int_0^{R_c} dR R [\rho(R) - \rho_b]$, i.e., it is normalized for each radius. Note the different (unnormalized) scale for the single wall adsorption in (a). For the capillaries, the liquid branch is also shown. Capillary condensation and layering transitions are indicated by vertical solid lines. For the $0 \rightarrow 1$ layer transition, the vertical line is dotted so that it may be distinguished from the nearly vertical adsorption isotherms in this region. (a) Single planar wall (we have not calculated beyond $\rho/\rho_{sat} = 0.87$). (b) Cylindrical capillary with radius $R_c = 15\sigma$. (c) $R_c = 7\sigma$. (d) $R_c = 4\sigma$.

the LDA histogram model (see Fig. 1) and lends support to the suggestion that these latter models are somehow stabilizing layering states artificially. It might also give some indication as to why hysteresis has not been reported in adsorption measurements which probe layering transitions (cf. the case of capillary condensation, where the broad loops in Γ calculated for this first order transition have been proposed[52] as the source of the hysteresis observed in adsorption measurements on mesoporous solids).

The results are summarized in the capillary phase diagram, Fig. 9, where we plot boundaries of coexistence as functions of capillary radius R_c and undersaturation, now in terms of chemical potential difference $\mu - \mu_{sat}$. Although capillary condensation soon supercedes higher order layering transitions, at small R_c the shift in the layering transitions is comparable to the shift in the bulk transition. The one layer–two layer transition is not preempted by conden-

sation until $R_c \lesssim 4\sigma$, and the $0 \rightarrow 1$ transition persists at least down to $R_c/\sigma = 1$. Note that capillary condensation is observed in extremely narrow pores $(R_c/\sigma \lesssim 1)$ at this temperature.[12,53] We did not observe any dependence of the layering critical temperatures T_{cj} on the radius. Although the $0 \rightarrow 1$ layer transition is shifted to smaller μ by confinement, due to an increase in the net wall–fluid attraction, the first order character of the transition is unaltered from that at a single wall. Finally we note that the dotted line in Fig. 9 denotes the coexistence between metastable two-layer and three-layer configurations.

V. SUMMARY AND DISCUSSION

We have used a nonlocal density functional theory to investigate layering transitions in the liquid-like film formed at an inert solid–gas interface. These transitions arise quite
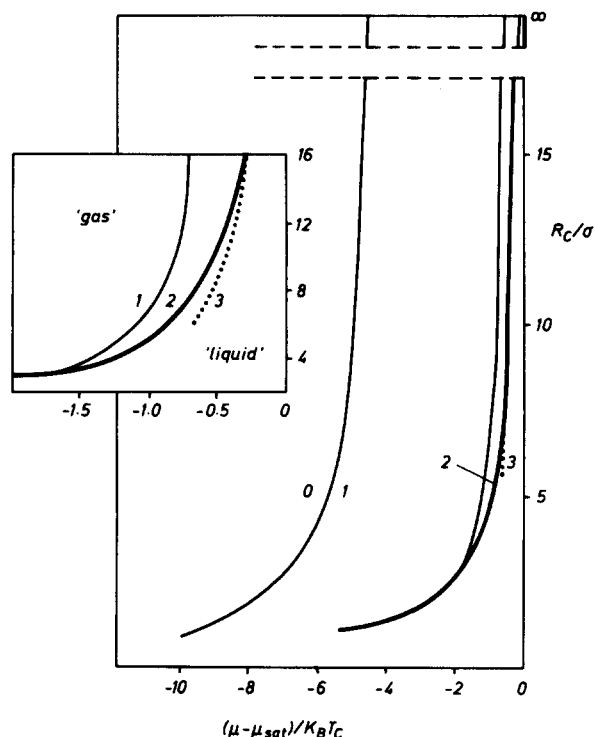
FIG. 9. Capillary phase diagram at $T = 0.5T_c$. The thick line denotes the capillary condensation phase boundary, while thin lines separate successive layering phases on the gas branch. The dotted line indicates layering transitions which occur on the metastable region of the gas branch, i.e., at pressures above that of capillary condensation.

