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Abstract. – Fluids adsorbed in 3D wedges are shown to exhibit two types of continuous interfacial unbinding corresponding to critical and tricritical filling, respectively. Analytic solution of an effective interfacial model based on the transfer-matrix formalism allows us to obtain the asymptotic probability distribution functions for the interfacial height when criticality and tricriticality are approached. Generalised random-walk arguments show that, for systems with short-ranged forces, the critical singularities at these transitions are related to 2D complete and critical wetting with random-bond disorder, respectively.

Recent studies of filling transitions for fluids in 3D wedges [1,2] have revealed the much stronger influence of interfacial fluctuations compared with wetting at flat and rough substrates [3–7]. Encouragingly effective Hamiltonian predictions for the critical exponents at continuous (critical) wedge filling with short-ranged forces have been confirmed in large-scale Ising model simulation studies [8]. Similar experimental verification of the predicted geometry-dominated adsorption isotherms at complete wedge filling [9] raise hopes that the filling transition itself and related fluctuation effects will be observable in the laboratory. Here we further develop the fluctuation theory of 3D filling and show that there is a rather deep and previously unrecognized connection with the theory of wetting in 2D systems with random-bond (RB) disorder. Our findings are based on the analytical solution of an effective model of 3D wedge filling and also generalised random-walk arguments [10]. First we show that there are actually two types of continuous-filling behaviour corresponding to critical and tricritical transitions, respectively, with the latter having stronger fluctuation effects. The phase diagram for these transitions together with the classification of fluctuation regimes and the allowed values of critical exponents resemble very closely those predicted for 2D wetting. More precisely 3D critical filling is related to 2D complete wetting whilst 3D tricritical filling is related to 2D critical wetting. Remarkably the particular value of the 3D wedge wandering exponent for pure systems (thermal disorder) implies that criticality at tricritical and critical filling is related to predictions for 2D critical and complete wetting with RB disorder.

Consider the interface between a bulk vapour at temperature T and saturation pressure with a 3D wedge characterised by a tilt angle α (see fig. 1). Macroscopic arguments dictate
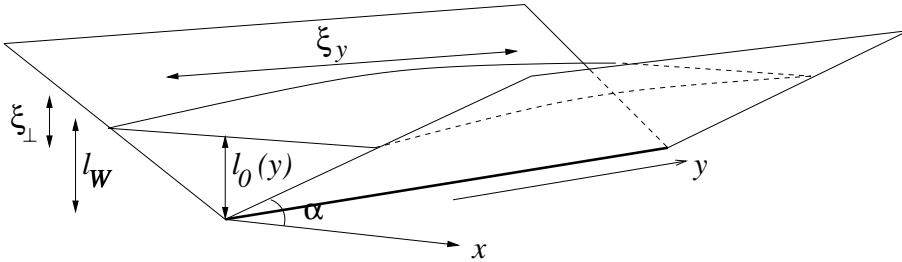
Fig. 1 – Schematic illustration of a typical interfacial configuration and relevant length scales for a fluid adsorption in a 3D wedge. The thick line marks the position of the wedge bottom.

that the wedge is partially filled by liquid if the contact angle $\theta > \alpha$ and completely filled if $\theta < \alpha$ [11] and is fully supported by both interfacial Hamiltonian [12] and exact Ising studies [13]. The filling transition refers to the change from microscopic to macroscopic liquid adsorption as $T \to T_f$, at which $\theta(T_f) = \alpha$, and may be first order or continuous (critical filling). Both these transitions can be viewed as the unbinding of the liquid-vapour interface from the wedge bottom. Characteristic length scales are the mean interfacial height above the wedge bottom l_W, the roughness $\xi_\perp$ and the longitudinal correlation length ξ_y, measuring fluctuations along the wedge (see fig. 1). The relevant scaling fields at critical filling are $\theta - \alpha$ and the bulk ordering field (partial pressure) h. In our discussion of filling we shall work exclusively at bulk coexistence ($h = 0$) since it is here that the connection with RB wetting emerges. However, calculations away from coexistence are not in any way problematic. At coexistence we define critical exponents by $l_W \sim (\theta - \alpha)^{-\beta_W}$ and $\xi_y \sim (\theta - \alpha)^{-\nu_y}$. The roughness can be related to ξ_y by the scaling relationship

$$\xi_\perp \sim \xi_y^{\zeta_W}, \tag{1}$$

where ζ_W is the wedge wandering exponent.

