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Finite-size effects on the approach of complete wetting

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Abstract. We perform an exact model calculation of the unbinding transition of a one-dimensional interface from a substrate on the approach of two-phase coexistence. This transition is modelled in a solid-on-solid (SOS) model with discrete columns which have a partition function calculated for a finite substrate area A. In the limits of large A and a small distance $|\Delta\mu|$ to coexistence, the partition function becomes a function of the the scaling variable $x = |\Delta\mu|^{2/3}A$. The interface-to-substrate distance l diverges as $l \propto |\Delta\mu|^{-\beta}$, with $\beta = -1/3$ if the two limits are taken at constant or diverging x. If x vanishes, a finite-size regime appears in which $\beta = -1$. A related interface model in continuous space was studied earlier by Kroll and Gompper and our scaling functions are identical to theirs.

1. Introduction

Consider a substrate which in contact with a coexisting liquid and vapour phase prefers to be covered by the liquid phase. If this substrate is in contact with a vapour phase which is undersaturated but close to the coexistence region, a microscopic liquid layer will already appear on the substrate. This layer will grow thicker as the vapour approaches the coexistence pressure and density such that, when the vapour has attained coexistence, a bulk liquid will have formed on the substrate. This growth mechanism is called complete wetting [1–3].

The divergence of the layer thickness l in complete wetting is characterized by an exponent β:

$$l \propto |\Delta\mu|^{-\beta} \tag{1.1}$$

where $|\Delta\mu|$ is the difference between the chemical potential of the undersaturated vapour and the chemical potential at liquid–vapour coexistence. This divergence has been studied extensively, mostly in the context of interface models such as the solid-on-solid (SOS) model in which the mechanism that drives the interface away from the wall becomes apparent [1–3]. That is, let $\bar{l}$ be the space-averaged height of an interface configuration and only allow an interface to fluctuate around $\bar{l}$ while keeping $\bar{l}$ fixed; the substrate will limit the extent of the local interface fluctuations around $\bar{l}$ since the interface cannot penetrate the substrate. This cut-off on the fluctuations will disappear with increasing $\bar{l}$ but the resulting gain in entropy has to be balanced by the cost of forming a liquid layer under thermodynamic conditions that favour the vapour phase. Such simple free-energy considerations predict $\beta = -1/3$ for $d = 2$ and $\beta = 0$ for $d = 3$. (The latter value implies a logarithmic divergence of the layer thickness. These predictions are for the case when there are no long-ranged forces and no random impurities in the system.) The predictions are supported by various model calculations [1–3] while we know of one affirmative experiment in $d = 3$ [4].

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These free-energy considerations assume that the interface collides with the substrate no matter how far away $\bar{l}$ is from the substrate. However, in the case of a finite substrate area A the extent of the interface fluctuations around $\bar{l}$ is limited by A when $\bar{l}$ is sufficiently far away from the substrate. Therefore, interfaces with a space-averaged height $\bar{l}$ far from the substrate will no longer collide with it. The entropy due to local fluctuations around $\bar{l}$ will be the same for all $\bar{l}$ sufficiently far away. Hence, the local fluctuations do not affect the relative statistical weights of such positions $\bar{l}$. We thus expect that, under these circumstances, the thickness of the liquid layer can be calculated as though the interface were rigid and completely flat. The divergence of the thickness of such an interface can trivially be calculated (as we will do in appendix A) and proceeds as the inverse of $|\Delta\mu|$, i.e. $\beta = -1$.

The entropy argument suggests that the average interface height of a rigid, flat interface forms a lower bound on the average height of an interface that can fluctuate around its space-averaged height $\bar{l}$. This can be proven rigorously for an SOS model in arbitrary dimensions, as we show in appendix A.

