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## Liquids at interfaces: what can a theorist contribute?

R Evans and A O Parry

H H Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, UK

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**Abstract.** This lecture reviews some recent theoretical and computer simulation studies of simple (atomic) fluids adsorbed at structureless substrates. Emphasis is placed on phase transitions, especially the various types of wetting transition. Criticality is associated with capillary-wave-like fluctuations in a continuously growing wetting film. This is of a subtle nature, which is best understood in terms of the pairwise correlation function of the fluid. Other surface phase transitions, such as prewetting and layering, occur out of bulk coexistence. Theory suggests that for sufficiently attractive substrates a sequence of first-order transitions, corresponding to the growth of new adsorbed *liquid* layers, should occur as the pressure of the bulk gas increases towards saturation at temperatures not too far above the bulk triple point. The extent to which such behaviour is found in adsorption experiments is discussed. We also argue that a simple fluid confined between two parallel hard-walls can exhibit surprisingly rich phase equilibria.

### 1. Introduction

One only has to weigh some recent summer school proceedings [1, 2, 3] and an edited volume [4] to realize that the subject of liquids at interfaces is enormous. Even if attention is restricted to equilibrium properties one finds that there has been a huge growth of interest in this area during the last decade. Significantly, many physicists have entered what was traditionally regarded as a part of physical chemistry. Clearly it would be inappropriate to attempt to give a detailed review, or even an overview, of the whole subject in this lecture. Since many speakers in various Symposia will describe experimental work on a wide variety of fluid interfaces and there will be talks on the theory of interfaces in complex systems such as polymers and amphiphilics, perhaps it is appropriate to present some theoretical work pertaining to extremely simple interfacial systems.

We will consider atomic (argon-like) classical fluids near solid substrates, i.e. we are concerned with the nature of the substrate–fluid interface for a gas or liquid in equilibrium with an inert spectator phase. The solid substrate is deemed to be rigid on relevant time scales and its boundary is deemed to be smooth and planar on relevant length scales. Such a spectator phase exerts an external potential  $V(\mathbf{r})$  on atoms in the fluid and acts as a geometrical constraint. The microscopic structure, thermodynamic properties and phase equilibria of the system are given by solving the statistical mechanics of the inhomogeneous fluid. Whether such a model of the substrate is realistic depends on the particular application but most theories of adsorption start with the above assumptions [5] and go on to specify  $V(\mathbf{r})$  appropriate to the experimental situation. Here we ignore

all effects associated with the atomic structure of the substrate and specialize to external potentials for which  $V(\mathbf{r}) \equiv V(z)$ , where  $z$  is measured normal to the substrate. Thus, we exclude from the outset the rich physics associated with commensurate and incommensurate (floating) surface phases. Moreover, we restrict ourselves to *fluid* phases so that the average one-body density  $\rho(\mathbf{r}) \equiv \rho(z)$ . In spite of these constraints, a variety of phenomena do occur which are especially interesting from the viewpoint of phase transitions. As is often the case in statistical physics, idealized models can exhibit surprising features and provide new insight into fundamental issues.

The paper is arranged as follows: in section 2 we recall some of the key results in the statistical mechanics of inhomogeneous fluids and apply these to the case of a fluid near planar hard-walls. For a single hard-wall the phenomenon of complete drying by gas of the wall-liquid interface occurs. This is an example of surface criticality in that long-ranged correlations develop at the interface and manifest themselves in a striking fashion in moments of the pairwise correlation function. When the liquid is confined between two hard-walls capillary-evaporation, which corresponds to the shifted bulk phase transition, occurs out of bulk coexistence. For sufficiently small wall separations the evaporation transition ends at a capillary-critical point which exhibits special features. By allowing the substrate potential to have an attractive as well as a repulsive component continuous wetting and drying transitions can occur when the fluid remains at bulk two-phase coexistence. Recent results from simulation and theory for such transitions in three dimensions are reviewed briefly in section 3. The accompanying critical fluctuations have no direct counterpart in bulk and lead to novel behaviour of the pairwise correlation function in the interface. In section 4 we mention some recent work on the prewetting and layering transitions. Adsorption at a strongly attractive substrate is sometimes characterized by a sequence of discrete layering transitions, each of which corresponds to the growth of a new, dense liquid layer, as the gas pressure is increased towards saturation. The extent to which such behaviour is found in continuum theories and in experiment and the nature of the critical points of the transitions is discussed. Section 5 contains concluding remarks.

## 2. Fluids near hard-walls

### 2.1. Sum rules for inhomogeneous fluids

We consider the fluid to be in contact with a reservoir with chemical potential  $\mu$  and temperature  $T$ . The hierarchy of distribution functions is generated by successive functional differentiation [6, 7] of the grand potential  $\Omega$  with respect to  $u(\mathbf{r}) \equiv \mu - V(\mathbf{r})$  at fixed  $T$ :

$$\delta\Omega/\delta u(\mathbf{r}) = -\rho(\mathbf{r}) \quad (1a)$$

and

$$\beta^{-1} \delta\rho(\mathbf{r}_1)/\delta u(\mathbf{r}_2) = G(\mathbf{r}_1, \mathbf{r}_2) \equiv \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)h(\mathbf{r}_1, \mathbf{r}_2) + \delta(\mathbf{r}_1 - \mathbf{r}_2)\rho(\mathbf{r}_1). \quad (1b)$$

Here  $\beta^{-1} \equiv k_B T$ ,  $\rho(\mathbf{r})$  is the average one-body density and  $G(\mathbf{r}_1, \mathbf{r}_2)$ , the density-density correlation function, is related to the total pairwise distribution function  $h$ . For a bulk,

homogeneous fluid  $h(\mathbf{r}_1, \mathbf{r}_2)$  reduces to  $g(|\mathbf{r}_1 - \mathbf{r}_2|) - 1$ , where  $g(r)$  is the usual radial distribution function. Manipulation of (1b) yields two key equations:

$$-\rho'(z_1) = \beta \int_{-\infty}^{\infty} dz_2 V'(z_2) G_0(z_1, z_2) \quad (2)$$

where the prime denotes differentiation with respect to  $z$ , and

$$\chi(z_1) \equiv \frac{1}{\beta \rho(z_1)} \left( \frac{\partial \rho(z_1)}{\partial \mu} \right)_T = \frac{1}{\rho(z_1)} \int_{-\infty}^{\infty} dz_2 G_0(z_1, z_2). \quad (3)$$

$\chi(z)$  is the (dimensionless) local susceptibility of the fluid in a fixed external potential  $V(z)$ . The zeroth transverse moment  $G_0$  is defined by the transverse Fourier transform:

$$\begin{aligned} G(z_1, z_2; \mathbf{Q}) &\equiv \int d\mathbf{R} \exp(i\mathbf{Q} \cdot \mathbf{R}) G(z_1, z_2; \mathbf{R}) \\ &= G_0(z_1, z_2) + Q^2 G_2(z_1, z_2) + \dots \end{aligned} \quad (4)$$

with  $G(z_1, z_2; \mathbf{R}) \equiv G(\mathbf{r}_1, \mathbf{r}_2)$  i.e.  $\mathbf{R}$  and  $\mathbf{Q}$  are transverse vectors, parallel to the substrate and  $R^2 = (x_1 - x_2)^2 + (y_1 - y_2)^2$  in three dimensions. Equation (3) is merely the generalisation to inhomogeneous fluids of the well-known compressibility sum rule.  $G_2$ , the second transverse moment of  $G$ , enters the formula for the surface tension  $\sigma$  of the fluid in the external potential:

$$\sigma = -\beta \int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} dz_2 V'(z_1) V'(z_2) G_2(z_1, z_2) \quad (5)$$

which is equivalent [7] to the Triezenberg–Zwanzig [8] formula. All of these equations are valid for arbitrary external potentials; they simplify considerably in the case of a hard-wall with

$$V_{\text{hw}}(z) = \begin{cases} \infty & z < 0 \\ 0 & z > 0. \end{cases} \quad (6)$$

