Universality classes for the critical wetting transition in two dimensions

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Universality classes and critical exponents for the wetting transition in two dimensions are determined with the use of a continuum planar solid-on-solid model. Effective substrate potentials \( BU(f) < 0 \) falling off no slower than \( f^{-2} \), where \( f \) is the distance from the substrate, are shown to lead to wetting transitions at finite potential strength \( B \). For potentials which go to zero at least exponentially fast with \( f \), the interface free energy \( F \) is analytic in the thermal scaling field \( t \). In the case of longer-range substrate potentials with a finite first moment, \( F \) remains proportional to \( t^\gamma \) to leading order, but higher-order nonanalytic terms in \( t \) appear, while in the borderline case \( |U(f)| \sim f^{-2} \), \( F \) has an essential singularity at the wetting transition. For potentials going to zero more slowly than \( f^{-2} \), there is no transition at finite \( B \). It is shown that \( F \sim B^{2/(a+1)} \) for \( B \rightarrow 0^+ \) for potentials asymptotically proportional to \( f^{-2-a}, a < 0 \).

I. INTRODUCTION

Our understanding of multilayer adsorption phenomena on attractive substrates is based largely on the analysis of simple Ising lattice-gas models originally introduced by de Oliveira and Griffiths.1 These models exhibit a wide range of phenomena, including layering, roughening, and wetting, many of which have been observed experimentally, and are believed to yield a realistic picture of the systemsatics of the surface phase diagrams.2 In particular, lattice-gas models should provide a good framework for investigating the so-called critical wetting transition, where the thickness of the adsorbed film diverges and the adsorbate-gas interface becomes diffuse.

However, analysis of even these relatively simple lattice-gas models beyond mean-field theory has proven to be very difficult, and it has been found useful to consider a simpler, closely related class of models based on the Onsager-Temperley sheet, or solid-on-solid (SOS) approximation. The SOS approximation provides a way of focusing attention on the interface fluctuations, which play the crucial role in adsorption phenomena, while ignoring irrelevant bulk fluctuations. The resulting models consist of a structureless (i.e., zero width) adsorbate-gas interface bound to a flat surface (the substrate) by a potential well. The wetting transition corresponds to the thermal unbinding of the interface from the well. For short-range potentials these models have proven to be remarkably successful in treating the wetting transition and have been found in fact to yield the correct critical singularities in two bulk dimensions \( (d = 2) \).3,4

Even for \( d = 2 \), however, no attention has been paid to long-range potentials and in particular, no attempt has been made to determine universality classes as a function of the range of the interaction potential. This is an important point; in the wetting problem the adatom-adatom and the adatom-substrate interaction is generally of the van der Waals type. This implies long-range tails in the lattice-gas interaction potentials. These long-range tails may well alter the form of the critical singularities at the wetting transition.

In this paper we investigate this problem for \( d = 2 \). The Hamiltonian we consider is given by

\[
H = \int d^{d-1} \! x \left[ \frac{1}{2} \left( \nabla f \right)^2 + BU(f) + hf \right],
\]

where \( f(x) \geq 1 \) denotes the perpendicular distance of the interface from point \( x \) on the substrate, located at \( f = 1 \). The energy contribution from the first term in (1) is proportional to the extra length of an interface which is not flat. The second term is the potential well, which localizes the interface below the transition temperature. In the last term \( h \) is proportional to \( \mu - \mu_0 \), the difference of the chemical potential of the adatom gas from its value at coexistence. In lattice-gas terms, this term is the bulk field. The critical wetting transition occurs at coexistence, i.e., \( h = 0 \).

The potential \( U(f) \) in (1) is given by the local free-energy density of a rigid interface located a distance \( f \) from the substrate in the original lattice-gas model. At \( T = 0 \), \( U(f) \) can be evaluated exactly. In the case of strong substrate potentials for which there is complete wetting at coexistence, \( U(f) \) is positive. Equation (1) then implies complete wetting for all finite \( B \). In the more interesting case of intermediate substrate potential strengths, \( U(f) \) can be negative. Generally, when a mean-field analysis of the original lattice-gas model predicts a state with finite coverage at coexistence, \( U(f) \) will be negative with a minimum at finite \( f \). This is the case we consider here. In particular, we parametrize the large-\( f \) behavior as

\[
U(f) \propto -1/f^{2+a},
\]

van der Waals interactions in \( d = 2 \) correspond then to \( a = 1 \).