The liquid-vapour interface across the wedge is aproximately flat and soft-mode fluctuations arise from local translations in the height of the filled region along the wedge [1]. The pseudo–one-dimensional nature of these means that ζ_W is greater than the wandering exponent defined for the asymptotically flat free interface ζ_3 in a 3D system. For systems with sufficiently short-ranged forces critical filling is fluctuation-dominated (*i.e.* $\xi_\perp \sim l_W$) and dimensional reduction arguments lead to the identification [2]:

$$\zeta_W = \frac{\zeta_2}{1 + \zeta_2 - \zeta_3} \tag{2}$$

with ζ_2 the 2D free-interface wandering exponent. Thus for pure (thermal) systems for which $\zeta_d = (3 - d)/2$ for $d \leq 3$, the 3D wedge wandering exponent $\zeta_W = 1/3$. In the fluctuation-dominated regime the value of ζ_W determines the other exponents, in particular

$$\nu_y = \frac{1}{2 - 2\zeta_W} \tag{3}$$

with $\beta_W = \nu_\perp = \zeta_W \nu_y$. Thus, for thermal forces $\nu_y = 3/4$, a value verified in Ising simulation studies [8].

There is, however, another example of continuous filling with even larger fluctuations characterized by different scaling fields and critical exponents. This corresponds to tricritical filling

and there are two ways the transition may be induced. The first mechanism occurs for wedges made from walls which themselves exhibit weakly first order wetting transitions [1]. The filling transition in these systems will be first order if $\alpha < \alpha^*$ and critical for $\alpha > \alpha^*$, where α^* is the tricritical wedge angle. A second mechanism exists, however, which is more practicable in simulation studies. Imagine a wedge made from a homogeneous chemical material which exhibits critical filling. Now micropattern a stripe along the wedge bottom (see fig. 1), so as to weaken the local wall-fluid intermolecular potential and therefore strengthen the interfacial binding potential, since locally liquid adsorption will not be favoured and consequently the vapour-liquid interface is more likely to be localized near the wedge bottom. This situation can be easily engineered in Ising model studies by modifying the strength of the surface field near the wedge bottom and indeed has been done on planar substrates in the laboratory. With this modification it may be possible to bind the interface to the wedge bottom even at the filling boundary $\theta = \alpha$ and at bulk coexistence. A continuous tricritical transition may then be induced as the strength of the modified wedge potential approaches a tricritical value.

For thermal systems, both critical and tricritical transitions can be modelled by the wedge Hamiltonian [1]

$$\mathcal{H}_W[l_0] = \int dy \left\{ \frac{\Sigma l_0}{\alpha} \left(\frac{dl_0}{dy} \right)^2 + V_W(l_0) \right\}, \tag{4}$$

where $l_0(y)$ is the local height of the interface at position y along the wedge bottom and Σ is the liquid-vapor surface tension. This expression arises from the identification of the interfacial breather modes which translate the interface up and down the sides of the confining geometry, as the only relevant fluctuations for the critical-filling transition, and corresponds to the excess free-energy contribution of a breather-mode configuration with respect to the planar case obtained from the usual capillary-wave model [1]. Note that the effective bending term resisting fluctuations along the wedge is proportional to the local interfacial height since the interfacial cross-section has a length $2l_0/\alpha$. At bulk coexistence, the effective binding potential $V_W(l_0)$, up to unimportant additive constants, is given by [1]

$$V_W(l_0) \approx \frac{\Sigma(\theta^2 - \alpha^2)l_0}{\alpha} + \Delta V_W(l_0), \tag{5}$$

where $\Delta V_W(l_0)$ has a hard-wall repulsion for $l_0 < 0$ and a long-ranged tail which decays when $l_0 \to \infty$. For short-ranged forces this can be modelled as a contact-like potential with strength u (i.e. $\Delta V_W \sim -u\delta(l_0)$, where $\delta(x)$ is Dirac's delta function). In general, there will be a tricritical value u_c such that for $u < u_c$ the interface unbinds from the wedge bottom when $\theta \to \alpha$ whilst for $u > u_c$, the interface remains bound to the wall in the same limit. A section of the phase diagram (at $h = 0$) for this is presented in fig. 2(a) and shows two continuous-filling transitions. Critical filling corresponds to $\theta \to \alpha$ for $u < u_c$ (route (iii)) and has the critical exponents described above. Tricritical filling corresponds to any thermodynamic path for which $u \to u_c$ and $\theta \to \alpha$ (routes (i) and (ii), for example). Along the path $\theta = \alpha$ the relevant length scales diverge as

$$l_W \sim (u - u_c)^{-\beta_W^*} , \quad \xi_y \sim (u - u_c)^{-\nu_y^*} \tag{6}$$

