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LETTER TO THE EDITOR

A disorder point for filling transitions in 1 + 1 dimensions

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Abstract

We study a continuum interfacial Hamiltonian model of fluid adsorption in a (1 + 1)-dimensional wedge geometry, which is known to exhibit a filling transition when the contact angle $\theta_\pi = \alpha$, with α the wedge angle. We extend the transfer matrix analysis of the model to calculate the interfacial height probability distribution function $P(l; x)$, for arbitrary positions x along the wedge. The asymptotics of this function reveal a fluctuation-induced disorder point (non-thermodynamic singularity) that occurs prior to filling when $\theta_\pi = 2\alpha$, where there is a change of length scales determining the decay of $P(l; x)$.

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Interfacial fluctuation effects occurring at filling transitions in wedge and cone-shaped non-planar geometries have recently attracted much attention [1–4]. The fluctuation theory confirms the elegant thermodynamic prediction [5] that filling occurs at a temperature T_F satisfying

$$\theta_\pi(T_F) = \alpha \tag{1}$$

where $\theta_\pi(T)$ denotes the temperature-dependent contact angle of the liquid drop (for example) on a planar surface and α is the wedge angle. The theory also predicts that continuous (critical) filling is characterized by large-scale, universal interfacial fluctuation effects associated with the unbinding of the liquid–vapour interface. In general, these fluctuation effects are much more pronounced than those occurring at wetting and reflect the influence of a soft-mode, breather fluctuation, which translates the interface up and down the sides of the confining geometry.

In this Letter we show how fluctuation effects also lead to a disorder point for wedge/cone filling in 1 + 1 dimensions occurring at a temperature $T_D < T_F$, where T_D satisfies the equally elegant condition

$$\theta_\pi(T_D) = 2\alpha. \tag{2}$$

As we shall show, T_D denotes a temperature at which there is an abrupt change in the α dependence of the length scale determining the aymptotic decay of the distribution function

$P(l;x)$. Here $P(l;x)$ denotes the probability for finding the interface a distance l from the wedge wall, at position x along it (measured from the apex).

Consider a wedge geometry in 1 + 1 dimensions comprising a (hard) wall whose height above the x-axis is described by the height function $z(x) = |x|\tan\alpha$. We suppose the wall is in contact with a bulk vapour phase at saturation chemical potential corresponding to bulk two-phase co-existence and that (at low temperatures) a thin film of liquid forms at the wall–vapour interface. Denoting the local height of the liquid–vapour interface above the x-axis by $y(x)$, the starting point of our analysis of filling in open wedges (corresponding to small α) is the interfacial model [1, 2]:

$$H[y] = \int \mathrm{d}x \left\{ \frac{\Sigma}{2}\left(\frac{\partial y}{\partial x}\right)^2 + W(y - \alpha|x|) \right\} \tag{3}$$

where Σ denotes the surface tension of the unbinding liquid–vapour interface and $W(l)$ is the usual binding potential describing the direct influence of wall–fluid and fluid–fluid forces, which is known from the theory of wetting in planar systems [6]. Notice that the binding potential is a function of the relative distance between the wall and the interface, denoted $l \equiv y - \alpha|x|$. This model can be readily studied using continuum transfer matrix techniques [2, 4] and is a straightforward extension of the method well known from the theory of wetting [7]. The main results are summarized below and form the starting point for our present analysis. We suppose that the wedge extends from $x = -L/2$ to $L/2$ and choose fixed end-point interfacial heights $l_{-\mathrm{e}}$ and l_{e} at these points. By splitting the partition function $\mathcal{Z}_{\mathcal{W}}$ into contributions to the left and right of the wedge apex and changing collective coordinates to the relative interfacial height it immediately follows that

$$\mathcal{Z}_{\mathcal{W}} \propto \int_0^\infty \mathrm{d}l_0\, \mathrm{e}^{2\alpha\Sigma l_0} \mathcal{Z}_\pi\left(l_{-\mathrm{e}}, l_0; \frac{L}{2}\right) \mathcal{Z}_\pi\left(l_0, l_{\mathrm{e}}; \frac{L}{2}\right) \tag{4}$$

where $l_0 = l(0)$ denotes the (mid-point) height of the interface above the apex. Here $\mathcal{Z}_\pi(l_1, l_2; X)$ corresponds to the partition function for an interface near a planar wall given by the usual spectral sum (or integral) [7]

