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Wetting phenomena with long-range forces: Exact results for the solid-on-solid model with the $1/r$ substrate potential

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Restricted solid-on-solid model for two-dimensional wetting transition, with the substrate potential decaying as c/r, is solved exactly. The wetting transition, which is second order for $c=0$, becomes smeared for $c<0$. For $c>0$, a new type of first-order transition is found, with divergent correlation lengths, with $\nu_\parallel = 2\nu_\perp = 1$ (as opposed to $\nu_\parallel = 2\nu_\perp = 2$ for $c=0$).

One of the central issues in the theory of wetting phenomena[1,2] is the effect of long-range forces on the nature and order of the wetting transitions. For three-dimensional (3D) systems with van der Waals potentials, a large number of studies have been reported.[1,3] The existing theories are mostly mean field and incorporate both substrate- and adatom-adatom interactions. For 2D systems, the theoretical efforts have focused on the asymptotically power-law substrate-adatom potentials. Typically, the fluctuations are stronger in lower dimensions so that many mean-field conclusions are not valid in 2D. Some general scaling considerations are known.[2] However, most of the specific results have been derived within the Schrödinger equation approach,[4] corresponding to the zero-dimensional field theory and inspired by the continuous limit of the solid-on-solid models.[2,4–6] We will term the appropriate results[4] quantum mechanical (QM); see below.

In this work we present an analytic solution for the *restricted*[5] *solid-on-solid model* with potential decaying like c/r for large distances r from the substrate. We consider weak potentials (small $|c|$). For $c<0$ potentials, causing attraction of the interface to the substrate, we find that the wetting transition is no longer sharp. The asymptotic scaling from describing this rounding is derived. A rich structure is discovered, with a nonscaling shift in the transition point, and logarithmic factors in some regimes. Much of this structure has been missed in the QM model calculations.[4] For $c>0$ potentials, which repel the interface from the substrate the wetting transition remains sharp. However, it becomes first order but with divergent correlation lengths. We find $\nu_\parallel = 2\nu_\perp = 1$ for $c>0$, which should be compared with $\nu_\parallel = 2\nu_\perp = 2$ for $c=0$.[2] Nonscaling critical-point shift and logarithmic factors are also found for the $c>0$ case.

The model is defined on the square lattice of unit spacing, in the half space $0 \le x < \infty$, $|y| < \infty$. The solid-on-solid configurations are specified by the number $n_y \ge 1$ of $-$spins near the wall at $x=0,1,\ldots,n_y-1$ for each fixed-y row. All the spins to the right at $x=n_y, n_y+1, \ldots$, are $+$. For the *restricted* model, only configurations with $|n_y - n_{y-1}| = 0$ or 1 are allowed. The interfacial energy is modeled by

$$H/kT = \sum_y [U|n_y - n_{y-1}| - W\delta_{1n_y} + E(n_y)] \ , \qquad (1)$$

for allowed configurations. Here $U>0$ represents the surface tension contribution. Short-range interactions attracting the interface to the wall at $x=0$ are represented by the "contact" term with $W>0$. The long-range substrate potential must satisfy $E(r) \approx c/r$ for $r \to \infty$. We use the notation

$$0 < u \equiv e^{-U} < 1, \quad w \equiv e^{W} > 1 \ , \qquad (2)$$

and denote by n and m the n_y values in two consecutive rows. Then the transfer matrix T can be defined to have nonzero elements $T_{nm} = u^{|n-m|} w^{\delta_{1n}} e^{-E(n)}$ for $|n-m| = 0,1$. The eigenequations $\sum_m T_{nm} g_m = \lambda g_n$ take the form

$$g_n + u(g_{n+1} + g_{n-1}) = \lambda g_n e^{E(n)} \ \text{for}\ n \ge 2 \ , \qquad (3)$$

$$w(g_1 + u g_2) = \lambda g_1 e^{E(1)} \ . \qquad (4)$$

Here g_n are the eigenvector elements, and $E(n)$ remains to be specified. We choose

$$E(n) = \ln\left(1 + \frac{c}{n}\right), \quad n \ge 1 \ , \qquad (5)$$

which behaves as c/n for small c/n.