Using the results that  $\rho(z) \exp(\beta V_{\text{hw}}(z))$  is continuous and  $(d/dz) \exp(-\beta V_{\text{hw}}(z)) = \delta(z)$ , equation (2) integrates to

$$G_0(z, 0) = \rho'(z) \quad z > 0 \quad (7)$$

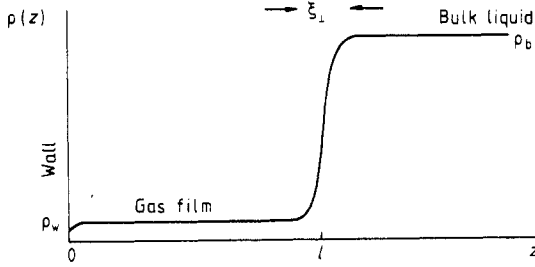
and (3) gives

$$\chi(0^+) \equiv (1/\beta \rho_w) (\partial \rho_w / \partial \mu)_T = \rho_b / \rho_w \quad (8)$$

where  $\rho_w \equiv \rho(0^+)$  is the density at the wall and  $\rho_b = \rho(\infty)$  is the density of the bulk fluid far from the wall. Integration of (5) yields

$$\beta \sigma = -G_2(0^+, 0^+) \quad (9)$$

i.e. the second moment of  $G$  evaluated for both particles at wall contact is proportional to the total surface tension of the hard-wall fluid interface. Equations (7) and (9) were



**Figure 1.** Schematic density profile for a liquid near a hard-wall. In the limit  $\mu \rightarrow \mu_{\text{sat}}^+$  the thickness  $l$  of the intruding film of gas and the interfacial roughness  $\xi_{\perp}$  both diverge.

derived by Henderson and van Swol [9], while (8) is simply a consequence of the familiar result for the contact density

$$\rho_w = \beta p \quad (10)$$

where  $p$  is the pressure of the bulk fluid. This set of results is not especially striking until one recognises that complete drying occurs at the wall-liquid interface.

## 2.2. Complete drying and its repercussions

When the bulk fluid is a dense liquid with  $\mu > \mu_{\text{sat}}(T)$ , the chemical potential at bulk coexistence, the density profile  $\rho(z)$  exhibits oscillations arising from packing effects near the wall. However, on reducing  $\delta\mu \equiv \mu - \mu_{\text{sat}}$  towards zero the oscillations disappear and a film of low density ‘gas’ intrudes between the wall and the bulk liquid. This is illustrated in figure 1. The thickness  $l$  of the film diverges as  $l \sim (\delta\mu)^{-\beta_s}$  in the limit  $\delta\mu \rightarrow 0$ , and the gas-liquid part of the interface is removed further from the wall exposing more of the wall-gas interface. For a three-dimensional fluid governed by van der Waals forces the exponent  $\beta_s = \frac{1}{3}$ , whereas for interatomic potentials of finite range  $\beta_s = 0$ , corresponding to logarithmic growth. At bulk coexistence,  $\mu = \mu_{\text{sat}}^+$ , the wall-liquid interface is a composite of the wall-gas (subscript wg) and the gas-liquid (subscript lg) interface with surface tension  $\sigma_{\text{wl}} = \sigma_{\text{wg}} + \sigma_{\text{lg}}$ ; the contact angle  $\theta$  in Young’s equation  $\sigma_{\text{wg}} = \sigma_{\text{wl}} + \sigma_{\text{lg}} \cos \theta$  is equal to  $\pi$ . This phenomenon of complete drying, or wetting by gas, was predicted by the simple density functional theory of Sullivan [10, 11] and was confirmed using more sophisticated versions [12–14]. The erosion of oscillations was found in some early computer simulations [15, 16] of liquids at hard-walls and the growth of thick drying films was observed in extensive simulations of a square-well liquid [7]. Complete drying is expected to occur at all temperatures for which bulk coexistence occurs.

What then are the implications of (7)–(10) in the limit  $\mu \rightarrow \mu_{\text{sat}}^+$ ? Equation (10) ensures that the density at contact  $\rho_w < \rho_g$ , the density of the coexisting gas at a given (low) temperature, consistent with the idea that drying should occur. That the local susceptibility at the wall  $\chi(0^+)$  should depend on  $\rho_l$ , the density of the bulk liquid that is macroscopically far from the wall, is the surprising feature in (8). Equation (7) is also somewhat startling since it states that  $G_0(l, 0)$  would be non-zero in the limit  $l \rightarrow \infty$  provided the density derivative in the edge of the film  $\rho'(l)$  remained non-zero in this limit. Indeed, this is the case for dimension  $d > 3$ , where mean-field theory is valid.

Capillary-wave arguments predict  $\rho'(l) \sim \xi_{\perp}^{-1}$  as  $\delta\mu \rightarrow 0$ , with the interfacial roughness  $\xi_{\perp}$ , which determines the width of the depinning liquid–gas interface, remaining finite for  $d > 3$  but diverging as  $(-\ln \delta\mu)^{1/2}$  in  $d = 3$ . Thus,  $G_0(l, 0)$  is predicted to vanish only very slowly, as  $(-\ln \delta\mu)^{-1/2}$ , in the approach to complete drying in  $d = 3$ . Perhaps the most striking result is that emerging from (9). In the limit  $\mu \rightarrow \mu_{\text{sat}}^+$  we find  $G_2(0^+, 0^+) = -\beta(\sigma_{\text{wg}} + \sigma_{\text{lg}})$ ; the second moment evaluated at the wall depends on the tension  $\sigma_{\text{lg}}$  of the liquid–gas interface that is macroscopically far from the wall. In order to appreciate the significance of these results it is useful to consider [17] the limit  $\mu \rightarrow \mu_{\text{sat}}^-(T)$  where now the bulk fluid is gas. The density profile is simply that of the wall–gas interface so that  $\rho_w$  and  $G_0(0^+, 0^+)$  are the same as in the limit  $\mu \rightarrow \mu_{\text{sat}}^+$ . However,  $\chi(0^+)$  is proportional to  $\rho_g$ , rather than  $\rho_l$ , and  $G_2(0^+, 0^+) = -\beta\sigma_{\text{wg}}$ . Note that  $\sigma_{\text{lg}} \gg \sigma_{\text{wg}}$  at low temperatures.