In Sec. II, after briefly discussing the transfer-matrix method in one dimension, the classes of potentials

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$U(f) \leq 0$ which lead to wetting transitions at finite $B = B^*$ are characterized and discussed. First, in order to make explicit the scaling behavior of the interface free-energy density $F_s$ at the critical wetting transition, results for the square-well potential

$$U(f) = \begin{cases} -1, & 1 < f < R \\ 0, & R < f \end{cases} \tag{2}$$

are reviewed. Next, it is shown in general that potentials $U(f) \leq 0$ with a finite first moment

$$\int_1^\infty f |U(f)| \, df < \infty$$

have a wetting transition at finite $B = B^*$. In this case a perturbative method is used to determine the dependence of $F_s$ on the thermal scaling field $\delta B = B - B^* > 0$. It is shown that if

$$\int_1^\infty e^{\alpha f} |U(f)| \, df < \infty$$

for some $\alpha > 0$, $F_s$ is analytic in $\delta B$, while if

$$\int_1^\infty df f^n |U(f)| \, df = \infty$$

for some $n > 1$, some derivations of $F_s$ diverge as the wetting transition is approached from below ($\delta B > 0$). Potentials asymptotically proportional to $f^{-2}$ are considered next. Taking $U(f) = -f^{-2}$ it is possible to obtain an exact solution, and we find that

$$F_s \sim \exp(-\delta B^{-1/2})$$

at the wetting transition. The transition is quite unusual in this case in that an infinite number of bound states breaks off from the continuum spectrum of the transfer matrix simultaneously at the transition.

Potentials which drop off asymptotically more slowly than $f^{-2}$ are considered in Sec. III. It is shown that the interface is bound to the substrate for all $B > 0$ in this case so that no wetting transition occurs. Further, we show that for

$$|U(f)| = f^{-2-a}, \quad a < 0,$$

we have

$$F_s \sim B^{2/(a+1)}$$

for $B \to 0^+$. In particular, for $|a| = 3 \{U(f) \sim f\}$ this result yields the dependence of $F_s$ on the bulk field $h \equiv B$

$$F_s \sim h^{2/3},$$

a result obtained by other methods in Sec. II.

II. CRITICAL WETTING TRANSITION

A. Square-well substrate potentials and scaling behavior

For $d = 2$, the partition function for (1) is rather easy to evaluate using transfer-matrix methods. In particular, the transfer-matrix technique allows us to replace the functional integration by an eigenvalue problem. In this one-dimensional case the eigenvalue problem can be reduced to a one-particle quantum-mechanical problem. This approach has been discussed by several authors and is simply related to Feynman's path-integral formulation of quantum mechanics.\(^3\)\(^-\)\(^5\)

For the present problem, the interface free-energy density $F_s$ is given in the thermodynamic limit by the lowest-energy eigenvalue of the Schrödinger equation

$$\left[-\frac{1}{2\beta^2} \frac{d^2}{df^2} + B U(f) + h f\right] \Phi_s(f) = E_s \Phi_s(f), \tag{3}$$

where $\beta = (k_B T)^{-1}$ and $f \geq 1$. Denoting the ground-state solution by subscript 0, we have

$$F_s = E_0 \tag{4}$$

and furthermore,

$$\langle f \rangle = \frac{\int_1^\infty df \Phi_s^*(f) \Phi_s(f)}{\int_1^\infty \Phi_s^*(f) \Phi_s(f)} = \frac{\partial F_s}{\partial h} \equiv m_s \tag{5}$$

At $h = 0$, the existence of a bound-state solution ($E_0 < 0$) to (3) means that $\langle f \rangle$ is finite, i.e., that the interface is localized and that we have finite coverage. When the bound state ceases to exist, $E_0 \to 0$ and $\langle f \rangle \to \infty$, signaling the critical wetting transition.

For the potential (2) the behavior near the critical wetting transition is easily determined in closed form. For $h = 0$ and $B = B^*$ we find $E_0 = 0$ for

$$\beta = \beta_0 = \frac{\pi}{2(R - 1)(2B^*)^{1/2}} \tag{6}$$

Deviations from the critical point are given by $t, h,$ and $\delta B$ (all greater than 0), where $t = B - B_0$ and $\delta B = B - B^*$. In fact, direct calculation shows that\(^4\)

$$F_s = t^2 \Omega(h/t^2) \tag{7}$$

where the scaling function $\Omega$ has the properties

$$\Omega(0) = \text{const} \quad \text{and} \quad \Omega(x) \to x^2/3, \quad \text{as} \quad x \to \infty.$$