and $\xi_\perp \sim \xi_y^{\zeta_W^*}$, with ζ_W^* the tricritical wandering exponent. These expressions define new critical exponents which are distinct from those at critical filling. Again for short-ranged forces we anticipate that the transition is fluctuation-dominated with $l_W \sim \xi_\perp$ and $\beta_W^* = \zeta_W^* \nu_y^*$. More generally, in the vicinity of the tricritical point (and at $h = 0$) we anticipate scaling,
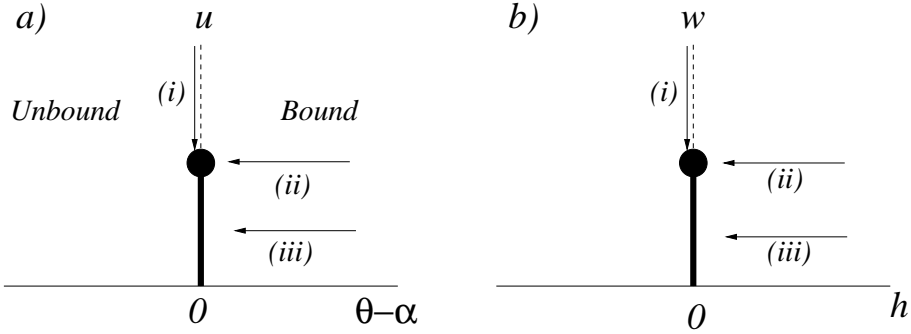
a)   *u*   *b)*   *w*

Unbound   *(i)*   *Bound*   *(i)*

(ii)   *(ii)*

(iii)   *(iii)*

0 $\theta-\alpha$ *0*   *h*

Fig. 2 – Phase diagrams for (a) filling and (b) wetting transitions in terms of the ordering fields $\theta - \alpha$ and h and the contact-like potential strengths u and w. The thick and dashed lines in both diagrams correspond to continuous and first-order boundaries between bound and unbound interfacial states, respectively. The arrows show representative paths along which continuous unbinding occurs. The filled circles represent the tricritical-filling and critical-wetting points, respectively.

e.g. $\xi_y \sim |u - u_c|^{-\nu_y^*} \Lambda \left[(\theta - \alpha)|u - u_c|^{-\Delta^*} \right]$ with the gap exponent Δ^*. Thus, along route (ii) $\xi_y \sim (\theta - \alpha)^{-\nu_y^*/\Delta^*}$.

To continue we evaluate these exponents for thermal systems by explicit transfer-matrix analysis before recasting them more generally in terms of the wandering exponent ζ_W. In the continuum limit the partition function is defined as a path integral [14]:

$$Z[l_b, l_a, Y] = \int \mathcal{D}l_0 \exp[-\mathcal{H}_W[l_0]], \tag{7}$$

where Y is the wedge length, $l_a = l_0(0)$ and $l_b = l_0(Y)$ are the endpoint heights and we have set $k_B T = 1$ for convenience. Due to the presence of a position-dependent stiffness some care must be taken with the definition of the path integral. This turns out to be of crucial importance for the the evaluation of the exponents at tricritical (but not critical) filling. This problem was already pointed out in ref. [15] and is related to the well-known ordering problem in the quantization of classical Hamiltonians with position-dependent masses. Similar issues also arise in solid-state physics [16]. Borrowing from the methods used to overcome these difficulties we use the following definition:

$$Z[l_b, l_a, Y] = \lim_{N \to \infty} \int dl_1 \ldots dl_{N-1} \prod_{j=1}^{N} K(l_j, l_{j-1}, Y/N), \tag{8}$$

where $l_0 \equiv l_a$ and $l_N \equiv l_b$, and $K(l, l', y)$ is defined as

$$K(l, l', y) = \sqrt{\frac{\Sigma \sqrt{ll'}}{\alpha \pi y}} \exp \left[-\frac{\Sigma \sqrt{ll'}}{\alpha y}(l - l')^2 - y V_W(l) \right]. \tag{9}$$