The dramatic behaviour of the correlation functions at complete drying predicted by the formal sum rules have been confirmed, at the mean-field level, in explicit analysis [17] of the Sullivan version of density functional theory. This analysis reveals the rather complex structure of  $G(z_1, z_2; Q)$  in a drying film. In addition to the (capillary-wave driven) small- $Q$  Wertheim behaviour [18] expected in the edge of the film:

$$G(z_1, z_2; Q) \sim G_0(z_1, z_2)(1 + \xi_{\parallel}^2 Q^2)^{-1} \quad z_1, z_2 \sim l \quad (11)$$

where the transverse correlation length  $\xi_{\parallel} = [-G_2(l, l)/G_0(l, l)]^{1/2}$  and

$$G_0(z_1, z_2) \sim \rho'(z_1)\rho'(z_2)\xi_{\parallel}^2/\beta\sigma_{\text{lg}} \quad z_1, z_2 \sim l$$

there is a separate coherent fluctuation of the whole film, present for all  $z_1$  and  $z_2$ . This contribution involves the total tension  $\sigma$  and has the form

$$G(z_1, z_2; Q) \sim \rho'(z_1)\rho'(z_2)(\rho'_w + \beta\sigma Q^2)^{-1} \quad (12)$$

at small  $Q$ . In the limit  $z_1, z_2 \rightarrow 0$  the capillary wave contribution (11) is damped to zero leaving (12), which is sufficient to account for the sum rule predictions (7) and (9).

It is important to recognise that the curious predictions of (8) and (9) at complete drying cannot be attributed to interfacial roughness. Although capillary-wave fluctuations lead to a diverging transverse correlation length  $\xi_{\parallel} \sim (\delta\mu)^{-\nu_{\parallel}}$ , with  $\nu_{\parallel} = (1 + \beta_s)/2$ , in *all* dimensions  $\xi_{\perp}$ , which in terms of  $\xi_{\parallel}$ , is given by [19]

$$\xi_{\perp}^2 = \begin{cases} \text{finite} & d > 3 \\ \omega \xi_b^2 \ln(\xi_{\parallel}/\xi_b)^2 & d = 3 \\ \text{constant } \xi_{\parallel}^{3-d} & d < 3 \end{cases} \quad (13)$$

where  $\xi_b$  is the bulk (gas) correlation length and  $\omega \equiv (4\pi\beta\sigma_{\text{lg}}\xi_b^2)^{-1}$ , diverges for  $d \leq 3$  only. By contrast (8) and (9) are valid for all dimensions. The sum rule predictions reflect the structure of  $G(z_1, z_2; Q)$  in the drying film, rather than any interfacial wandering. We return to this issue in section 3 where we consider correlation functions at wetting and drying transitions for more general potentials.

### 2.3. Sum rules for a fluid confined between two hard-walls

Suppose that the fluid is confined between two identical parallel substrates which have (infinite) surface area  $A$  but which are separated by a finite distance  $L$ . The system is

open so that atoms can pass freely in and out of a reservoir at fixed  $\mu$  and  $T$ . An atom in the confined fluid experiences an external potential

$$V(z; L) = V_s(z) + V_s(L - z) \quad (14)$$

where  $V_s$  is the potential due to a single substrate. Confinement gives rise to the solvation force  $f(L)$ . This is defined [6] as an excess pressure:

$$f = -(1/A)(\partial\Omega/\partial L)_{\mu,T} - p \quad (15)$$

where  $p(\mu, T)$  is the pressure of the fluid in the reservoir. Clearly  $f \rightarrow 0$  as  $L \rightarrow \infty$ . Using (1a) and (14)  $f$  can be re-expressed [20, 21] as

$$f = -\int_{-\infty}^{\infty} dz \rho(z) \frac{\partial V(z; L)}{\partial L} - p = -\int_{-\infty}^{\infty} dz \rho(z) V'_s(z) - p \quad (16)$$

where we have used the property  $\rho(L - z) = \rho(z)$ . Another important result [21] follows using (1b):

$$\left(\frac{\partial\rho(z_1)}{\partial L}\right)_{\mu,T} = \int d\mathbf{r}_2 \frac{\delta\rho(\mathbf{r}_1)}{\delta u(\mathbf{r}_2)} \left(\frac{\partial u(\mathbf{r}_2)}{\partial L}\right)_{\mu} = -\beta \int_{-\infty}^{\infty} dz_2 G_0(z_1, z_2) V'_s(L - z_2). \quad (17)$$

As was the case for a single substrate these results simplify considerably when  $V_s = V_{hw}$ . The solvation force reduces to [21]

$$f = \beta^{-1}(\rho_{w,L} - \rho_{w,\infty}) \quad (18)$$

where  $\rho_{w,L} \equiv \rho(0^+) \equiv \rho(L^-)$  is the contact density for finite wall separation and  $\rho_{w,\infty}$  is the corresponding quantity for a single wall,  $L = \infty$ , with the fluid maintained at the same  $\mu$  and  $T$ . Formula (18) provides an elegant means of understanding the origin of the oscillatory solvation force that occurs for small separations. When the fluid is a dense liquid  $\rho_{w,L}$  will reflect the packing of the atoms between the two walls. If  $L \geq$  an integral number of atomic diameters  $\rho_{w,L}$  is significantly larger than the unconfined density  $\rho_{w,\infty}$  and  $f$  is large and positive. When  $L$  is out of registry with the packing  $\rho_{w,L} < \rho_{w,\infty}$  and negative  $f$  results. As  $L$  increases the packing effects become less pronounced and  $f \rightarrow 0$ . Although there is no direct counterpart of (18) for arbitrary substrate potential, similar considerations apply [6] and the genesis of oscillatory solvation forces in liquids is readily understood via (16).

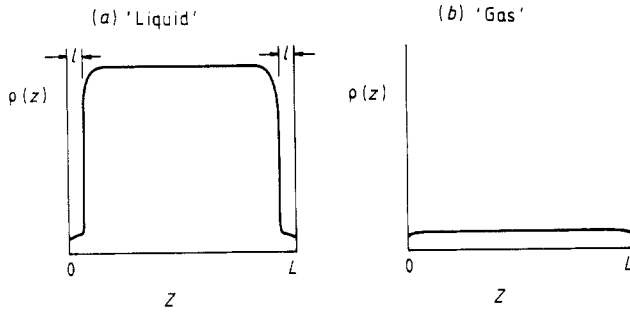
The derivative of  $f$  with respect to  $L$  is proportional to the zeroth moment  $G_0$ , evaluated with a particle at each (hard) wall. From (17) and (18)

$$(\partial f/\partial L)_{\mu,T} = \beta^{-1}(\partial\rho_{w,L}/\partial L)_{\mu,T} = \beta^{-1}G_0(0, L). \quad (19)$$

The local susceptibility at each wall depends on  $(\partial f/\partial\mu)_{L,T}$ , i.e.

$$\chi(0^+) = \chi(L^-) \equiv (1/\beta\rho_{w,L})(\partial\rho_{w,L}/\partial\mu)_{L,T} = (1/\rho_{w,L})[(\partial f/\partial\mu)_{L,T} + \rho_b]. \quad (20)$$

These last two results are important at a capillary critical-point, where both derivatives of  $f$  are divergent. In order to understand how such a critical point can arise it is necessary to consider the phase equilibria of a fluid confined by hard-walls. Complete wetting and



**Figure 2.** Schematic density profiles for the two phases that coexist at a point of capillary evaporation for a fluid confined between two hard-walls separated by a distance  $L$ . (a) 'Liquid' with drying films of thickness  $l$ . (b) 'Gas'. The chemical potential  $\mu_{\text{co}}(T)$  is slightly greater than  $\mu_{\text{sat}}(T)$ —see text.

wetting transitions are precluded as these necessitate films of macroscopic thickness, which cannot develop for finite  $L$ . Nevertheless, interesting phase behaviour does occur.