$$\mathcal{Z}_\pi(l_1, l_2; x) = \sum_n \psi_n(l_1)\psi_n(l_2)\mathrm{e}^{-E_n x} \tag{5}$$

where the eigenfunctions (labelled $n = 0, 1, \ldots$) satisfy the Schrödinger equation (with $k_{\mathrm{B}}T \equiv 1$)

$$-\frac{1}{2\Sigma}\frac{\partial^2}{\partial l^2}\psi_n(l) + W(l)\psi_n(l) = E_n\psi_n(l). \tag{6}$$

From the expression (4) for the wedge partition function it is transparent that in the thermodynamic limit of an infinite wedge the probability distribution function for the mid-point height is given by

$$P(l;0) = \frac{\mathrm{e}^{2\Sigma\alpha l}|\psi_0(l)|^2}{\langle 0|\mathrm{e}^{2\Sigma\alpha l}|0\rangle} \tag{7}$$

where

$$\langle n|f(l)|m\rangle = \int \psi_n(l) f(l) \psi_m^*(l)\,\mathrm{d}l \tag{8}$$

is the inner product with respect to the planar eigenfunctions. The result for the mid-point distribution function is very simple and from it one can readily obtain the thermodynamic prediction phase boundary (1) for filling for arbitrary choices of binding potential $W(l)$. To see this, note that the ground state planar wavefunction decays as $\mathrm{e}^{-\Sigma\theta_\pi l}$ as $l \to \infty$ since the eigenvalue E_0 is equivalent to the planar excess free energy. This quantity is hence related to the contact angle by $E_0 \approx -\Sigma\theta_\pi^2/2$ by approximating Young's equation in the small-angle limit. Thus $P(l; 0)$ only describes a localized interface provided $\theta_\pi(T) > \alpha$. Hereafter we specialize to binding potentials that decay faster than $\sim 1/l$, which correspond to the fluctuation-dominated regime for filling and represent the universality class for systems with short-ranged forces [4]. For this case we can follow standard methods [7], drop the binding potential term in the Schrödinger equation and replace it with the boundary condition on the planar wavefunction

$$\frac{\partial}{\partial l} \ln \psi(l)|_{l=0} = -\tau \tag{9}$$

where τ is a suitable linear measure of the deviation from the critical wetting temperature. For this system we can identify $\theta_\pi = \tau/\Sigma$ and write the explicit form of the mid-point distribution function as

$$P(l; 0) = 2\Sigma(\theta_\pi - \alpha)\mathrm{e}^{2\Sigma(\alpha-\theta_\pi)l}. \tag{10}$$

Thus the divergence of the mean mid-point height $\langle l_0 \rangle$ and roughness $\xi_\perp$ as $\theta_\pi \to \alpha$ in the fluctuation-dominated regime of filling is characterized by critical exponents that are identical to the equivalent exponents describing the divergence of the interface height and roughness at critical wetting in 1 + 1 dimensions belonging to the strong-fluctuation regime [2, 6]. This remarkable connection extends to the full scaling form of the distribution function since for the planar system

$$P_\pi(l) = 2\Sigma\theta_\pi \mathrm{e}^{-2\Sigma\theta_\pi l} \tag{11}$$

which is clearly of the same form as $P(l; 0)$ with θ_π replaced by $\theta_\pi - \alpha$ [4].

The central question addressed in this Letter concerns the position dependence of the full probability distribution $P(l; x)$. In the limit corresponding to distances infinitely far from the wedge bottom (after the limit $L \to \infty$ has been taken, of course) we can identify

$$\lim_{x\to\infty} P(l; x) = P_\pi(l) = |\psi_0(l)|^2 \tag{12}$$

corresponding to the standard quantum mechanical result. Here we seek to understand how $P(l; x)$ changes its form from (10) to (11) as we move away from the wedge bottom. The full distribution function also allows us to calculate the equilibrium profile $\langle l(x) \rangle$, which has not previously been studied (see figure 1).