In the continuum limit the partition function becomes

$$Z(l_b, l_a, Y) = \sum_n \psi_n(l_b) \psi_n^*(l_a) e^{-E_n Y}, \tag{10}$$

where the complete orthonormal set of functions satisfies

$$\left(-\frac{\alpha}{4\Sigma} \frac{\partial}{\partial l} \left[\frac{1}{l} \frac{\partial}{\partial l} \right] + V_W(l) - \frac{3\alpha}{16\Sigma l^3} \right) \psi = E\psi. \tag{11}$$
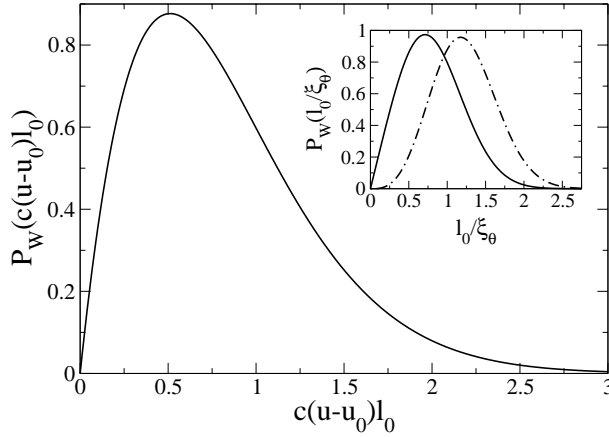
Fig. 3 – Scaled interfacial height PDF $P_W(c(u - u_c)l_0)$ as a function of the scaled wedge midpoint interfacial height $c(u - u_c)l_0$ for $\theta = \alpha$. Inset: plot of the scaled PDF along routes (ii) and (iii) in fig. 2(a), *i.e.* for $\epsilon \approx 1.086$ (continuous line) and $\epsilon \approx 1.639$ (dot-dashed line), respectively.

In the thermodynamic limit $Y \to \infty$ we obtain the probability distribution function (PDF) for the midpoint interfacial height $P_W(l_0) = |\psi_0(l_0)|^2$ and the longitudinal correlation length $\xi_y = 1/(E_1 - E_0)$. We have obtained the analytical solution to the transfer-matrix operator for short-ranged forces determining the crossover from tricritical to critical filling. We present without proof some of our findings. A more complete and detailed description of our results will be published elsewhere.

Along route (i) we find that there is only one bound solution to eq. (11) for $u > u_c$ with $E_0 \propto (u - u_c)^3$ and associated PDF

$$P_W(l_0) \propto l_0 \text{Ai}^2[c(u - u_c)l_0] \qquad (12)$$

with c an unimportant constant while $\text{Ai}(x)$ is the Airy function. Thus, $l_W \sim \xi_\perp \propto (u - u_c)^{-1}$ and $\xi_y \propto (u - u_c)^{-3}$ identifying $\beta_W^* = 1$, $\nu_y^* = 3$ and confirming that the tricritical wandering exponent coincides with the critical wandering exponent $\zeta_W^* = \zeta_W = 1/3$. A numerical plot of the PDF is shown in fig. 3. On the other hand, the scaling of the PDF along the route (ii) is given by

$$P_W(l_0) \propto l_0 \exp\left[\frac{2\epsilon l_0}{\xi_\theta} - \frac{2l_0^2}{\xi_\theta^2}\right] H_s^2\left(\sqrt{2}\frac{l_0}{\xi_\theta} - \frac{\epsilon}{\sqrt{2}}\right), \qquad (13)$$

where $\xi_\theta = \Sigma^{-1/2}[(\theta/\alpha)^2 - 1]^{-1/4}$, $s = \epsilon^2/4 - 1/2$ with $\epsilon = -\Sigma E_0 \xi_\theta^3/\alpha \approx 1.086$ and $H_s(z)$ is the Hermite function [17]. The value of ϵ is obtained by imposing appropriate boundary conditions at $l_0 = 0$. Thus along this route $l_W \sim \xi_\perp \propto (\theta - \alpha)^{-1/4}$ similar to critical filling. From analysis of the spectrum it is also possible to show that $\xi_y \propto (\theta - \alpha)^{-3/4}$. As anticipated, in the vicinity of the tricritical point the divergent length scales show scaling with tricritical gap exponent $\Delta^* = 4$. Whilst the exponents for critical filling are already known the exact scaling form for the PDF has not been given previously. For thermodynamic paths (iii) far from the tricritical point we have found that the scaling of the PDF is of the form shown in eq. (13) but with $\epsilon \approx 1.639$. We remark that the PDFs at critical and tricritical filling have distinct short-distance expansions when $l_0/l_W \to 0$ and our results (cubic and linear powers, respectively) are consistent with exact thermodynamic requirements [2].