#### 2.4. Capillary evaporation and criticality

We begin by recalling the Kelvin equation [22, 23] for the shift of the first-order liquid-gas transition arising from confinement at fixed  $T$  below the bulk critical temperature  $T_{\text{c},\infty}$ . This predicts coexistence between 'liquid' and 'gas' at a chemical potential  $\mu_{\text{co}}$  given by

$$\Delta\mu_{\text{co}} \equiv \mu_{\text{sat}} - \mu_{\text{co}} = 2(\sigma_{\text{wg}} - \sigma_{\text{wl}})/L(\rho_{\text{l}} - \rho_{\text{g}}). \quad (21)$$

If  $\sigma_{\text{wg}} > \sigma_{\text{wl}}$ , i.e. the walls favour liquid and  $\cos \theta > 0$ , capillary condensation of dilute 'gas' to a dense 'liquid', filling the slit occurs at  $\mu_{\text{co}} < \mu_{\text{sat}}$ . The less familiar situation occurs when the walls favour gas so that  $\sigma_{\text{wg}} < \sigma_{\text{wl}}$  and  $\cos \theta < 0$ , then capillary *evaporation* of the dense 'liquid' to a dilute 'gas' phase takes place for  $\mu_{\text{co}} > \mu_{\text{sat}}$ , i.e. the fluid in the reservoir is a liquid. It is the second situation which pertains with hard-walls since we have seen  $\cos \theta = -1$  in this case. Figure 2 shows the density profiles of the two coexisting phases. For sufficiently large  $L$  and, therefore, small  $\Delta\mu_{\text{co}}$ , drying films of thickness  $l$  will develop in the 'liquid' phase at coexistence. However, we expect  $l$  to be small ( $\sim 1$  atomic diameter), even for  $L \sim 40$  diameters [14].

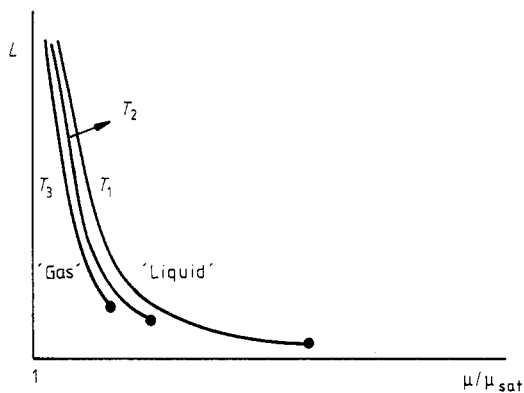
The Kelvin equation (21) is exact in the limit  $L \rightarrow \infty$ . Density functional results [14] for a model fluid between two hard-walls indicate that it remains accurate down to  $L \sim 20$  atomic diameters for  $T/T_{\text{c},\infty} = 0.7$ . For  $L$  less than a certain critical value  $L_{\text{c}}$  there is no phase transition and only one phase is present in the slit; the line of capillary evaporation ( $\mu_{\text{co}}, L$ ) ends a critical point ( $\mu_{\text{c}}, L_{\text{c}}$ ), as sketched in figure 3. Other critical points will occur for different temperatures giving rise to a line of capillary critical points in  $(\mu, L, T)$  space [22].

The thermodynamics of capillary condensation and critical points has been discussed in some detail [24]. Here we merely summarize the features that are relevant to the hard-wall system. Capillary evaporation is signalled by a discontinuous fall in the adsorption

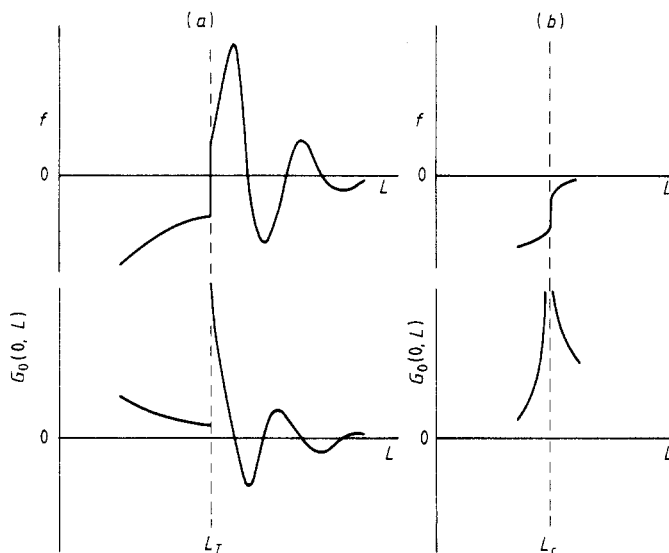
$$\Gamma = \int_0^L dz (\rho(z) - \rho_{\text{b}}) \quad (22)$$

from a 'liquid'-like value to a 'gas' like value as  $L$  is reduced at fixed  $\mu$  or as  $\mu$  is reduced





**Figure 3.** Lines of capillary evaporation  $\mu_{co}(L)$  plotted (schematically) for different temperatures,  $T_3 > T_2 > T_1$ . These lines terminate in capillary critical points  $(\mu_c, L_c, T)$  which can be regarded as shifted bulk critical points. As  $T \rightarrow T_{c,z}$  the critical wall separation is given by  $T_{c,z} - T \sim L_c^{-1/\nu}$ , where  $\nu \approx 0.63$  is the bulk correlation length exponent.



**Figure 4.** (a) The solvation force  $f(L)$  for a liquid undergoing capillary evaporation at fixed temperature  $T$  and  $\mu < \mu_c(T)$ , and the corresponding plot of the zeroth moment  $G_0(0, L)$ . It is assumed that the transition occurs at a sufficiently small wall separation  $L_T$  that  $f(L)$  is oscillatory in the liquid phase for  $L > L_T$ . (b) The behaviour of  $f(L)$  and  $G_0(0, L)$  at a capillary critical point. As  $L$  is increased at fixed  $\mu_c(T)$   $(\partial f/\partial L)$  and  $G_0(0, L)$  diverge at the critical value  $L_c$ . At low temperatures  $L_c$  may be sufficiently small that  $f(L)$  is oscillatory for  $L > L_c$ .

