Tricritical wedge filling transitions with short-ranged forces

J. M. Romero-Enrique[†] and A. O. Parry[‡]

† Departamento de Física Atómica, Molecular y Nuclear, Area de Física Teórica, Universidad de Sevilla, Apartado de Correos 1065, 41080 Sevilla, Spain
‡ Department of Mathematics, Imperial College 180 Queen's Gate, London SW7 2BZ, United Kingdom

Abstract. We show that the 3D wedge filling transition in the presence of short-ranged interactions can be first-order or second order depending on the strength of the line tension associated with to the wedge bottom. This fact implies the existence of a tricritical point characterized by a short-distance expansion which differs from the usual continuous filling transition. Our analysis is based on an effective one-dimensional model for the 3D wedge filling which arises from the identification of the breather modes as the only relevant interfacial fluctuations. From such analysis we find a correspondence between continuous 3D filling at bulk coexistence and 2D wetting transitions with random-bond disorder.
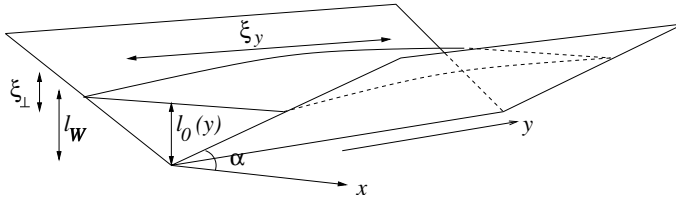
Figure 1. Schematic illustration of a typical interfacial configuration and relevant lengthscales for a fluid adsorption in a 3D wedge.

Fluid adsorption in micropatterned and sculpted geometries has become the subject of intense study over the last decade. Highly impressive technological advances which allow the tailoring of micro-patterned and structured solid surfaces on the nanometer to micrometer scale [1] are a landmark in the development of the emerging microfluidic industry [2] which aims at minituarizing chemical synthesis plants or biological analysis equipment in much the same way the silicon chip brought about the electronics revolution. However, the theoretical understanding of this phenomenon is far from being complete. Recent studies of filling transitions for fluids in 3D wedges show that interfacial fluctuations are greatly enhanced compared with wetting at flat substrates [3, 4]. The control of such enhanced interfacial fluctuations is crucial for the effectiveness of the microfluidic devices. Fortunately, there are simple theoretical approaches which take into account these effects. For example 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 [5]. Similar experimental verification of the predicted geometry-dominated adsorption isotherms at complete wedge filling [6] raise hopes that the filling transition itself and related fluctuation effects will be observable in the laboratory. We further develop the theory of wedge filling in this paper, focussing on the emergence of a new type of continuous filling: tricritical filling.

First we briefly review the fluctuation theory of 3D wedge filling. Consider the interface between a bulk vapour at temperature T and saturation pressure with a 3D wedge characterised by a tilt angle α. Macroscopic arguments dictate that the wedge is partially filled by liquid if the contact angle $\theta > \alpha$ and completely filled if $\theta < \alpha$ [7]. 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 of 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 Figure 1). The relevant scaling fields at critical filling are $\theta - \alpha$ and the bulk ordering field h (which is proportional to the pressure difference with the saturation value). At coexistence ($h = 0$) 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 $\xi_\perp \sim \xi_y^{\zeta_W}$, where ζ_W is the wedge wandering exponent. For short-ranged forces, $\zeta_W = 1/3$.

For shallow wedges, i.e. $\alpha \ll 1$, the free energy of an interfacial configuration can be modelled by an effective Hamiltonian based on the capillary wave model for wetting of planar substrates [8]. However, an analysis of this model [3] shows that 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. These *breather modes* are the only relevant fluctuations in the continuous filling phenomena, and can be taken into account by the following effective Hamiltonian [3]

$$\mathcal{H}_W[l_0] = \int dy \left\{ \frac{\Sigma l_0}{\alpha} \left(\frac{dl_0}{dy} \right)^2 + V_W(l_0) \right\} \tag{1}$$