We can now place the results for tricritical filling in a more general context. For short-ranged forces the tricritical transition belongs to a general class of strong-fluctuation regime interfacial unbinding since the transition occurs at a finite value of the binding potential u. The critical singularities at such transitions can be very elegantly modelled using random-walk methods which previously have been succesfully used to understand 2D critical wetting (at flat walls) [10]. By modelling the interface as a sequence of bound and unbound regions (the so-called bead-necklace picture), the critical exponent for the correlation length along the interface at the strong-fluctuation transition can be related to the appropriate wandering exponent. Details will be published elsewhere, so we just mention our main results. Following this argument for the tricritical-filling transition and making allowance for the position-dependent stiffness, we find

$$\nu_y^* = \frac{1}{1 - 2\zeta_W} \ , \quad \Delta^* = \frac{2 - 2\zeta_W}{1 - 2\zeta_W}, \tag{14}$$

from which all other critical exponents follow. For thermal systems, $\zeta_W = 1/3$, implying $\nu_y^* = 3$ and $\Delta^* = 4$, in agreement with our explicit calculations. Equations (12), (13) and (14) are the main results of our paper and together with eq. (3) completely determine the critical singularities at fluctuation-dominated 3D filling occuring at bulk coexistence.

A remarkable connection with the theory of 2D complete and critical wetting is now apparent. These transitions correspond to the continuous unbinding of an interface from a planar wall and can be modelled by the interfacial Hamiltonian

$$\mathcal{H}[l] = \int \mathrm{d}x \left[\frac{\tilde{\Sigma}}{2} \left(\frac{\mathrm{d}l}{\mathrm{d}x} \right)^2 + W(l) \right], \tag{15}$$

where $l(x)$ is the interfacial height at a position x along the wall, $\tilde{\Sigma}$ is the 2D stiffness and $W(l)$ is the binding potential. In general $W(l) = hl + \Delta W(l)$ where h is proportional to the bulk ordering field (partial pressure) and for short-ranged forces $\Delta W(l)$ can be modelled as a contact potential of strength w (*i.e.* $\Delta W(l) = -w\delta(l)$). Disorder arising from bulk random bonds can also be allowed for by including a stochastic term in $W(l)$. The phase diagram is shown in fig. 2(b), and shows two continuous transitions referred to as complete wetting (path (iii)) and critical wetting (*e.g.*, path (i) and (ii)), at which the mean interfacial height l_π, roughness $\xi_\perp$ and transverse correlation length $\xi_\parallel$ all diverge. For short-ranged forces the transitions are fluctuation-dominated and $l_\pi \sim \xi_\perp \sim \xi_\parallel^{\zeta_2}$. More specifically, for complete wetting we write $\xi_\parallel \sim h^{-\nu_\parallel^{co}}$ whilst for critical wetting $\xi_\parallel \sim (w - w_c)^{-\nu_\parallel}$ with associated gap exponent Δ off coexistence. The values of these exponents can be expressed explicitly in terms of the wandering exponent ζ_2 as [18]

$$\nu_\parallel^{co} = \frac{1}{2 - \zeta_2} \ , \quad \nu_\parallel = \frac{1}{1 - \zeta_2} \ , \quad \Delta = \frac{2 - \zeta_2}{1 - \zeta_2}. \tag{16}$$

There is therefore a qualitative and quantitative connection between critical singularities at 3D filling and 2D wetting. The phase diagrams are equivalent (see fig. 2) with the field $\theta - \alpha$ playing the role of the ordering field h at wetting. Further, writing the 2D wetting exponents in terms of ζ_2, *e.g.* $\nu_\parallel^{co} = \nu_\parallel^{co}(\zeta_2)$, etc., we have from eqs. (3) and (14) the dimensional reduction relations for the critical exponents

$$\nu_y = \nu_\parallel^{co}(2\zeta_W) \ , \quad \nu_y^* = \nu_\parallel(2\zeta_W) \ , \quad \Delta^* = \Delta(2\zeta_W). \tag{17}$$

Most remarkably for thermal forces the numerical value $2\zeta_W = 2/3$ means that 3D filling is related to 2D wetting with RB disorder, since $\zeta_2 = 2/3$ for this case [19].

A full account of our study, including the analysis of the presence of long-ranged forces, will be presented elsewhere.

In summary, we have identified a second example of continuous-filling transition corresponding to tricritical behaviour. For systems with short-ranged forces and thermal disorder only we have exactly found the critical singularities and associated probability distribution function for the interfacial height. A random-walk analysis reveals a remarkable connection between the critical exponents for thermal 3D filling and random-bond 2D wetting for systems with short-ranged forces. These predictions may certainly be tested in Ising model simulation studies and would be a stringent test of the theory of 3D wedge filling. Experimental studies of tricritical (and critical) filling similar to those already performed for complete filling would be very welcome.

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