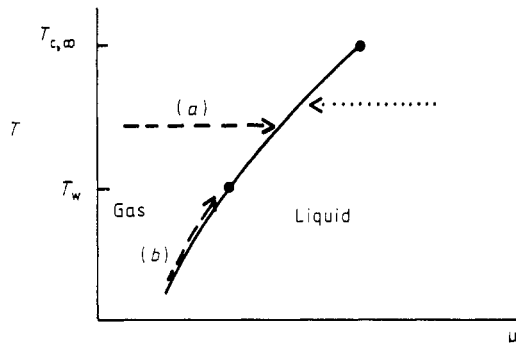
at fixed  $L$ . The solvation force also exhibits a discontinuity—see figure 4(a). A critical point is characterized by  $(\partial\Gamma/\partial\mu)_{T, L_c}$  or  $(\partial\Gamma/\partial L)_{T, \mu_c}$  diverging. Alternatively, one can require  $(\partial f/\partial\mu)_{T, L_c}$  or  $(\partial f/\partial L)_{T, \mu_c}$  to diverge—see figure 4(b). We now see that sum rules (19) and (20) make certain explicit predictions regarding the microscopic nature

of criticality for the particular case of hard-walls. Equation (20) indicates that the surface susceptibility  $\chi(0^+)$  diverges as  $(\partial f/\partial\mu)_T$ , while (19) implies that the zeroth moment  $G_0(0, L)$  is also divergent, as illustrated in figure 4(b). The latter result is quite striking, once one recognises that  $L_c$  can be made arbitrarily large by increasing  $T$  towards  $T_{c,\infty}$ . The former becomes significant when we realize that the susceptibility at mid-point  $\chi(L/2)$  diverges as  $(\partial\Gamma/\partial\mu)_T$ ; this follows directly from (22), assuming the integral over the finite slit does not introduce any additional singularities.

The implication is that the fluid manifests its criticality throughout the slit, i.e. there is a single transverse correlation length  $\xi_{\parallel}$  characterizing all relevant fluctuations. Since the correlation length can only diverge parallel to the substrates and the order-parameter for evaporation is simply the difference in  $\Gamma$  (or in  $f$ ) between the two phases, capillary-criticality, for any type of substrate, should lie in the two-dimensional Ising universality class. Thus, at fixed  $T$  and  $L = L_c$ , the adsorption should have the form  $\Gamma - \Gamma_c \sim |\mu - \mu_c|^{1/\delta}$  and, at fixed  $T$  and  $\mu = \mu_c$ , the solvation force should vary as  $f - f_c \sim |L - L_c|^{1/\delta}$ , with critical exponent  $\delta = 15$ , the Onsager value. This is the behaviour sketched in figure 4(b). The line of critical points referred to above is a line of Onsager critical points.

### 3. Criticality at wetting transitions

In this section we consider a fluid near a single planar substrate that exerts an attractive, as well as a repulsive, external potential on the atoms of the fluid. Various types of surface phase transitions can occur for such a system—see the reviews [25–27]. The wetting transition is the transition from partial to complete wetting of the interface between the substrate, or any spectator phase, and a fluid phase by a second fluid phase that coexists with the first. The transition is often induced by varying the temperature  $T$ , staying along the coexistence curve. For  $T < T_w$  the thickness  $l$  of the film of intruding phase is finite, whereas for  $T \geq T_w$   $l$  is of macroscopic extent.  $l$  may diverge discontinuously (first-order transition) or continuously; then the transition is termed ‘critical wetting’. If the bulk fluid, far from the substrate, is gas at  $\mu = \mu_{\text{sat}}^-$  partial wetting by the liquid, for  $T < T_w$ , corresponds to contact angle  $\theta > 0$  and complete wetting, for  $T \geq T_w$ , has  $\theta = 0$ . At a drying transition, on the other hand, the bulk is liquid at  $\mu = \mu_{\text{sat}}^+$  and partial wetting by gas, for  $T < T_D$ , has  $\theta > 0$  whereas complete wetting by gas (drying), for  $T \geq T_D$ , has  $\theta = \pi$ . In a complete wetting regime  $l$  diverges continuously as  $\mu$  approaches  $\mu_{\text{sat}}(T)$ . (The approach to complete drying at a hard-wall, discussed in section 2.2, was a particular example of this latter behaviour.) Mean-field theories [25, 26] for continuum fluids and lattice-gas models predict both first-order and critical wetting transitions: which type occurs depends on the choice of substrate–fluid and fluid–fluid potential functions. Computer simulations for continuum fluids in  $d = 3$  have determined first-order wetting and drying transitions. van Swol and Henderson [28] studied, using molecular dynamics, a square-well liquid at a hard-wall with a weakly attractive square-well portion of depth  $\varepsilon$ . By varying  $\varepsilon$ , at fixed temperature, they observed a weak first-order drying transition in which fluctuations play a major role [29]. Sikkenk *et al* [30] performed massive simulations, using the Delft Molecular Dynamics Processor, for a (truncated) Lennard-Jones fluid adsorbed at a ‘live’ substrate composed of Lennard-Jones atoms. By varying the ratio of the well depths for substrate–fluid and fluid–fluid interatomic potentials they found evidence for first-order wetting and drying transitions in their system. This was confirmed in later simulations [31] which made a



**Figure 5.** The two types of wetting transition. Complete wetting from off-bulk coexistence corresponds to path (a)  $\mu \rightarrow \mu_{\text{sat}}(T)$  for  $T > T_w$ . Critical wetting is associated with path (b) where the wetting transition temperature  $T_w$  is approached along bulk coexistence,  $\mu = \mu_{\text{sat}}(T)$  (full curve). Complete drying (dotted line) occurs when the bulk phase is liquid and  $\mu \rightarrow \mu_{\text{sat}}(T)$ .

direct determination of contact angles. We are not aware of any simulation for a continuum fluid that yields a critical wetting transition in  $d = 3$ . Some early Monte Carlo simulations [32] for lattice-gas models in  $d = 3$  found signatures of a first-order transition. Recent, more systematic, Monte Carlo studies [33] for a nearest-neighbour lattice gas with a contact surface field  $h_1$  showed that first-order, critical and tricritical wetting transitions do occur in such models. Experimental work on wetting transitions is reviewed in [25–27]. As yet there is no direct evidence for any type of transition occurring at a temperature above the bulk triple point  $T_{\text{tr}}$  in a single-component fluid at a substrate. There is ample evidence for the phenomenon of triple-point wetting, whereby complete wetting of the substrate–gas interface occurs exactly at  $T_{\text{tr}}$ ; for  $T \geq T_{\text{tr}}$  the substrate is completely wet by liquid whereas for  $T < T_{\text{tr}}$  solid films of finite thickness are adsorbed.

Our present interest concerns the nature of the critical behaviour associated with the continuous growth of a wetting film. As indicated above we can consider two different thermodynamics paths—see figure 5. Path (a) corresponds to complete wetting from off bulk coexistence at  $T \geq T_w$ , where the relevant control field is  $\mu_{\text{sat}}(T) - \mu$ . Path (b) denotes the approach to a critical wetting transition, where the control field is  $T_w - T$  at  $\mu = \mu_{\text{sat}}$ . As was mentioned for the simulation studies, it is often more convenient to fix  $T$  and vary the strength  $\varepsilon$  of the attractive substrate–fluid potential to induce critical wetting. The relevant field is  $\varepsilon_w(T) - \varepsilon \equiv \delta\varepsilon$ , which is equivalent, thermodynamically, to  $T_w - T$ . On both paths the interfacial profile would have the form shown in figure 1 (for drying) so that the film thickness diverges as

$$l \sim |\delta\mu|^{-\beta_s}(\text{complete}) \quad l \sim |\delta\varepsilon|^{-\beta_s}(\text{critical}).$$

Capillary-wave-like fluctuations develop in the liquid–gas edge of the films leading to a diverging transverse correlation length

$$\xi_{\parallel} \sim |\delta\mu|^{-\nu_{\parallel}}(\text{complete}) \quad \xi_{\parallel} \sim |\delta\varepsilon|^{-\nu_{\parallel}}(\text{critical}).$$