For the scaling analysis, we will regard c as a *small parameter*. Indeed, we wish to investigate the effect of the long-range tail in the potential on the wetting transition. The short-range structure of $E(n)$ must be a weak perturbation or else it may lead to additional effects depending on the precise form of $E(n)$. For the scaling analysis, the variables t and ε defined by

$$u^{-1} = u_c^{-1} - \frac{w}{w-1} t, \quad u_c \equiv \frac{w-1}{2-w} \ , \qquad (6)$$

$$\lambda_{\max} = (2u+1) + 2u\varepsilon \ , \qquad (7)$$

will also be assumed small. Here $\lambda_{\max}$ is the largest eigenvalue of T. For the $c=0$ system[5] and provided we fix w in the range $1 < w < \frac{3}{2}$, there is a wetting transition at $0 < u_c < 1$. For $t<0$ $[u < u_c(w)]$ there exists a "nonwet" solution with the finite layer of $-$ spins at the substrate. The eigenvector is given by

$$g_n \propto \gamma^n, \quad \gamma \equiv 1 + \varepsilon - \sqrt{\varepsilon(2+\varepsilon)} \ , \qquad (8)$$

with $\gamma < 1$ for $\varepsilon > 0$. For the eigenvalue we list only the scaling (small $|t|$) result

$$\varepsilon(t,c=0)\approx \tfrac{1}{2}t^2 \text{ or } 0 \tag{9}$$

for $t\leq 0$ and $t\geq 0$, respectively. Generally, there is a continuum of delocalized states for the λ range

$$1-2u\leq \lambda_{\text{delocalized}}\leq 1+2u \ . \tag{10}$$

The "nonwet" solution corresponds to the discrete state with $\lambda_{\max}>1+2u$. It disappears by merging with the continuum (10) as $u\to u_c^-$. In the scaling regime, the singular part of the free energy f_s and the longitudinal and transverse correlation lengths $\xi_\parallel$ and $\xi_\perp$ can be represented as[7]

$$f_s=(-\ln\lambda_{\max})_s=-\frac{2(w-1)}{w}\varepsilon \ , \tag{11}$$

$$\xi_\parallel\equiv\left[\ln\frac{\lambda_{\max}}{1+2u}\right]^{-1}\approx\frac{w}{2(w-1)}\varepsilon^{-1} \ ,$$
$$\xi_\perp\equiv(-\ln\gamma)^{-1}\approx(2\varepsilon)^{-1/2} \ . \tag{12}$$

Relation (9) then corresponds to the exponents $\nu_\parallel=2$ and $\nu_\perp=1$ for $c=0$. Our calculations for $c\neq 0$ outlined below indicate that relations (11) and (12) can be used for $c\neq 0$ as well.[8] The form of $\varepsilon(t,c)$ is, however, modified yielding new critical properties.

We now turn to the solution of the eigenproblem (3)-(5). We *do not* assume small ε, t, and c here [$c\neq -1$ is needed to avoid singularity in (5)]. The final result, the eigenvalue Eq. (20) below, is exact. Consider first the relation (3) with (5) without the boundary condition (4). We define the generating function

$$G(z)=\sum_{n=1}^{\infty}g_n z^{n-1} \ , \tag{13}$$

then multiply (3) by nz^{n-1}, and sum over $n=2,3,\ldots$.

After some algebra, the result can be represented as

$$[z^2-2(1+\varepsilon)z+1]G'+[2(z-1-\varepsilon)-\lambda c/u]G = G_0'-[2(1+\varepsilon)+\lambda c/u]G_0 \ , \tag{14}$$

where $G\equiv G(z)$, $G'\equiv dG(z)/dz$, $G_0\equiv G(0)=g_1$, and $G_0'\equiv G'(0)=g_2$. The G_0,G_0' terms on the right side of (14) make it homogeneous in G, as is (3) in g_n. Let $J(z)$ denote the solution of the differential equation obtained by replacing the right side of (14) by zero. Up to an arbitrary coefficient, we have

$$J(z)=(1-z\gamma)^{-1+p}(1-z\gamma^{-1})^{-1-p} \ , \tag{15}$$

where γ was defined in (8) and

$$p\equiv\frac{\lambda c}{2u\sqrt{\varepsilon(2+\varepsilon)}}\approx\frac{w}{2(w-1)}\frac{c}{\sqrt{2\varepsilon}} \ . \tag{16}$$