naturally as a consequence of the pronounced structure, due to packing effects, in the fluid density profile near the wall. To our knowledge this is the first observation of layering transitions in a continuum theory, and is in consequence free from the ambiguities inherent from the "imposed structure" of the lattice gas model. We anticipate qualitative differences in the phase diagrams of the two models. In particular, the absence of imposed structure in a continuum model leads us to suspect that layering transitions will not occur when the density profiles are rather smooth, e.g., at the edge of a thick adsorbed wetting film far from the wall or in a gas-like drying film. These suggestions remain to be verified. Mean field nearest-neighbor lattice theories suggest[6] that successive layering transitions are ordered in a manner reflecting the decay of the wall potential [Eq. (9)]. The SDA results in Fig. 3 do not conform to this simple pattern, i.e. the relative pressures at each transition do not follow the predicted pattern $\mu_j - \mu_{sat} \sim - e^{-j}$. This may reflect the fact that the range of fluid–fluid forces is equal to that of wall–fluid forces. Further work, using wall potentials that decay algebraically with distance, might provide more insight into this aspect of the transitions.

The global characteristics of single wall systems may prove to be very rich, and warrant further attention. It has been suggested[6] for lattice models that the transitions may not always remain sequential, e.g., that triple points may be found at which three layering phases coexist. The pattern of critical points is worthy of investigation; it seems that all of these, or at least those of lower order transitions, lie very close together. For higher temperatures and weaker substrates layering transitions in the lattice model merge into a

single prewetting transition.[6,13] Whether this remains true in the SDA theory is yet to be ascertained. We believe that all SDA results presented here pertain to complete wetting situations for which the transition is first order. Therefore, prewetting is certainly a possibility in each case. It appears that layering occurs in preference to, rather than in addition to, prewetting; however, we should emphasize that prewetting is difficult to locate since it occurs over a very small region of the phase diagram.

In capillaries the phase diagrams may be richer still, since layering is now in competition with capillary condensation. In small pores the surface transitions are influenced by confinement. Note that in cylindrical capillaries the curvature of the surface may also play a role, so that the shift in layering transitions may be less pronounced in slit-like pores with planar walls.[54]

Caution must be exercised in interpreting the results for cylindrical pores. Since the SDA is a mean-field theory we must expect it to predict the same type of phase equilibria for cylinders as for slits and this is what is found in our calculations and in earlier work on condensation and prewetting.[11,12] Dimensionality must manifest itself when one goes beyond a mean-field approximation, and in the cylinder, which is quasi-one dimensional, *all* phase transitions should be smeared by finite-size effects. Surface transitions (layering and prewetting) and capillary condensation are characterized by a jump in the adsorption; in each case the order parameter is $\Gamma_\alpha - \Gamma_\beta$, where α and β refer to the relevant phases. Thus all transitions should be Ising-like and a transition in a cylinder would correspond to an Ising transition in an infinite strip, which cannot occur for $T > 0$. While it should be possible to estimate the degree of "rounding" of the various first-order transitions, at least for large radii R_c, using finite size scaling theory[55] we are not aware of any explicit calculations. Because of the Ising character we expect the condensation transition to be rounded (in $\Delta\mu$, say) on the scale $\exp[- (R_c /\sigma)^2]$, which implies very sharp "transitions" in all but the very smallest cylinders. This argument appears to be supported by the results of simulation[14] which find very abrupt jumps in adsorption with no obvious rounding. The rounding of the surface transitions is more subtle and fluctuations may tend to wash these out. However, the competition between layering and condensation leading to triple points remains a viable scenario beyond mean field for slit geometry.

The present theory gives no indication of the transverse structure within the layers themselves. In this respect the structure of the solid surface will be a significant factor, and it has been suggested[1,49] that this may provide a template for crystalline ordering of the first adsorbed layer. Since most layering transitions occur at low temperatures (close to the bulk triple point) this is not unexpected. Experimentally, the monolayer may exhibit a wide range of different structures, some of which persist in the bilayer also.[4,7,9,35,36]

Explicit layering transitions have not been reported in computer simulations of a continuum fluid. Given the close correspondence between simulation and the results of SDA theory found elsewhere[23,24] we anticipate that simulation studies performed for similar potential functions and tem-

peratures could prove most fruitful. They would certainly test many of the predictions made here.