The same fluctuations give rise to a singular contribution to the substrate–fluid interfacial tension (or excess grand potential)

$$\sigma^{\text{sing}} \sim |\delta\mu|^{2-\alpha_s}(\text{complete}) \quad \sigma^{\text{sing}} \sim |\delta\varepsilon|^{2-\alpha_s}(\text{critical}).$$

Although the same notation is employed for the critical exponents their values are

different for the two different paths. Moreover, their values depend on the form of the substrate–fluid and fluid–fluid attractive potentials. For algebraically decaying potentials the upper critical dimension  $d_c < 3$  [26, 27] so that the critical exponents for real systems, governed by van der Waals forces, should be described correctly by mean-field theories and the values are known, e.g.  $\beta_s = \frac{1}{3}$  for complete wetting, as quoted in section 2.2. Fluctuation effects are insufficient, in  $d = 3$ , to alter the critical exponents from their mean-field values when the substrate–fluid or fluid–fluid potential is long-ranged. For potentials that are exponentially decaying or of finite range, as one would usually employ in computer simulations,  $d_c = 3$  for both complete and critical wetting. The incorporation of fluctuation effects has been tackled within the context of approximate renormalisation group (RG) calculations for effective interfacial Hamiltonians of the type

$$H\{l\} = \int d\mathbf{R} \left[ \frac{1}{2} \sigma_{\text{lg}} (\nabla l(\mathbf{R}))^2 + U(l(\mathbf{R})) \right] \quad (23)$$

where  $U(l)$  represents the interaction potential for the fluctuating film thickness  $l(\mathbf{R})$ . These predict [34] that the exponents for complete wetting in  $d = 3$  retain their mean-field values ( $\beta_s = O(\ln)$ ,  $\nu_{\parallel} = \frac{1}{2}$  and  $\alpha_s = 1$ ) but the amplitudes of  $l$  and  $\xi_{\parallel}$  are dependent on the parameter  $\omega \equiv (4\pi\beta\sigma_{\text{lg}}\xi_b^2)^{-1}$  (see (13)) which measures the interfacial stiffness. More significantly, for critical wetting, RG predicts that the critical exponents should be non-universal, i.e. dependent on  $\omega$  in  $d = 3$ , when all potential functions are short-ranged. Mean-field gives  $\beta_s = O(\ln)$ ,  $\nu_{\parallel} = 1$  and  $\alpha_s = 0$ . Monte Carlo simulations [35] for the same interfacial Hamiltonian find values of  $\nu_{\parallel}$  that are consistent with the RG results, at least for the small values of  $\omega$  investigated. Thus, fluctuations would seem to play a major role at the marginal dimension  $d = 3$ . The situation is confused, however, by the Monte Carlo results of Binder and Landau [33, 36], for the  $d = 3$  Ising model with contact surface field, which appear to yield only the mean-field value  $\nu_{\parallel} = 1$  for a situation where  $\omega$  was estimated to be about 1 and RG for (23) would predict  $\nu_{\parallel} \sim 6$ . Various explanations have been proposed to explain the discrepancy, including the idea that the asymptotic scaling regime is very small for the  $d = 3$  Ising model and had not been entered in the simulations of [33]. Very recently Gompper *et al* [37] have reported Monte Carlo results for the solid-on-solid limit of the  $d = 3$  Ising model with a surface. They show that this model lies in the same universality class as the Hamiltonian (23) with the parameter  $\omega \approx \frac{1}{4}$  for all temperatures greater than the roughening temperature. With this value of  $\omega$ ,  $\nu_{\parallel} \sim 1.3$ , a result which Gompper *et al* claim is not inconsistent with the data of Binder and Landau [33]. Thus, there are signs that the controversy might soon be resolved.

From the viewpoint of liquid state theory it is of some interest to enquire whether the striking results for critical behaviour obtained from effective interfacial Hamiltonians, which treat the fluctuating film thickness as the relevant order parameter, can be derived by methods appropriate to a full many-body Hamiltonian for a realistic continuum fluid adsorbed at a substrate. The effective Hamiltonian approaches do not provide a description of the density profile, nor of the pairwise correlation of the inhomogeneous fluid. How much information about criticality at wetting transitions can we obtain from statistical mechanical sum-rules and thermodynamic arguments? That progress was made in section 2.2 for the particular case of complete drying at a hard-wall persuades us that this is a meaningful query. In a recent paper [38] we were able to provide answers for both types of wetting transition when all relevant forces are short-ranged. We summarize the main conclusions here, omitting all details; the interested reader is

**Table 1.** Singular contributions to the transverse moments of the density–density correlation function  $G$  and the local susceptibility  $\chi(z)$  at the two types of wetting transition. Note that the thickness  $l$  of the wetting film and the transverse correlation length  $\xi_{\perp}$  diverge at the transition in all dimensions  $d$ , whereas the derivative of the density profile  $\rho'(l) \sim \xi_{\perp}^{-1}$  vanishes only for  $d \leq 3$ .  $a$  is a microscopic distance. All unimportant factors of proportionality have been suppressed in this table.  $\delta\varepsilon$  measures the deviation of the field  $\varepsilon$  from its value at the (critical) transition.

	Complete	Critical
$G_0(l, l)$	$(\rho'(l))^2 \xi_{\perp}^2$	$(\rho'(l))^2 \xi_{\perp}^2$
$G_0(l, a)$	$\rho'(l)$	$\rho'(l)(\partial l/\partial \varepsilon)_{\mu, T}$
$G_0(a, a)$	0	$ \delta\varepsilon ^{-\alpha_s}$
$G_2(l, l)$	$-(\rho'(l))^2 \xi_{\perp}^4$	$-(\rho'(l))^2 \xi_{\perp}^4$
$G_2(a, a)$	$-\sigma_{lg}$	$-\sigma_{lg}(\partial l/\partial \varepsilon)_{\mu, T}^2$
$\chi(l)$	$\rho'(l) \xi_{\perp}^2$	$\rho'(l) \xi_{\perp}^2$
$\chi(a)$	$\rho_b$	$(\partial l/\partial \varepsilon)_{\mu, T}$

referred to [38]. The only assumptions which are made are that (i) the Wertheim form (11) for  $G$  is valid in the liquid–gas portion of the interface ( $z_1, z_2 \sim l$ ) and (ii) hyperscaling is valid, i.e.  $2 - \alpha_s = (d - 1)\nu_{\parallel}$ . (In the surface problem hyperscaling asserts  $\xi_{\perp}^{d-1} \sigma^{\text{sing}} \sim k_B T$ .)

For complete wetting, path (a), use of the Gibbs adsorption equation for  $\Gamma$ , the sum rule for  $(\partial\Gamma/\partial\mu)_T$  and the two assumptions above are sufficient to determine the critical exponents uniquely, i.e. for  $d \leq 3$ ,  $\nu_{\parallel} = 2/(d + 1)$ ,  $\alpha_s = 4/(d + 1)$  and  $\beta_s = (3 - d)/(d + 1)$ . In  $d = 2$  these agree with the exact results determined for a solid-on-solid model in an external field. In  $d = 3$  they reduce to the mean-field results quoted earlier. It is not possible to determine singular contributions to the transverse moments of  $G$ , except where  $z_1, z_2 \sim l$ , by formal manipulations for potentials other than the hard-wall. However, the explicit mean-field analysis for the Sullivan model, mentioned in section 2.2, is not restricted to purely hard-walls. These results imply that the singularities obtained for hard-walls should apply quite generally to complete wetting. Table 1 lists the various singular contributions that are expected.