For later use, we indicated the critical region asymptotic form for p. Equation (14) can then be integrated to yield

$$G(z)=J(z)\left[G_0+\{G_0'-[2(1+\varepsilon)+\lambda c/u]G_0\}\int_0^z\frac{dv}{[v^2-2(1+\varepsilon)v+1]J(v)}\right] \ , \tag{17}$$

where we used $J(0)=1$. One can verify the consistency conditions $G(0)=G_0$ and $G'(0)=G_0'$. Thus, G_0 and G_0' are arbitrary at this stage. The overall coefficient in $G(z)$ is not important since (3) and (4) are homogeneous in g_n. However, the relative magnitude of the two linearly independent terms in (17) may be restricted in some regimes to yield solutions g_n which do not diverge exponentially for large n. One can show that for the λ range (10) there is a continuous spectrum of delocalized solutions. [In this regime γ is complex, with $|\gamma|=1$ and $\gamma^{-1}=\gamma^*$. The point $\varepsilon=0$ requires special care, as (15)-(17) do not apply there. We omit these mathematical technicalities.] We focus our consideration on the $\lambda>1+2u$ solutions corresponding to $\varepsilon>0$ and real $0<\gamma<1$. Both terms in (17) have singularities at $z=\gamma^{\pm 1}$. In order to have the "nonwet" solution with exponentially vanishing g_n for large n, we must select the relative coefficient to cancel the singularity at $z=\gamma$, to let the $z=\gamma^{-1}>1$ singularity dominate the convergence of the series (13). One can show that for the calculation of $\lambda_{\max}$, $p>-1$ can be assumed. The appropriate choice yields, after some algebra,

$$G(z)\propto(1-z\gamma)^{-1+p}(1-z\gamma^{-1})^{-1-p}\times\int_\gamma^z dv\left[\frac{1-v\gamma^{-1}}{1-v\gamma}\right]^p \ . \tag{18}$$

That (18) is regular at $z=\gamma$, can be most easily seen from the representation (up to a z-independent coefficient),

$$G(z)\propto {}_2F_1\left[2,1,2+p,\frac{\gamma-z}{\gamma-\gamma^{-1}}\right] \ , \tag{19}$$

in terms of the standard hypergeometric function which has a singularity in the complex plane of the fourth argument at 1, i.e., for $z=\gamma^{-1}$, but is analytic at the origin corresponding here to $z=\gamma$. Finally, we impose the boundary condition (4); recall that $g_2/g_1=G_0'/G_0$. After some algebra, one gets

$$\int_0^\gamma dv\left[\frac{1-v\gamma^{-1}}{1-v\gamma}\right]^p=\frac{uw}{\lambda(w-1)(1+c)} \ . \tag{20}$$

This is an equation for $\varepsilon(t,c;w)$. Note that λ, γ, and p depend on ε and w, via (6)-(8) and (16). We seek the largest solution satisfying $\varepsilon>0$ (with $p>-1$).

We now proceed to analyze (20) for *small* c, t, and ε. We decompose the integrand on the left side in the form

$$\left(\frac{1-v\gamma^{-1}}{1-v\gamma}\right)^p = 1+p\ln\frac{1-v\gamma^{-1}}{1-v\gamma}+\left[\left(\frac{1-v\gamma^{-1}}{1-v\gamma}\right)^p-1-p\ln\frac{1-v\gamma^{-1}}{1-v\gamma}\right] . \quad (21)$$

The first two terms can be integrated explicitly while in the third term we change the integration variable so that the left side of (20) takes the form

$$\gamma+p(\gamma^{-1}-\gamma)\ln(1-\gamma^2) + p^2\gamma(1-\gamma^2)\int_0^1 d\tau\frac{\tau^p-1-p\ln\tau}{p^2(1-\gamma^2\tau)^2} . \quad (22)$$

For small ε, we have $\gamma\approx 1-\sqrt{2\varepsilon}$. The second term in (22) can be replaced by $[wc/(w-1)]\ln\sqrt{8\varepsilon}$, where we used (16). The *coefficient* of the integral can be similarly approximated by $w^2c^2/(w-1)^2\sqrt{8\varepsilon}$. In the $\gamma\rightarrow 1$ limit the integral in (22) approaches a function $f(p)$ which is bounded for all $-1<p<\infty$, and in fact is given by $f(p)\equiv p^{-1}[\psi(p)+K+p^{-1}]$. Here $\psi(p)$ is the logarithmic derivative of the gamma function, $\psi(p)=d\ln\Gamma(p)/dp$, while $K=0.5752156649\ldots$ is Euler's constant. The right side of (20), when expanded, reduces to $1+t-c+\ldots$. In summary, the eigenvalue equation in the critical region is