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. Note that the effective bending term resisting fluctuations along the wedge is proportional to the local interfacial height. The effective binding potential $V_W(l_0)$ for $l_0 \gg l_\pi$, where l_π is the mean wetting film thickness for a planar substrate, is given (up to irrelevant additive constants) by [3]:

$$V_W(l_0) \approx \frac{h(l_0 - l_\pi)^2}{\alpha} + \frac{\Sigma(\theta^2 - \alpha^2)l_0}{\alpha} + \int_{-(l_0-l_\pi)/\alpha}^{(l_0-l_\pi)/\alpha} dx W(l_0 - \alpha|x|) \tag{2}$$

where $W(l)$ is the binding potential between the gas-liquid interface and a planar substrate. Note that the mean field result for l_W is recovered by minimizing $V_W(l_0)$ for $l_0 > l_\pi$, which is an important check on the self-consistency of the method [3]. In addition to a hard wall repulsion for $l_0 < 0$, the potential $V_W(l_0)$ contains a short-ranged attraction which may be modified by micropatterning a stripe along the wedge bottom, so as to weaken the local wall-fluid substrate and therefore strengthen the interfacial binding. This observation will be crucial for the existence of tricritical filling, since with this decoration it may be possible to bind the interface to the wedge bottom at the filling boundary $\theta = \alpha$ and $h = 0$. For latter convenience, hereafter we will set $h = 0$ in our discussion of continuous filling.

The quasi-one-dimensional nature of the effective Hamiltonian Equation (1) allows us to use the transfer-matrix formalism. In the continuum limit the partition function is defined as a path integral [9] (setting $k_B T = 1$ for convenience)

$$Z[l_b, l_a, Y] = \int \mathcal{D}l_0 \exp(-\mathcal{H}_W[l_0]) \tag{3}$$

where Y is the wedge length and l_a and l_b are the endpoint heights. The position-dependent stiffness introduces some ambiguity in the definition of the path integral. This problem was already pointed out in Ref. [10] 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 [11]. Borrowing from the methods used to overcome these difficulties we use the following definition
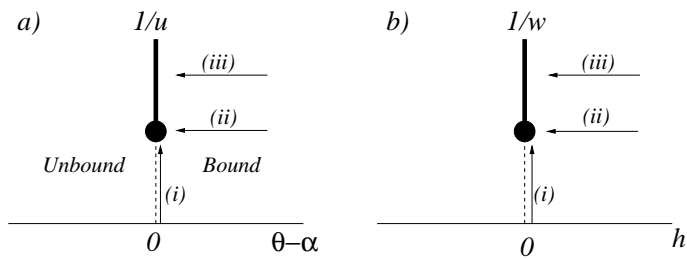
$$Z[l_b, l_a, Y] = \lim_{N \to \infty} \int dl_1 \dots dl_{N-1} \prod_{j=1}^{N} K(l_j, l_{j-1}, Y/N) \tag{4}$$

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

$$K(l, l', y) = \sqrt{\frac{\Sigma\sqrt{ll'}}{\alpha\pi y}} \exp \left(-\frac{\Sigma\sqrt{ll'}}{\alpha y}(l - l')^2 - y V_W(l) \right) \tag{5}$$

In the continuum limit the partition function becomes

$$Z(l_b, l_a, Y) = \sum_n \psi_n(l_b)\psi_n^*(l_a)e^{-E_n Y} \tag{6}$$

Figure 2. Phase diagrams for (a) filling and (b) wetting transitions. 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 occur: (i) and (ii) for tricritical filling (critical wetting) and (iii) for critical filling (complete wetting), respectively. The filled circles represent the tricritical filling and critical wetting points, respectively. See text for explanation.

where the complete orthonormal set satisfy

$$\left(-\frac{\alpha}{4\Sigma}\frac{\partial}{\partial l}\left[\frac{1}{l}\frac{\partial}{\partial l}\right] + V_W(l) - \frac{3\alpha}{16\Sigma l^3} \right)\psi = E\psi \tag{7}$$

In the thermodynamic limit $Y \to \infty$ we obtain the probability distribution function (PDF) for the midpoint interfacial height $P_W(l_0) = |\psi_0(l_0)|^2$, the wedge excess free energy $f_W = E_0$ and the longitudinal correlation length $\xi_y = 1/(E_1 - E_0)$. At this point we must remark that *any* definition of the path integral which is invariant upon exchanging l_a and l_b leads to an Schrödinger equation similar to Equation (7) but with a different coefficient for the extra $1/l^3$ term in the effective binding potential [10].