We now distinguish between two situations in which the limit $|\Delta\mu| \to 0$ can be taken: one can first take the limit $A \to \infty$ followed by $|\Delta\mu| \to 0$ or one can take the limit $|\Delta\mu| \to 0$ at finite A. In the first case we expect to observe the 'classical' value for β as the intrinsic width of the interface is no longer bounded by A; the interface will thus collide with the wall no matter how far away from the wall its space-averaged position $\bar{l}$ is. In the second case we expect $\beta = -1$ as the interface will no longer collide with the substrate for $|\Delta\mu|$ small enough. In the more general process of taking the limits $|\Delta\mu| \to 0$ and $A \to \infty$ simultaneously, we expect that if A increases quickly enough we will stay within the classical regime; if, however, A increases too slowly we expect to crossover into the non-classical or finite-size regime.

The existence of two such regimes has been observed before by Kroll and Gompper [5] in the framework of a renormalization-group (RG) calculation of wetting transitions. The two regimes have been demonstrated in an exact solution of a one-dimensional interface model in continuous space [5]. We aim to demonstrate this finite-size effect in an exact solution of a one-dimensional SOS model with discrete columns. This is the subject of the next section. Concluding remarks are given in section 3.

2. Complete wetting in a one-dimensional SOS model

We solve a one-dimensional SOS model with continuous column heights in the presence of an external field H (note that H plays the role of the chemical potential difference $|\Delta\mu|$ [1–3]) with periodic boundary conditions.

The Hamiltonian of the model reads

$$\mathcal{H}(\{h_i\}) = J \sum_{i=1}^{N} |h_{i+1} - h_i| + H \sum_{i=1}^{N} h_i \tag{2.1}$$

where $\{h_i\}$ is a set of N continuous height variables in the interval $0 < h_i < \infty$, $h_{N+1} = h_1$ and J and H are positive.

The partition function is given by

$$Z = \int_0^\infty \mathrm{d}h_1 \ldots \int_0^\infty \mathrm{d}h_N \, \exp\{-\beta\mathcal{H}\} \tag{2.2}$$

where $\beta = 1/k_B T$ and k_B is Boltzmann's constant (unfortunately, β also denotes the wetting exponent but there will be no danger of confusing the two).

The partition function can be written as the trace over the Nth power of a transfer matrix:

$$Z = \int_0^\infty \mathrm{d}h\, T^N(h,h) \tag{2.3}$$

with

$$T^N(h,h') = \int_0^\infty \mathrm{d}h_2 \ldots \int_0^\infty \mathrm{d}h_N \prod_{i=1}^{N} T(h_i, h_{i+1}) \tag{2.4}$$

with $h_1 = h$, $h_{N+1} = h'$ and

$$T(h,h') = \exp\{-\beta(J|h-h'| + Hh')\}. \tag{2.5}$$

Note that we may symmetrize the transfer matrix but the choice of (2.5) turns out to be equally convenient for our purposes. To calculate the trace we determine the eigenvalues λ of T from the eigenvalue equation

$$\int_0^\infty \mathrm{d}h'\, T(h,h')\psi(h') = \lambda\psi(h). \tag{2.6}$$

This integral equation can be turned into a differential equation [6] by differentiating it twice with respect to h, employing

$$\frac{\partial}{\partial h}\exp\{-\beta J|h-h'|\} = -\beta J \operatorname{sgn}(h-h')\exp\{-\beta J|h-h'|\} \tag{2.7}$$

$$\frac{\partial^2}{\partial^2 h}\exp\{-\beta J|h-h'|\} = (-2\beta J\delta(h-h') + \beta^2 J^2)\exp\{-\beta J|h-h'|\}. \tag{2.8}$$

With (2.8) we find that ψ satisfies

$$-2\beta J\exp\{-\beta Hh\}\psi(h) + \beta^2 J^2\lambda\psi(h) = \lambda\psi''(h) \tag{2.9}$$

where a prime stands for differentiation with respect to h. Boundary conditions at $h = 0$ for this differential equation can be constructed by differentiating (2.6) once with respect to h and taking $h = 0$. We furthermore impose that ψ vanishes for large h. In this way we have specified ψ, apart from a multiplicative constant, by

$$\begin{cases} -\psi''(h) + \left(-\dfrac{2\beta J}{\lambda}\exp\{-\beta Hh\} + \beta^2 J^2\right)\psi(h) = 0 \\ \psi'(0) = \beta J\psi(0) \\ \lim\limits_{h\to\infty}\psi(h) = 0 \end{cases} \tag{2.10}$$

which has to be solved on the positive axis $h > 0$.