Finally one must ask how these results relate to experiment. In the vast majority of cases, sharp layering transitions are seen below the bulk triple point T_{tr} of the adsorbate. One therefore expects the adsorbed film to be solid-like, with the sequence developing as $p \to p_{sg}$, where p_{sg} is the saturated vapor pressure at solid-gas coexistence. Our version of the SDA does not allow for the formation of a bulk solid phase, so that the theory does not make reference to p_{sg}. [Calculations performed for low temperatures would associate p_{sat} with the analytic continuation of the liquid-gas bulk coexistence line below the (hypothetical) triple point.]

However, it is known that the melting temperature of adsorbed solid layers may be significantly below that of the bulk solid (in thin films melting has two-dimensional character). It is therefore quite possible to find liquid-like adsorbed films close to but below the bulk triple point. First order layering transitions have been seen to persist above the melting point of such films, i.e., between liquid-like adsorbed phases.[35,36] We have shown that packing effects near the wall may provide a mechanism for these transitions.

At least two cases have been reported of layering transitions above T_{tr}. Ethylene adsorbed on graphite is a particularly well studied system.[36,56,57] There are certainly transitions above $T_{tr} = 104$ K, but the precise number and behavior very close to T_{tr} is not entirely clear. Drir et al.[56] were able to resolve eight discrete steps at 104.6 K and six at 107.8 K in an ellipsometric study. Kim et al.[57] located the critical points of the first five transitions in heat capacity measurements. They find $T_{c2} = 115.3$ K, $T_{c3} = 111$ K, $T_{c4} = 108.4$ K, and $T_{c5} \sim 105$ K and suggest that the sequence will approach T_{tr} ($\equiv T_R$) from above. Kim et al. point out that x-ray and ellipsometric measurements indicate that films corresponding to three or more layers are liquid-like on formation and that the melting temperature of the monolayer and bilayer are well below T_{tr}. In other words, all the layering transitions for $T \gtrsim T_{tr}$ occur between liquid-like adsorbed phases. While we had anticipated that the large number of transitions calculated in the SDA (at least nine in Fig. 3) was a consequence of the mean-field approximation it appears that the latter is mimicing the experimental situation rather well. We speculate that incorporating roughening will ensure that the sequence is not infinite but will otherwise not be very significant. There is certainly no compelling reason why the critical temperatures of a (large) number of the layering transitions should not lie above T_R; only the asymptotic ($j \to \infty$) behavior of the T_{cj}'s is determined by T_R. Other models [see, e.g., Fig. 21(b) of Ref. 6] show several critical points above T_R. Thus, we might envisage a phase diagram of the type shown schematically in Fig. 10 with layering transitions occurring both below T_{tr}, but above the melting temperature of the films, and above T_{tr}. We have implied that both solid and liquid films might grow continuously beyond a certain finite number of layering transitions. The actual situation for ethylene[58] is somewhat different since there is no freezing of the trilayer or thicker layers; the liquid films persist to the bulk gas-solid phase boundary.
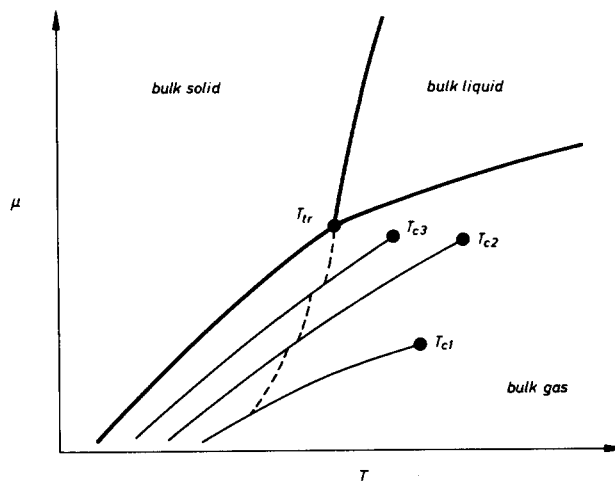