The change of variables $\lambda = \sqrt{8\Sigma/\alpha}l^{3/2}/3$ and $\psi(l) = (2\Sigma l/\alpha)^{1/4}\phi(\lambda(l))$ [12] transforms the Equation (7) to:

$$-\frac{1}{2}\frac{d^2\phi(\lambda)}{d\lambda^2} + \left(V_W[l(\lambda)] - \frac{5}{72\lambda^2} \right)\phi(\lambda) = E\phi(\lambda) \tag{8}$$

with $l(\lambda) = \left(3\lambda/\sqrt{8\Sigma/\alpha}\right)^{2/3}$. In general, there will be an interfacial bound state at bulk coexistence for $\theta = \alpha$ if the strength of the small l_0 attraction between the gas-liquid interface and the substrates, which we will denote as u, is greater than some value u_c. Consequently, the filling transition is first-order if $u > u_c$ and critical if $u < u_c$. Tricritical filling is observed when $u - u_c$ emerges as a new relevant field (in the renormalization-group sense). If $W(l) \sim -a/l^p + b/l^q$, different scenarios may arise as the range of the binding potential is varied. In particular, for $p > 4$ the long-range behaviour of V_W is dominated by the $1/l^3$ term for $\theta = \alpha$, so the filling phenomena are fluctuation-dominated. This finding is consistent with the existence of two different fluctuation regimes for critical filling: mean-field if $p < 4$ and fluctuation-dominated regime if $p > 4$ [3]. In the fluctuation-dominated regime, examination of Equation (8) shows that there is an analogy between 3D continuous filling and 2D continuous wetting (see Figure 2), where the role at wetting of the bulk ordering field h and the potential strength w are played by $\theta - \alpha$ and u for filling phenomena, respectively. In particular, 3D tricritical (critical) filling is analogous to 2D critical (complete) wetting, respectively. Different critical exponents which characterize the divergence of length scales can be defined. In addition to the critical filling critical exponents β_W and ν_y

defined along route (ii) in Figure 2(a) (see above), we can define new critical exponents for tricritical filling at $\theta = \alpha$ (route (i) in Figure 2(a)) as:

$$l_w \sim (u - u_c)^{-\beta_W^*} \ , \ \xi_y \sim (u - u_c)^{-\nu_y^*} \tag{9}$$

and $\xi_\perp \sim \xi_y^{\zeta_W^*}$, where ζ_W^* is the tricritical wandering exponent which in general may be different from ζ_W (in contrast with the wetting case). More generally, in the vicinity of the tricritical point we anticipate scaling 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) $\xi_y \sim (\theta - \alpha)^{-\nu_y^*/\Delta^*}$.

We focus now on the case of short-ranged forces as the prototype of the fluctuation-dominated regime. In addition to the hard-wall condition, $V_W(l_0)$ can be modelled as a contact-like attraction with strength u. An analysis of Equation (7) for $l_0 \to 0$ shows that the short-distance expansion of the PDF is either $P_W \sim l_0$ or $P_W \sim l_0^3$. We anticipate that the former corresponds to tricritical behaviour and the latter to critical filling. It is remarkable that thermodynamic consistency at critical filling is ensured as the local density at the wedge bottom is non-singular, i.e. $\rho_w(0) - \rho_l \sim T - T_f$, where ρ_l is the bulk liquid density [14]. This property is only obtained if the partition function is defined by Equation (4) and Equation (5). Thus, the ambiguity in its definition can be removed by imposing this regularity condition on the short-distance expansion of the interfacial height PDF.

We report now our explicit results (details will be presented elsewhere). Along route (i) we find that there is only one bound solution to Equation (7) for $u > u_c \approx 1.358$ with $E_0 \propto (u - u_c)^3$ and associated PDF

$$P_W(l_0) = \frac{6\sqrt{3}\pi}{\xi_u} \frac{l_0}{\xi_u} \left[\mathrm{Ai} \left(\frac{l_0}{\xi_u} \right) \right]^2 \tag{10}$$

where $\mathrm{Ai}(x)$ is the Airy function and in the scaling limit $\xi_u \sim |u - u_c|^{-1}$. 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 obtaining $\zeta_W^* = \zeta_W = 1/3$. As predicted, the short-distance behaviour of the PDF is linear with l_0.

On the other hand, the scaling of the PDF for $\theta > \alpha$ is given by (see also Figure 3):

$$P_W(l_0) \propto l_0 \exp \left[\frac{2\epsilon l_0}{\xi_\theta} - \frac{2l_0^2}{\xi_\theta^2} \right] H_\nu^2 \left(\sqrt{2}\frac{l_0}{\xi_\theta} - \frac{\epsilon}{\sqrt{2}} \right) \tag{11}$$

where $\xi_\theta = \Sigma^{-1/2}[(\theta/\alpha)^2 - 1]^{-1/4}$, $\epsilon = \Sigma E_0 \xi_\theta^3/\alpha$, $\nu = \epsilon^2/4 - 1/2$ and $H_\nu(x)$ is the Hermite function [13]. The value of ϵ is obtained as the smallest solution of the following equation:

$$\pm \frac{\Gamma\left[-\frac{1}{3}\right] 3^{-2/3}}{\Gamma\left[\frac{1}{3}\right]} \frac{\xi_\theta}{\xi_u} = \epsilon + \left(\frac{\epsilon^2}{\sqrt{2}} - \sqrt{2} \right) \frac{H_{\frac{\epsilon^2}{4} - \frac{3}{2}}\left(-\frac{\epsilon}{\sqrt{2}} \right)}{H_{\frac{\epsilon^2}{4} - \frac{1}{2}}\left(-\frac{\epsilon}{\sqrt{2}} \right)} \tag{12}$$

where the positive (negative) sign corresponds to $u > u_c$ ($u < u_c$), respectively. The inset of Figure 3 plots the solution of this equation. As anticipated, note that scaling is obeyed in the vicinity of the tricritical point as the wedge excess free energy $f_W \sim \xi_\theta^{-3} F_\pm(\xi_\theta/\xi_u)$. For $u > u_c$ and $\xi_\theta/\xi_u \gg 1$, we have checked numerically that the PDF (11) converges to the expression given by Equation (10) for the corresponding value of ξ_u given by Equation (12). Thus, the interface remains bound to the substrate when $\theta \to \alpha$, in agreement to the first-order character of the filling transition. The thermodynamic path (ii) to the tricritical point corresponds to $\xi_u \to \infty$, which corresponds to $\epsilon \approx 1.086$. Thus along this route $l_W \sim \xi_\perp \propto (\theta - \alpha)^{-1/4}$ similar
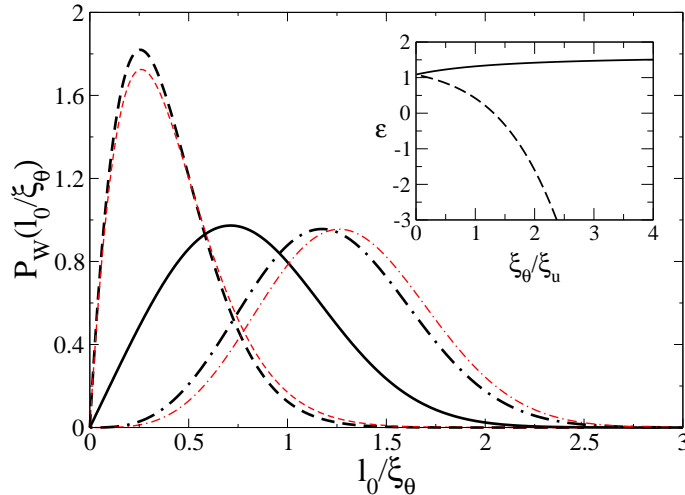
Figure 3. Plot of the scaled PDF for $\epsilon = -1.5$ (thick dashed line), and along routes (ii) and (iii) in Figure 2(a), i.e. for $\epsilon \approx 1.086$ (thick continuous line) and $\epsilon \approx 1.639$ (thick dot-dashed line), respectively. For comparison, the PDF from Equation (10) with $\xi_u \approx 1.968\xi_\theta$ (which corresponds to $\epsilon = -1.5$, see inset) is also plotted (thin dashed line). Finally, the scaled PDF obtained in Ref. [10] is also shown (thin dot-dashed line). Inset: Plot of ϵ as a function of ξ_θ/ξ_u for $u < u_c$ (continuous line) and $u > u_c$ (dashed line).

to critical filling. From analysis of the spectrum it is also possible to show that $\xi_y \propto (\theta - \alpha)^{-3/4}$, so the tricritical gap exponent $\Delta^* = 4$. Finally, for thermodynamic paths (iii) far from the tricritical point, i.e. $\xi_u \to 0$, we have found that the scaling of the PDF is of the form shown in Equation (11) with $\epsilon \approx 1.639$. Note that $P_W \sim l_0^3$ as $l_0 \to 0$, in agreement with our previous statement. This condition is not fullfilled by the solution presented in Ref. [10], although globally it does not differ too much from our exact solution (see Figure 3).

We finish by mentioning a remarkable connection for short-ranged forces between 3D wedge filling and 2D wetting with random-bond disorder [15]. The critical exponents corresponding to tricritical and critical wedge filling can be obtained from generalized random-walk methods [16] in terms of the wedge wandering exponent ζ_W. In particular, they are found to have the same dependence of the critical exponents for critical and complete wetting, respectively, but in terms of an effective 2D wandering exponent equal to $2\zeta_W$. For short-ranged forces ($\zeta_W = 1/3$), this implies that the set of critical exponents is the same as for 2D random-bond disorder [17]. These predictions may certainly be tested in Ising model simulation studies and would be a stringent test of the theory of 3D wedge filling.

Acknowledgments

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