$$-\sqrt{2\varepsilon}+\frac{wc}{w-1}\ln\sqrt{8\varepsilon}+\frac{w^2c^2f(p)}{(w-1)^2\sqrt{8\varepsilon}}\approx t-c , \quad (23)$$

with p given by (16). Note that we consistently kept the leading terms in $\sqrt{\varepsilon}$ and t. However, we kept terms of $O(c)$ in addition to $O(c\ln\varepsilon)$ or, equivalently, $O(c\ln c)$. The reason for this will become apparent later. Since $f(p)$ is bounded, the $c\rightarrow 0$ limit of (23) is straightforward. We get simply $-\sqrt{2\varepsilon}\approx t$, reproducing the known result[5] that the $\varepsilon>0$ solution exists only for $t<0$ with $\varepsilon\approx t^2/2$. For $c\neq 0$, let us replace all the $\sqrt{\varepsilon}$ dependence in (23) by c/p via (16). After some algebra, we get

$$L(p)\equiv\psi(p)+\frac{1}{2p}-\ln|p|\approx\frac{w-1}{w}\frac{\bar{t}}{c} \quad (24)$$

with

$$\bar{t}\equiv t-\frac{w}{w-1}c\ln|c|-\left[1+\frac{w}{w-1}\left(K+\ln\frac{w}{w-1}\right)\right]c . \quad (25)$$

By solving (24) for p as a function of $\bar{t}/\bar{c}$ and using (16), we will obtain a *universal* scaling form

$$\varepsilon\approx\bar{c}^2P^{(\pm)}(\bar{t}/\bar{c}), \quad \bar{c}\equiv wc/(w-1) \quad (26)$$

where there will be two functions $P^{(\pm)}=(8p^2)^{-1}$, corresponding to $c>0$ and $c<0$ (see Fig. 1). All the parametric dependence on w has been absorbed in the scale of $\bar{c}$ and in the shifted variable $\bar{t}$.

Let us consider first in detail the $c<0$ case. By (16), p must be negative. The function $L(p)$ defined in (24), is monotonically increasing for all $-1<p<0$. As $p\rightarrow -1^+$, $L(p)\rightarrow -\infty$ according to $L(p)\approx -(1+p)^{-1}$. For $p\rightarrow 0$, $L(p)\rightarrow +\infty$ according to $L(p)\approx -(2p)^{-1}$. Thus, for *each* $\bar{t}/\bar{c}$, there is a *unique* value of $-1<p<0$, determined by (24). There is no sharp wetting transition. The results of the QM model calculations by Kroll and Lipowsky[4] for the $c<0$ case can be summarized by the following: ε scales $\propto c^2$, and since for $c=0$ we have $\varepsilon\sim t^2$, t must scale with c. This is generally consistent with (26). However, the conclusion $\varepsilon\propto c^2$ is oversimplified. The function $P^{(-)}$ is shown in Fig. 1. For $\bar{t}/\bar{c}$ taking positive values of ~ 1 or any negative values including the limit $\bar{t}/\bar{c}\rightarrow -\infty$, $P^{(-)}$ remains finite, suggesting that indeed $\varepsilon\propto c^2$. This regime corresponds, via (25), to

$$t>\frac{w}{w-1}c\ln|c|-O(|c|)>0 ,$$

i.e., to the "wet" side of the $c=0$ critical region. Thus, the $c<0$ potential "pins" the otherwise unbound interface at the distance $\xi_\perp\sim|c|^{-1}$, and cuts the longitudinal fluctuations at $\xi_\parallel\sim c^{-2}$. However, for large positive $\bar{t}/\bar{c}$, $P^{(-)}\approx\frac{1}{2}(\bar{t}/\bar{c})^2$ and thus $\varepsilon\approx\frac{1}{2}\bar{t}^2$. This result is reminiscent of the $t<0$, $c=0$ relation (9), but with the shifted $\bar{t}$. To have $\bar{t}/\bar{c}$ large and positive, we must have $[w/(w-1)]c\ln|c|-t\gg O(|c|)$. Thus, t can be negative or positive but not exceeding $[w/(w-1)]c\ln|c|-O(|c|)$. This regime covers the "nonwet" side of the $c=0$ critical region and also includes the $c=0$ critical point $t=0$. Specifically,

$$\varepsilon(t\equiv 0,c<0)\approx\frac{w^2}{2(w-1)^2}c^2\ln^2|c| . \quad (27)$$

We now turn to the $c>0$ case. The appropriate p values must be positive. The function $L(p)$ defined in (24) is monotonically increasing for all $p>0$. As $p\rightarrow 0^+$, $L(p)\rightarrow -\infty$ according to $L(p)\approx -(2p)^{-1}$.