A formal expression for $P(l; x)$ follows from the expression for the partition function which explicitly integrates over the interface coordinate (written $l_x = l(x)$)

$$\mathcal{Z}_\mathcal{W} \propto \int_0^\infty \mathrm{d}l_0 \int_0^\infty \mathrm{d}l_x\, \mathcal{Z}_\pi\left(l_{-\mathrm{e}}, l_0; \frac{L}{2}\right) \mathrm{e}^{2\Sigma\alpha l_0} \mathcal{Z}_\pi(l_0, l_x; x) \mathcal{Z}_\pi\left(l_x, l_\mathrm{e}; \frac{L}{2} - x\right). \tag{13}$$

If we now take the limit $L \to \infty$ and substitute for the appropriate wavefunctions within the model defined by (9) we obtain

$$P(l; x) = \frac{\psi_0(l) \int_0^\infty \mathrm{d}l'\, \mathrm{e}^{2\Sigma\alpha l'} \psi_0^*(l') \mathrm{e}^{-x\tau^2/2\Sigma} \mathcal{Z}_\pi(l, l'; x)}{\langle 0|\mathrm{e}^{2\Sigma\alpha l}|0\rangle}. \tag{14}$$

To proceed we use the known closed-form expression for the planar propagator [7]

$$\mathcal{Z}_\pi(l, l'; x) = 2H(\tau)\tau \mathrm{e}^{-\tau(l+l')+\tau^2 x/2\Sigma} + \int_{-\infty}^\infty \frac{\mathrm{d}p}{2\pi} \mathrm{e}^{-p^2 x/2\Sigma} \left\{ \mathrm{e}^{\mathrm{i}p(l-l')} + \frac{\mathrm{i}p + \tau}{\mathrm{i}p - \tau} \mathrm{e}^{-\mathrm{i}p(l+l')} \right\} \tag{15}$$

where $H(\tau)$ denotes the usual Heaviside step function. The p integration can now be performed by a simple contour integration (see footnote in [7]) and the result inserted into the above

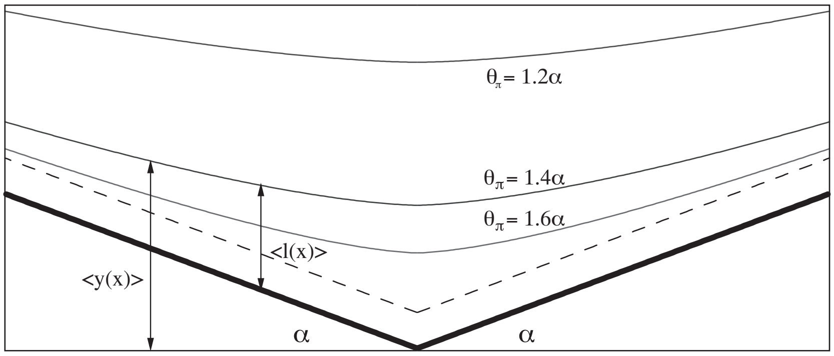

Figure 1. Plot showing the mean interfacial profile, $\langle l(x)\rangle \equiv \int_0^\infty l P(l;x)\,\mathrm{d}x$, computed by numerical integration. The plots have been generated with $\alpha = 0.3$, $\Sigma = 1$ and with θ_π having three values in multiples of α: 1.6, 1.4 and 1.2. The dashed curve shows the expected planar profile in the case $\theta_\pi = 1.6\alpha$.

expression for the wedge propagator (14). We find

$$P(l;x) = \frac{\psi_0(l)}{\langle 0|\mathrm{e}^{2\Sigma\alpha l}|0\rangle}\int_0^\infty \mathrm{d}l' \left(\mathrm{e}^{2\Sigma\alpha l'}\mathrm{e}^{-\tau l'}\mathrm{e}^{-\tau^2 x/2\Sigma}\left\{\sqrt{\frac{\Sigma}{2\pi x}}(\mathrm{e}^{-\Sigma(l-l')^2/2x} + \mathrm{e}^{-\Sigma(l+l')^2/2x})\right\}\right.$$
$$\left. +\tau \mathrm{e}^{\tau^2 x/2\Sigma - \tau(l+l')}\mathrm{erfc}\left(\sqrt{\frac{\Sigma}{2x}}(l+l') - \sqrt{\frac{x}{2\Sigma}}\tau\right)\right) \quad (16)$$