The differential equation can be transformed into a Bessel equation by the substitution

$$x = \left(\frac{8J}{\lambda\beta H^2}\right)^{1/2}\exp\left\{\frac{-\beta Hh}{2}\right\}. \tag{2.11}$$

Note that, from an analogy with the Schrödinger equation, we do not expect solutions for $\lambda < 0$: this would be analogous to looking for bound states of a particle which experiences a purely repulsive external potential. However, we can include the possibility of such solutions by allowing x to be complex.

In terms of x, (2.10) reads

$$\begin{cases} x^2\psi''(x) + x\psi'(x) + \left(x^2 - \dfrac{4J^2}{H^2}\right)\psi(x) = 0 \\ \psi' = -\left(\dfrac{\lambda\beta J}{2}\right)^{1/2}\psi \qquad \text{at } x = \left(\dfrac{8J}{\lambda\beta H^2}\right)^{1/2} \\ \lim\limits_{x\to 0}\psi(x) = 0 \end{cases} \tag{2.12}$$

which has to be solved in the interval $0 < x < \sqrt{8J}/\sqrt{\lambda\beta H^2}$.

The general solution of this differential equation is a linear combination of $J_\nu(x)$ and $J_{-\nu}(x)$ with J_ν the Bessel function of order ν and $\nu = 2J/H$ [7]. However, any combination with $J_{-\nu}$ violates the boundary condition at $x = 0$ as $J_{-\nu}$ diverges at $x = 0$, whereas $J_\nu(0) = 0$ so $\psi = cJ_\nu$ with an arbitrary multiplicative constant c.

The spectrum of λ values can be inferred from the boundary condition at $x = \sqrt{8J}/\sqrt{\lambda\beta H^2}$. With the identity

$$J'_\nu = -\frac{\nu}{x}J_\nu + J_{\nu-1} \tag{2.13}$$

this boundary condition becomes

$$J_{\nu-1}\left(\left(\frac{8J}{\lambda\beta H^2}\right)^{1/2}\right) = 0 \qquad \nu = \frac{2J}{H} \tag{2.14}$$

i.e. the eigenvalues λ are given by the zeros of $J_{\nu-1}$. Since ν is positive, $J_{\nu-1}$ has an infinite number of simple real zeros. If we denote the positive zeros as $\{j_{\nu-1,i}\}$, $i = 1, 2, \ldots$, with $0 < j_{\nu-1,1} < j_{\nu-1,2} < \ldots$ (the negative zeros are given by $\{-j_{\nu-1,i}\}$) then the spectrum of the eigenvalues is

$$\lambda_i = \frac{8J}{\beta H^2}\frac{1}{j^2_{\nu-1,i}} = \frac{2\nu^2}{\beta J}\frac{1}{j^2_{\nu-1,i}} \tag{2.15}$$

where $\lambda_1 > \lambda_2 > \ldots$.

The trace of the Nth power of the transfer matrix is the sum over the Nth powers of the eigenvalues:

$$Z = \left(\frac{2}{\beta J}\right)^N \sum_{i=1}^{\infty}\left(\frac{\nu}{j_{\nu-1,i}}\right)^{2N}. \tag{2.16}$$

We will now inspect the sum in (2.16) in the limit $H \to 0$ and $N \to \infty$. Since the limit $H \to 0$ corresponds to $\nu \to \infty$ we inspect the behaviour of the $\{j_{\nu-1,i}\}$ for large ν. The positive zeros of J_ν can be expanded as [8]

$$j_{\nu,i} = \nu - 2^{-1/3}a_i\nu^{1/3} + \mathcal{O}(\nu^{-1/3}) \tag{2.17}$$

where the a_i are the zeros of the Airy function. These are all real, negative and ordered as $0 > a_1 > a_2 > \ldots$ [8].