In the case of critical wetting, path (b), surface thermodynamics, sum rules etc. are not sufficient to determine exponents uniquely. Now there are two relevant scaling fields,  $\delta\mu$  and  $\delta\varepsilon$ , rather than the single field  $\delta\mu$  which governs complete wetting. Nevertheless, one can determine a rigorous relationship between exponents:  $2 - \alpha_s = 2\nu_{\parallel} - 2\beta_s$ , which is the analogue of the Rushbrooke relationship for bulk critical exponents. When this is combined with hyperscaling we find  $\beta_s = (3 - d)\nu_{\parallel}/2$  for  $d \leq 3$ . All critical exponents can be expressed in terms of a single independent exponent. The technical reason for such a simplification is that the analogue of the exponent  $\eta$  is zero for wetting transitions [26, 27]. Singular contributions to moments of  $G$  and the local susceptibility  $\chi$  can be ascertained by making use of two extra sum rules [39, 40], involving derivatives of  $\Gamma$  and of  $\sigma$  with respect to  $\varepsilon$ , the strength of the attractive part of the substrate potential. The results for critical wetting are also given in table 1. Once again an explicit mean-field analysis [38] agrees with the predictions of the sum-rules. A comparison of critical and complete wetting shows that while these transitions might seem similar at first sight, they have a very different character when examined in detail. Although correlations have the

same form, i.e. the same dependence on  $\rho'(l)$  and  $\xi_{\parallel}$ , when both particles lie near  $l$ , this is not the case when one or both particles move away from the edge of the film to lie within a microscopic distance  $a$  of the substrate. In critical wetting  $G_0(l, a)$ ,  $G_2(a, a)$  and  $\chi(a)$  are divergent quantities, whereas they remain finite for complete wetting. Fluctuations manifest themselves in a more pronounced fashion for critical wetting, extending throughout the whole film. Indeed, it is possible to show that the transverse correlation length for particles close to the substrate defined by  $\xi_{\parallel}^{\#} = (-G_2(a, a)/G_0(a, a))^{1/2}$ , diverges as  $(\delta\varepsilon)^{-\nu_{\parallel}}$ , i.e. in the same fashion as  $\xi_{\parallel}$ . In the case of complete wetting there is no such divergent correlation length; the structure of  $G(z_1, z_2; Q)$  is somewhat more complex (see section 2.2), due to the modulation of the fluctuations.

The predictions of the sum rule analysis have been confirmed for a solid-on-solid model in  $d = 2$  that exhibits a critical wetting transition. Explicit analysis [41] yields the following results:

$$\begin{aligned} \chi(z_1) &\sim \delta\varepsilon^{-2} z_1 & z_1 \ll l \\ G_0(z_1, z_2) &\sim z_1 z_2 & z_1, z_2 \ll l \\ G_2(a, a)/G_0(a, a) &\sim \delta\varepsilon^{-4} & a \sim 0. \end{aligned} \quad (24)$$

These agree with the predictions in table 1, since  $\beta_s = 1$ ,  $\nu_{\parallel} = 2$  and  $\alpha_s = 0$  are exact results [42] for critical wetting in  $d = 2$ . The  $z$  dependence is in accord with general scaling arguments [41], valid in the strong-fluctuation regime ( $d < d_c$ ):

$$\begin{aligned} \chi^{\text{sing}}(z_1) &\sim \delta\varepsilon^{-(1+\beta_s)} z_1^{(1-\alpha_s)/\beta_s} & z_1 \ll l \\ G_0(z_1, z_2) &\sim \delta\varepsilon^{-\alpha_s} (z_1 z_2)^{(1-\alpha_s)/\beta_s} & z_1, z_2 \ll l \end{aligned} \quad (25)$$

A scaling argument for complete wetting gives

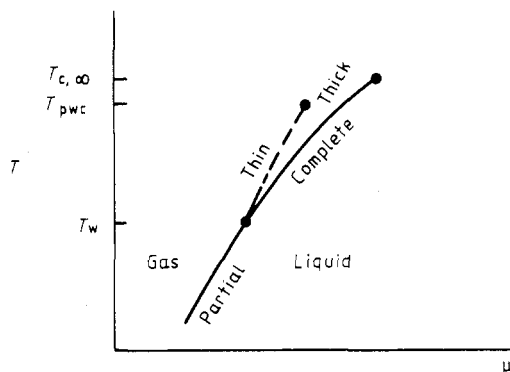
$$\chi^{\text{sing}}(z_1) \sim z_1^{(d+1)/(3-d)} \quad z_1 \ll l \quad (26)$$

which has also been confirmed by an explicit calculation for the  $d = 2$  solid-on-solid model [41].

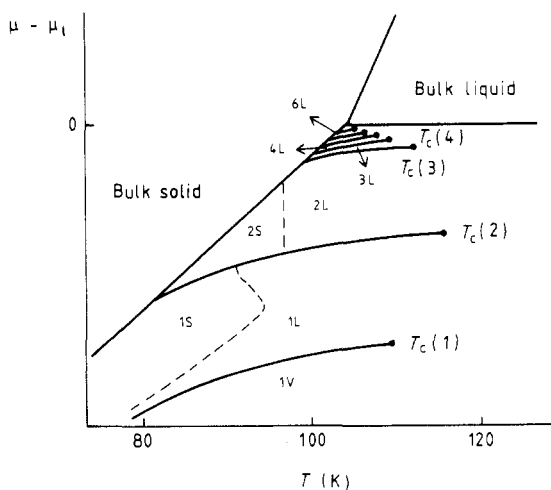
Finally, we note that while it is not possible to derive explicit exponents for critical wetting using purely formal techniques, it is possible to derive a relationship between the two lengths  $l$  and  $\xi_{\parallel}$  by effecting a Gaussian unfreezing of capillary-wave-fluctuations on the mean-field density profile [40, 38]. Use of sum-rules yields the result [38]

$$l = (2 + \omega - 1/\nu_{\parallel}) \xi_b \ln(\xi_{\parallel}/\xi_b) \quad \omega < 2; d = 3. \quad (27)$$

The RG results [34] for the Hamiltonian (23) are consistent with (27). Thus, we are confident that if a critical wetting transition were to be found in  $d = 3$  for a continuum fluid with short-ranged forces, the critical exponents would be non-universal, i.e.  $\omega$  dependent. For  $d < 3$ , however, where fluctuations are very strong and  $\xi_{\perp}$ , the interfacial roughness, is of the same order as  $l$ , the film thickness, Gaussian unfreezing is expected to fail [43].



**Figure 6.** Schematic phase diagram for a fluid exhibiting a first-order wetting transition at  $T = T_w$ . The dashed line is the prewetting line  $\mu_{pw}(T)$  where thin and thick films coexist. The full curve is the bulk coexistence curve  $\mu_{sat}(T)$ .



**Figure 7.** Schematic phase diagram for ethylene adsorbed on graphite. The chemical potential relative to that of the bulk liquid ( $\mu_l$ ) is plotted vertically. Only the multilayer region is described; other phases exist at low coverage and low temperature. Solid lines represent first-order layering transitions terminating at critical temperatures  $T_c(n)$ . 2L, 3L etc denote bilayer, trilayer liquids. The dashed lines represent (continuous) melting transitions from solid (s) to liquid (L) phases. This diagram is based on data from [52, 53].