which only leaves some standard integrals. These are all of the form

$$I_1(a,b) = \int_0^\infty \mathrm{e}^{ax}\mathrm{e}^{-b^2x^2}\mathrm{d}x \Rightarrow I_1(a,b) = \frac{\sqrt{\pi}}{2b}\mathrm{e}^{a^2/4b^2}\mathrm{erfc}\left(-\frac{a}{2b}\right) \quad (17)$$

$$I_2(a,b,c) = \int_0^\infty \mathrm{e}^{ax}\mathrm{erfc}(bx+c)\,\mathrm{d}x \Rightarrow I_2(a,\pm b,c)$$
$$= \frac{1}{a}\left(\pm \mathrm{e}^{a^2/4b^2}\mathrm{e}^{-ac/b}\mathrm{erfc}\left(\mp\frac{a}{2b}+c\right) - \mathrm{erfc}(c)\right) \quad (18)$$

where (17) is a modification of a standard integral and (18) is analogous to one for normal error functions [8]. Note that the second integral is valid only for $b > 0$. Our final expression for the distribution function is written

$$P(l;x) = \Sigma(\theta_\pi - \alpha)\mathrm{e}^{2\Sigma(\alpha-\theta_\pi)l}\mathrm{e}^{2\Sigma\alpha x(\alpha-\theta_\pi)}\mathrm{erfc}\left(\sqrt{\frac{\Sigma x}{2}}(\theta_\pi - 2\alpha) - \sqrt{\frac{\Sigma}{2x}}l\right)$$
$$-\Sigma\alpha \mathrm{e}^{-2\Sigma\alpha l}\mathrm{e}^{2\Sigma\alpha x(\alpha-\theta_\pi)}\mathrm{erfc}\left(\sqrt{\frac{\Sigma x}{2}}(\theta_\pi - 2\alpha) + \sqrt{\frac{\Sigma}{2x}}l\right)$$
$$+\Sigma\theta_\pi \mathrm{e}^{-2\Sigma\theta_\pi l}\mathrm{erfc}\left(-\sqrt{\frac{\Sigma x}{2}}\theta_\pi + \sqrt{\frac{\Sigma}{2x}}l\right) \quad (19)$$

which is the main result of this Letter. It is straightforward, though tedious, to check that this result is fully normalized $\forall x$ and reduces to known cases (10) and (11) for $x \to 0$ and $x \to \pm\infty$ respectively.

From (19) we can evaluate the equilibrium profile $\langle l(x)\rangle$ using simple (numerical) integration. Some representative plots of this are shown in figure 1 and show the expected flatness of the profile in the central filled region. Notice also that as x is increased away from

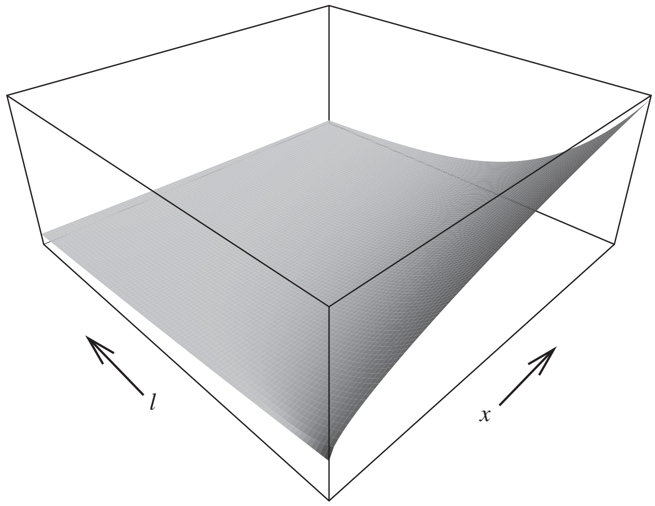

Figure 2. A plot of the probability density function for x and l with $\alpha = 0.3$, $\Sigma = 1$ and $\theta_\pi = 1.6\alpha$. Notice how the distribution becomes more localized as the distance from the wedge centre is increased (see the text).

the wedge apex the local distribution function $P(l; x)$ becomes increasingly localized (see figure 2).