FIG. 10. Possible phase diagram for a system which exhibits layering transitions in liquid-like adsorbed films. Thick solid lines denote bulk first order transitions, and thin solid lines denote layering transitions; the latter end at critical points T_{cj}. Dashed lines indicate film melting transitions—the melting point of an adsorbed film may lie substantially below the bulk triple point. Adsorption isotherms correspond to the vertical approach from below to a bulk solid-gas or a liquid-gas phase boundary. Only three layering transitions are sketched here; in general, there may be more (see the text).

O_2 on graphite also exhibits layering transitions[37,59] above $T_{tr} = 54.35$ K. Adsorption isotherm measurements[37] found monolayer to bilayer and bilayer to trilayer transitions at temperatures up to 60 K, and diffraction experiments[60] indicate melting of the multilayers occurs below T_{tr}. Ellipsometric studies[59] found seven steps for T slightly above T_{tr} and ~ 6 at $T = 60.2$ K. It is possible that T_{cj} may be roughly constant ~ 60 K for these few layers. Other physisorbed systems exhibit layering critical points but these are often below T_{tr}; however, ethane on graphite is another recently investigated case[63] where several transitions with critical points above T_{tr} have been observed.

It is likely that experiment has now reached the stage where its results can help the theorist make intelligent selections from the many theoretical variations that are possible.

As a final remark we should mention that the adsorption Γ is not the only useful order parameter for describing phase transitions in confined fluids. In planar geometry (a slit-like pore) the solvation force

$$f = -\frac{1}{A}\left(\frac{\partial \Omega}{\partial H}\right)_{\mu,T,A} - p,$$

where A is the area and H is the separation of the walls, is equally valid. Monitoring $f(H)$ at fixed μ and T is complementary[61] to monitoring $\Gamma(\mu)$ at fixed H and T. First order transitions of the fluid are characterized by discontinuous jumps in f at a particular H. The magnitude of the jump $f_\alpha - f_\beta$ is given by[61]

$$f_\alpha - f_\beta = (\Gamma_\beta - \Gamma_\alpha)\left(\frac{\partial \mu_t}{\partial H}\right)_T,$$

where α and β refer to the two phases coexisting at μ_t, the chemical potential of the transition. Reference to Fig. 9 suggests that the low-order layering transitions could be identified (in simulations, say) by calculating $f(H)$ at small H. Whether measurements of solvation forces using crossed mica cylinders immersed in gases could provide a means of

studying such transitions remains to be seen.

After the completion of this work we received a preprint[62] from the Cornell group reporting results of SDA calculations and computer simulations for capillary condensation in cylindrical pores. As their results refer to weaker wall–fluid potentials and higher temperatures than those considered here, they did not observe layering transitions.[62]

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[45] It appears common practice amongst experimentalists to assume that layering transitions occur at relative pressures determined by an inverse cube law: $\ln(p_j/p_{sat}) \sim -j^{-3}$ (see, for example, Ref. 29). This corresponds to Eq. (9) for the specific case of van der Waals walls, $V(z) \sim -z^{-3}$.

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[51] This high degree of structure provides the possibility of packing transitions between liquid states as the pore radius is changed, allowing different numbers of layers to pack into the pore. Although packing effects may induce oscillations in the capillary coexistence curve within the SDA theory (Ref. 12), simulation results (Ref. 49) suggest that first order transitions are only possible when the wall itself has an underlying lattice structure.

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[53] This is an artifact of mean-field theory, which permits first order transitions to persist in systems which are pseudo-one dimensional. See also Ref. 62. For fluids confined between parallel walls (a capillary slit) capillary condensation will occur as the wall separation $\to 0$, provided $T < T_c^{2d}$, the two-dimensional bulk critical temperature (Ref. 12).

[54] The effects of curvature on the capillary condensation and prewetting transitions in pores are discussed in Ref. 11. Similar consideration will apply for layering transitions.

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