#### 4. Other phase transitions

Wetting (or drying) is not the only phase transition that can occur at a substrate-fluid interface. Under certain circumstances layering or prewetting transitions will occur.

If the wetting transition is first-order it is accompanied by a line of first-order prewetting transitions out of bulk coexistence, i.e. at  $\mu_{pw}(T) < \mu_{sat}(T)$ —see figure 6. The adsorption  $\Gamma$  jumps discontinuously from a value characteristic of a thin adsorbed film to one characteristic of a thick liquid film. On increasing  $\mu$  further  $\Gamma$  increases and

diverges as  $\mu \rightarrow \mu_{\text{sat}}^-(T)$ . At low temperatures the prewetting line meets the bulk coexistence curve tangentially at  $T = T_w$  while, at high temperatures, it terminates at the prewetting critical temperature  $T_{\text{pwc}}$ , where the distinction between thin and thick vanishes. For  $T > T_{\text{pwc}}$ ,  $\Gamma$  increases continuously with  $\mu$ . First-order wetting and associated prewetting were first predicted by Cahn [44] and Ebner and Saam [45]. Monte Carlo simulations for a lattice-gas model [32] and for a Lennard-Jones gas at a substrate [46] confirm the existence of the prewetting transition. There is, as yet, no compelling experimental evidence for such a transition. Theory and simulation predict that the prewetting line lies very close to bulk coexistence,  $|\mu_{\text{pw}}(T) - \mu_{\text{sat}}(T)|$  is only a few per cent of  $\mu_{\text{sat}}(T)$ , and is short in temperature, i.e.  $T_{\text{pwc}} - T_w$  may be only a few degrees. Prewetting criticality is expected to lie in the  $d = 2$  Ising universality class since (i) the order parameter is the difference in film thickness or adsorption and (ii) only the parallel correlation length  $\xi_{\parallel}$  can diverge (the film thickness remains finite at  $T_{\text{pwc}}$ ). This conjecture has been confirmed by extensive Monte Carlo simulations, in conjunction with a finite-size scaling analysis, for a lattice-gas model [47]. The resulting exponents are, to within statistical error, equal to the Onsager values.

Layering transition is the name given to the discontinuous increase in adsorption, associated with the growth of a new adsorbed layer of a dense phase, that occurs when the gas pressure, or chemical potential, is increased at fixed temperature for sufficiently attractive substrates. The existence of a series of such transitions at temperatures below the bulk triple point has been established in many adsorption experiments for rare-gases and small molecules adsorbed on graphite—see e.g. [48, 49] and references therein. If solid-like layers develop it is not too surprising that the growth takes place in discontinuous jumps. Lattice-gas models of adsorption predict [50, 32] an infinite sequence of first-order transitions, provided  $T_w$  is located at  $T = 0$ . Each of these transitions has its own critical temperature  $T_c(n)$ , above which the new layer grows continuously with increasing  $\mu$ . As  $n \rightarrow \infty$   $T_c(n)$  approaches the roughening temperature  $T_R$  of the lattice model. For  $T > T_R$  there are no layering transitions. One might suspect that the discreteness of the transitions is imposed by the discreteness of the lattice. It is of interest to enquire whether such transitions occur in a continuum treatment, as would be appropriate to gas adsorption at temperatures above the bulk triple point  $T_{\text{tr}}$ . Whilst it should be impossible to have *infinitely* many transitions for  $T > T_{\text{tr}}$ , since the liquid–gas interface is always rough, is it possible to have several transitions between layered liquid films? Density functional calculations [51], based on a non-local treatment of the hard-sphere free-energy functional [6], have found a large number of layering transitions, similar to those obtained in lattice-gas models. The layering arises from the packing of the atoms in the presence of the substrate potential. The critical temperatures  $T_c(n)$  are calculated to be no more than 20 or 30 K above  $T_{\text{tr}}$ . Theory predicts discrete transitions from a highly structured *liquid* film with  $n$  layers, to one with  $n + 1$  layers. Since the theory is of mean-field character it omits the effects of roughening. It would be important to confirm such layering behaviour by computer simulation [60]. There is a growing amount of experimental evidence, for gases adsorbed on graphite, that transitions between layered liquid films do take place for  $T > T_{\text{tr}}$ . Ethylene [52, 53], ethane [54] and oxygen [55] are cases, see figure 7, where up to seven or eight discrete steps in the adsorption have been resolved in ellipsometric measurements or heat-capacity studies. Note that the criticality of layering transitions should also lie in the  $d = 2$  Ising universality class. Heat-capacity measurements for methane on graphite [56] obtain a value of  $\beta = 0.127 \pm 0.02$  for the order-parameter exponent at the sub-monolayer liquid-gas transition. For the monolayer-bilayer transition in  $\text{C}_2\text{D}_4$  on graphite the experimental data [57] are consistent with  $\beta$  between 0.08 and 0.17. Recall that the Onsager value is  $\beta = \frac{1}{8}$ .



## 5. Concluding remarks

We have attempted to show that the theory of simple fluids at substrates remains an ebullient subject. For those more accustomed to working with bulk phase transitions and critical phenomena it might seem surprising that purely formal techniques (sum rules and surface thermodynamics) can be made to yield so much information about the nature of criticality at interfaces. It is, of course, the presence of a spatially varying external potential, which induces surface phase transitions in the first place, that gives rise to a new battery of statistical mechanical techniques and allows us to make progress.

The theoretical work has posed several challenges for computer simulation. We have mentioned already the need to understand layering transitions in the vicinity of the bulk triple point. Determining the locus of the line of critical temperatures  $T_c(n)$  would be particularly relevant to experiments on multilayer adsorption, see figure 7. Testing the detailed predictions made for critical wetting will be extremely demanding. First one has to find the transition! The recent work of Henderson and van Swol [29] shows that even sophisticated density functional theories cannot be relied upon to predict the correct order of the drying transition for given potential functions. Even if a suitable system were found it would be an enormous effort to measure the appropriate correlation functions and thermodynamic functions with sufficient accuracy to determine critical exponents etc. Although the effects of capillary-wave fluctuations are especially rich at this transition these are not readily amenable to investigation in continuum fluids. For confined fluids simulations should be significantly easier. Capillary condensation has already been investigated in some detail (see [58] for a brief review), and evaporation is essentially the same phenomenon. Nevertheless, confirming the two-dimensional character of the capillary critical point is certainly a challenge!

The experimentalists must decide for themselves what, if anything, from this story is relevant to them. They will argue, not unreasonably, that there are no hard-walls in nature, or that the contact angle  $\theta$  will never equal  $\pi$  so complete drying cannot occur. But this does not mean our results for the idealized cases are irrelevant. Complete drying is equivalent to complete wetting, which certainly does occur for real fluids at real substrates. Capillary evaporation does not require two hard-walls; it will occur provided  $\theta > \pi/2$ . Thus, if one can find a pure liquid that has a contact angle  $> \pi/2$  on mica, solvation force measurements, of the type pioneered by Israelachvili [59] for liquids between two crossed mica cylinders, should show the features illustrated in figure 4.

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