Substituting $\nu - 1$ for ν in (2.17) we can expand the sum in (2.16) term by term as

$$\sum_{i=1}^{\infty}\left(\frac{\nu}{j_{\nu-1,i}}\right)^{2N} = \sum_{i=1}^{\infty}(1 + 2^{-1/3}a_i\nu^{-2/3} + \mathcal{O}(\nu^{-1}))^{2N}. \tag{2.18}$$

Eliminating ν in favour of $x \equiv N/\nu^{2/3}$ and taking the limit $N \to \infty$ yields

$$\sum_{i=1}^{\infty}\left(\frac{\nu}{j_{\nu-1,i}}\right)^{2N} \to \mathcal{Z}(x) \equiv \sum_{i=1}^{\infty}\exp\{2^{2/3}a_i x\} \qquad \text{for} \begin{cases} N \to \infty \\ \nu \to \infty \\ x = N/\nu^{2/3} \text{ fixed.} \end{cases} \tag{2.19}$$

In the limit $x \to \infty$ the first term of the sum in (2.19) will dominate and hence $\mathcal{Z}$ behaves as

$$\mathcal{Z}(x) \simeq \exp\{2^{2/3}a_1 x\}(1 + \mathcal{O}(\exp\{2^{2/3}(a_2 - a_1)x\})) \qquad \text{for } x \to \infty \tag{2.20}$$

whereas in the limit $x \to 0$ the sum will be determined by the behaviour of the terms for large i. In this limit we can replace the a_i by their asymptotic expansion for large i [8]: $a_i \simeq -(3\pi i/2)^{2/3} + \mathcal{O}(i^{-1/3})$ and replace the sum in (2.19) by an integral

$$\mathcal{Z}(x) \simeq \int_1^\infty \mathrm{d}y\, \exp\{-(3\pi y)^{2/3}x\} \qquad \text{for } x \to 0. \tag{2.21}$$

The integral is easily calculated and gives

$$\mathcal{Z}(x) \simeq \frac{1}{4\pi^{1/2}}\frac{1}{x^{3/2}} \qquad \text{for } x \to 0. \tag{2.22}$$

The average height l of the interface can be calculated as

$$l = -\frac{1}{\beta N}\frac{\partial}{\partial H}\log Z. \tag{2.23}$$

With

$$\frac{\partial}{\partial H} = \frac{2N}{3(2J)^{2/3}}\frac{1}{H^{1/3}}\frac{\partial}{\partial x} \tag{2.24}$$

we obtain in the limits $H \to 0$ and $N \to \infty$, while keeping x fixed,

$$l \simeq -\frac{2}{3\beta(2J)^{2/3}}\frac{1}{H^{1/3}}\frac{\partial}{\partial x}\log\mathcal{Z}(x) \qquad \text{for } \begin{cases} N \to \infty \\ H \to 0 \\ x = N/\nu^{2/3} \text{ fixed.} \end{cases} \tag{2.25}$$

This scaling form is the same as that obtained from the RG calculation of [5] (this can be seen from the authors' expression for $\langle z^q \rangle$ at the top of page 437 with $q = 1$, $\zeta = 1/2$, $\lambda_h = 3/2$ and $\xi_\parallel \sim h^{-2/3}$). This shows that l diverges as $l \sim H^\beta$ with $\beta = -1/3$ when the limits $N \to \infty$ and $H \to 0$ are taken at constant x.