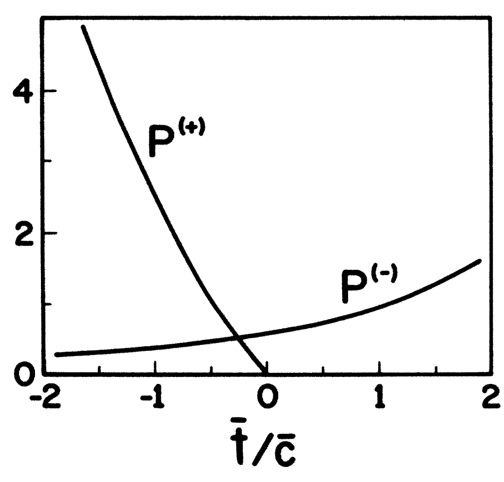

FIG. 1. The scaling functions $P^{(+)}$ and $P^{(-)}$, defined in (26), obtained by numerical solution of Eq. (25) (Ref. 9). Note that $P^{(-)}(-\infty)=\frac{1}{8}$.

However, for $p \rightarrow +\infty$, $L(p) \rightarrow 0^-$ according to $L(p) \approx -(12p^2)^{-1}$. Thus, there is a *unique* value of $p>0$ *only for* $\bar{t}/\bar{c}<0$. At $\bar{t}=0$, there is a *sharp* wetting transition. The critical-point shift with respect to the $c=0$ case, is given by the value of t corresponding to $\bar{t}=0$, which by (25) is $-[w/(w-1)]c|\ln|c||+O(c)$. For small negative $\bar{t}$, we find

$$\varepsilon \approx \tfrac{3}{2}\bar{c}(-\bar{t}) \;, \tag{28}$$

while for $\bar{t} \geq 0$ there is no "nonwet" solution and $\varepsilon \equiv 0$. The derivative $d\varepsilon/d\bar{t}$ is discontinuous at $\bar{t}=0$, reminiscent of the bulk first-order transitions. However, the correlation lengths diverge, by (12), with $\nu_{\parallel}=1$ and $\nu_{\perp}=\frac{1}{2}$ on the "nonwet" side ($\bar{t}<0$). They remain infinite in the "wet" phase ($\bar{t} \geq 0$). For negative $\bar{t}/\bar{c} \sim -1$, we find $\varepsilon \approx \bar{c}^2 P^{(+)}(\bar{t}/\bar{c})$, with $P^{(+)} \sim 3$ (see Fig. 1).[9] However, for large negative $\bar{t}/\bar{c}$, we find $\varepsilon \approx \frac{1}{2}\bar{t}^2$, similarly to one of the asymptotic limits in the $c<0$ case. To have such behavior, t must be negative and satisfy $|t|-[w/(w-1)]\times c|\ln|c|| \gg O(c)$, which corresponds to the "nonwet" side of the $c=0$ critical region.

In summary, we found a new type of wetting transition (for $c>0$) with kinklike free energy (i.e., surface tension) singularity, but with divergent correlation lengths $\xi_{\perp}$ and $\xi_{\parallel}$. The experimental verification of the wetting theories in three dimensions is still rather limited[1] and for the first-order wetting only the surface tension (capillary rise) measurements seem to confirm *some* mean-field-type predictions. It is therefore important to find and classify new wetting mechanisms which may then be looked for in more realistic (but not exactly solvable) three-dimensional models.

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[8]Regarding relation (12) for $\xi_{\parallel}$, it no longer represents the leading gap correlation length for $c<0$ since there are additional bound states. However, based on universality we will use this definition to study the scaling of the parallel correlations. In relations (8), g_n is modified by a power-law prefactor which does not, however, effect the identification $\xi_{\perp}=(-\ln\gamma)^{-1}$ in (12), via $g_n \sim \exp[-n/\xi_{\perp}+O(\ln n)]$.

[9]Formally, $P^{(+)}(\bar{t}/\bar{c}) \equiv 0$ for $\bar{t}/\bar{c}>0$.