A rather unexpected and intriguing feature of the full distribution function is the appearance of the term $(\theta_\pi - 2\alpha)$, which acts as the discriminant for the asymptotic decay of $P(l; x)$ as $x \to \infty$ at fixed l. Depending on the sign of this discriminant, the asymptotics of $P(l; x)$ pick up quite distinct contributions from the error functions. Explicitly for $\theta_\pi > 2\alpha$ we find

$$P(l; x \to \infty) \sim 2\Sigma\theta_\pi e^{-2\Sigma\theta_\pi l} + x^{-\frac{3}{2}} e^{-\frac{1}{2}\Sigma\theta_\pi^2 x} e^{-\Sigma\theta_\pi l} \times \left[\sqrt{\frac{8\Sigma}{\pi}} (2\Sigma\theta_\pi l - 1) \frac{\alpha(\alpha - \theta_\pi)}{\theta_\pi^2(\theta_\pi - 2\alpha)^2} \right] + \cdots \tag{20}$$

whilst for $\alpha < \theta_\pi < 2\alpha$ we find

$$P(l; x \to \infty) \sim 2\Sigma\theta_\pi e^{-2\Sigma\theta_\pi l} + e^{2\Sigma\alpha x(\alpha-\theta_\pi)} 2\Sigma[(\theta_\pi - \alpha)e^{2\Sigma(\alpha-\theta_\pi)l} - \alpha e^{-2\Sigma\alpha l}] + \cdots. \tag{21}$$

Defining an appropriate length scale ξ_F from the asymptotic decay of $P(l; x)$ we can thus identify $\xi_F \sim \xi_\parallel$ for $\theta_\pi > 2\alpha$ and $\xi_F \sim l_0$ for $\alpha < \theta_\pi < 2\alpha$ [1]. In terms of the contact angle we can express ξ_F as

$$\xi_F = \begin{cases} \dfrac{2}{\Sigma\theta_\pi^2} & \theta_\pi > 2\alpha \\ \dfrac{1}{2\Sigma\alpha(\theta_\pi - \alpha)} & \alpha < \theta_\pi < 2\alpha \end{cases} \tag{22}$$

which identifies $\theta_\pi = 2\alpha$ as a non-thermodynamic singularity prior to filling. Notice that ξ_F is continuous at the disorder point, $\theta_\pi = 2\alpha$.

To conclude our Letter we suggest that the location of the disorder point has a geometrical interpretation which is closely related to the thermodynamic condition for filling. One way

[1] Interestingly for $\alpha < \theta_\pi < 2\alpha$, ξ_F can be identified *precisely* as the the correlation length across the system defined via the curvature as $\sqrt{l(0)/l_{xx}(0)}$.

of deriving the thermodynamic result (1) is to notice that at $\theta_\pi = \alpha$ one may imagine a macroscopically flat meniscus of arbitrary size extending from one side of the wedge to the other, which satisfies the local Young equation at both regions of contact. This suggests that in the present grand canonical ensemble there is therefore no surface free-energy restriction to translations in the interface height up or down the wedge and that therefore the wedge is completely filled. This is indeed what is found when effective models are constructed to account for the breather mode which translates the interface up and down the wedge [3]. Now consider the fluctuation contributions to the free energy when the wedge is partially filled, corresponding to $\theta_\pi > \alpha$. These fluctuations are highly important for filling, since we know that the roughness and film thickness are comparable. Let us suppose that the interface runs down the left side of the wedge wall and leaves at some arbitrary point of contact. The most prevalent fluctuations of this type will leave the wall with local contact angle θ_π (relative to the tilted wall). Depending on the sign of the discriminant $(\theta_\pi - 2\alpha)$ such a configuration will either be directed towards or away from the other side of the wedge. Given that the configuration must eventually reach the other side of the wedge, we conclude that if $\theta_\pi > 2\alpha$ the length scale controlling this decay will not depend on the geometry and will be intrinsic to the properties of an interface at a flat wall (since the wedge bottom plays no role). In contrast, for $\theta_\pi < 2\alpha$ the geometry is essential and one may anticipate that a different length scale emerges. These qualitative remarks are entirely in keeping with the explicit results of the transfer matrix analysis. This geometrical picture is also suggestive that a similar phenomena happens in the three-dimensional wedge although it may be very difficult to prove this.

In summary we have derived a closed-form expression for the full position-dependent probability distribution function $P(l; x)$ for filling in 1 + 1 dimensions and have shown that a non-thermodynamic singularity precedes the filling transition. The simplicity of the exact condition for this disorder point suggests a geometrical interpretation in terms of fluctuation contributions.

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