We obtain the same exponent $\beta = -1/3$ in the 'classical regime' in which we first let N go to infinity at fixed H, i.e. $x \to \infty$, before we take H to zero. From (2.20) we find

$$l \simeq -\frac{2a_1}{3\beta J^{2/3}}\frac{1}{H^{1/3}} \qquad \text{for } \begin{cases} N \to \infty \\ H \to 0 \\ x = N/\nu^{2/3} \to \infty. \end{cases} \tag{2.26}$$

In the 'finite-size regime' $H \to 0$ at fixed N, i.e. $x \to 0$, we obtain from (2.22)

$$l \simeq \frac{1}{N\beta H} \qquad \text{for } \begin{cases} N \to \infty \\ H \to 0 \\ x = N/\nu^{2/3} \to 0 \end{cases} \tag{2.27}$$

and thus an exponent $\beta = -1$.

A solution of a spatially continuous version of the one-dimensional SOS model has been proposed previously by Kroll and Gompper [5]. The authors do not pursue the calculation to the point that their expression for Z can be compared with (2.16) or (2.19) directly. We show in appendix B, however, that their expression is, apart from a different metric prefactor, equal to (2.19). This confirms the expectation that finite-size scaling functions are universal for this transition.

3. Conclusions

We have demonstrated, by means of an exact calculation, the appearance of a finite-size regime in the unbinding of a one-dimensional interface. We calculated the scaling functions for the partition function and the layer thickness and showed that they depend on a single scaling variable only. A previous calculation [5] on a slightly different interface model yielded the same scaling functions and, apart from a metric prefactor, the same scaling variable. This correspondence confirms the universal character of the transition. Both models illustrate the predictions of a RG calculation [5].

We have proven that in a system of finite size the interface height diverges at least as fast as $\propto 1/|\Delta\mu|$ in dimensions larger than two. This shows that the crossover from the usual (infinite-size) regime to a finite-size regime also occurs in higher dimensions; this is because the infinite-system exponents predict a slower divergence.

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Appendix A.

We prove that the average height above a substrate of a SOS interface is always larger than the average height of an interface that is held completely flat.

The Hamiltonian of a d-dimensional SOS model is a straightforward generalization of (2.1):

$$\mathcal{H}(\{h_i\}) = J\sum_{(i,j)}|h_i - h_j| + H\sum_i h_i \tag{A.1}$$

where the height variables $\{h_i\}$ are now defined on a d-dimensional square lattice and the sum over (i, j) is over all the nearest-neighbour columns in the lattice. The lattice contains $A = N^d$ *columns and has periodic boundary conditions in all directions.*

The probability that a randomly chosen interface configuration has an average height h is

$$P(h; H) = \frac{w(h)\exp\{-\beta N^d Hh\}}{\int_0^\infty \mathrm{d}h\, w(h)\exp\{-\beta N^d Hh\}} \tag{A.2}$$

(because we will keep N fixed in this appendix we do not list it as an argument of P) with

$$w(h) = \int_0^{\infty,*} \mathrm{d}h_1 \ldots \int_0^{\infty,*} \mathrm{d}h_{N^d}\, \exp\{-\beta J\sum_{(i,j)}|h_i - h_j|\} \tag{A.3}$$

in which the stars indicate that the integration is restricted to those configurations $\{h_i\}$ that satisfy

$$\frac{1}{N^d}\sum_{i=1}^{N^d} h_i = h. \tag{A.4}$$

Since the number of configurations that satisfy (A.4) will become larger when h is chosen to be larger and the Bolzmann factor in (A.3) is invariant under translations of a configuration normal to the substrate, we have

$$\frac{\partial w(h)}{\partial h} > 0. \tag{A.5}$$

The probability that an interface that is forced to remain flat is at a height h is

$$p_{\mathrm{fl}}(h;\, H) = \frac{\exp\{-\beta N^d H h\}}{\int_0^\infty \mathrm{d}h\ \exp\{-\beta N^d H h\}}. \tag{A.6}$$

The average heights of the two types of interface are

$$l(H) = \int_0^\infty \mathrm{d}h\, h P(h;\, H) \tag{A.7}$$

$$l_{\mathrm{fl}}(H) = \int_0^\infty \mathrm{d}h\ h p_{\mathrm{fl}}(h;\, H) = \frac{1}{N^d \beta H} \tag{A.8}$$

and we can express the difference in average heights as

$$l - l_{\mathrm{fl}} = -\frac{1}{N^d \beta}\frac{\partial}{\partial H} \log \int_0^\infty \mathrm{d}h\ w(h) p_{\mathrm{fl}}(h;\, H). \tag{A.9}$$

Due to (A.5) and the fact that p_{fl} is a simple exponential with a decay length proportional to $1/H$, we know that

$$\frac{\partial}{\partial H} \int_0^\infty \mathrm{d}h\ w(h) p_{\mathrm{fl}}(h;\, H) < 0 \tag{A.10}$$

and thus

$$l > l_{\mathrm{fl}}. \tag{A.11}$$

From this it follows that in the limit $H \to 0$ at N fixed, l will diverge at least as fast as $1/H$, i.e. $\beta \leqslant -1$. From the physical picture sketched in the introduction it may safely be concluded that $\beta = -1$ and that (A.8) is the exact leading-order behaviour in the finite-size region (as is true for the one-dimensional model, see (2.27)).

Appendix B.

Kroll and Gompper [5] previously solved a one-dimensional SOS model in continuous space. We show that their solution for the partition function has the same form as the scaling function (2.19) for our model with continuous height variables but discrete columns.

In [5], the surfaces are represented by continuous functions $h(x)$, where h represents the height of the surface above the substrate at the position x along the substrate. For the case where the one-dimensional interface moves in an external field $U(h) = Hh$ the Hamiltonian reads

$$\mathcal{H}[h] = \int_0^L \mathrm{d}x\ \left\{\sigma\left(1 + h'(x)^2\right)^{1/2} + Hh(x)\right\} \tag{B.1}$$

where the substrate has a length L and the integral over the first term gives the surface tension σ times the area of the surface (the prime denotes differentiation with respect to x). This term is expanded with the argument that only the long-wavelength fluctuations with mild variations of h will be relevant. Thus one obtains

$$\mathcal{H}[h] = \int_0^L \mathrm{d}x\ \left\{\frac{\sigma}{2} h'(x)^2 + Hh(x)\right\} \tag{B.2}$$

omitting the h-independent contribution σL.

The partition function Z is a functional integral of the functional $\exp\{-\beta\mathcal{H}[h]\}$ over all contours that satisfy the periodic boundary condition $h(0) = h(L)$ and respect the presence of the substrate: $h(x) > 0$. Gompper and Kroll calculate this functional integral [9, 10] as

$$Z = \sum_i \exp\{-L\beta E_i\} \tag{B.3}$$

where the E_i are the eigenvalues of a Schrödinger-type equation:

$$-\frac{1}{2\beta\sigma}\phi_i''(h) + \beta(Hh - E_i)\phi_i(h) = 0 \tag{B.4}$$

and the boundary conditions are $\phi_i(0) = 0$ and $\lim_{h\to\infty}\phi_i(h) = 0$. The solutions of (B.4) are Airy functions:

$$\phi_i(h) = \mathrm{Ai}((2\beta^2\sigma H)^{1/3}h + a_i) \tag{B.5}$$

$$\beta E_i = -\frac{(\beta H)^{2/3}}{(2\beta\sigma)^{1/3}}a_i \tag{B.6}$$

where the $\{a_i\}$ are the zeros of the Airy function Ai, ordered as $0 > a_1 > a_2 > \ldots$. Hence, the partition function becomes

$$Z = \sum_{i=1}^{\infty} \exp\{2^{2/3}a_i x'\} \tag{B.7}$$

with the variable x' defined as

$$x' = \frac{\beta^{1/3}}{2\sigma^{1/3}}H^{2/3}L. \tag{B.8}$$

The partition function (B.7) is of the form (2.19) and the variables x and x' contain the characteristic combination $NH^{2/3}$ and $LH^{2/3}$ respectively, although with different metric prefactors.

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