Thus $F_s \sim t^2$ for $h = 0$ and $F_s \sim h^{2/3}$ for $t = 0$. As can already be seen directly from (3), $\delta B$ is a so-called nonordering field and

$$m_1 \equiv \frac{\partial F_s}{\partial B} \sim \frac{\partial F_s}{\partial t} \tag{8}$$

is a nonordering density.\(^6\) In other words, $\delta B$ has the same scaling dimension as $t$. Generally, the interface free-energy density $F_s$ has the scaling form

$$F_s = t^{2-a_1} \Omega(h/t^b) \tag{9}$$

and the exponent governing the behavior of $m_1 \sim t^{b_1}$ is called $\beta_1$.\(^7\) In the present case we therefore have $a_1 = 0$ and $\Delta = 3$, and since $\beta_1 = 2 - a_1 - \Delta$, $\beta_1 = -1$. For the singular part of the nonordering density $m_1 \sim t^{b_1}$ we obtain $b_1 = 1 - a_1 = 1$, and similarly

$$\frac{\partial^2 F_s}{\partial B^2} \equiv t^{-a_1} \sim t^{-a_1}, \tag{10}$$
implying $\gamma_{11}=0$ for $h=0$. Other exponents follow by differentiation and various scaling relations can be derived in the usual manner.

There are thus two independent exponents, $a_*$ and $\Delta$, and in general they may both be determined by considering (3) with $h=0$ if we determine both the ground-state energy $E_0$ and the asymptotic behavior of the corresponding wave function $\Phi_0(f)$. $a_*$ is determined by (4) and $\beta_*$, and therefore $\Delta$ is determined by (5). This is the approach we shall apply here.

**B. General substrate potentials with finite first moment**

For general $U$, it is not possible to solve Eq. (3) explicitly. However, general properties of the spectrum and the dependence of the lowest eigenvalue on $t$ can be determined as follows. Equation (3) has the generic form

$$\frac{d^2\varphi}{dx^2} - \kappa^2 \varphi - BU(x) \varphi = 0,$$

(6)

where $\kappa^2 = -E_0$ and $x \equiv f \geq 1$. We are interested in the ground-state solution to (6), and in particular how $\kappa^2 \rightarrow 0$ as $\delta B \rightarrow 0$+, where $\delta B = B - B^*$ and $\kappa^2(B^*) = 0$. To lowest order, $\delta B$ is equivalent to the thermal scaling field $t$. (The factor $2\beta^2$ has been adsorbed in $B$.)

Utilizing the boundary condition $\phi(1) = 0$, (6) can be rewritten as a Fredholm integral equation

$$\varphi(x) = B \int_1^\infty G(x,y) \left| U(y) \right| \varphi(y) dy,$$

(7)

where the Green's function

$$G(x,y) = \frac{1}{2\kappa} \left( e^{-\kappa|x-y|} - e^{2\kappa(x-y)} \right),$$

is the finite solution of

$$\frac{d^2G}{dx^2} - \kappa^2 G = -\delta(x-y),$$

(8)

with boundary condition $G(1,y) = 0$. Defining $\psi(x) = \left| U(x) \right|^{1/2} \varphi(x)$, (7) reduces to a Fredholm equation with symmetric kernel $K(x,y)$:

$$\psi(x) = B \int_1^\infty K(x,y) \psi(y) dy,$$

(9)

where

$$K(x,y) = \left| U(x) \right|^{1/2} G(x,y) \left| U(y) \right|^{1/2}.$$  

The trace of the integral operator on the right-hand side of (9) is given by

$$\int_1^\infty K(x,x) dx.$$  

Since

$$K(x,x) = \frac{1}{2\kappa} \left( 1 - e^{2\kappa(x-1)} \right) \left| U(x) \right| \\
< (x-1) \left| U(x) \right| < x \left| U(x) \right|$$

for all $\kappa \geq 0$, the trace is bounded by

$$\int_1^\infty x \left| U(x) \right| dx,$$

independent of $\kappa$. If this integral is finite, the integral operator in (9) is trace class, and it follows immediately that (9) has a real, discrete, infinite spectrum $0 < B_0 < B_1 < \cdots$ (the operator is positive) with a point of accumulation at $B^{-1} = 0$. Each eigenvalue has finite multiplicity and the eigenvectors $\{ \varphi_n \}, n = 0,1, \ldots, \infty$, form a complete orthonormal basis on $[1, \infty)$.

In fact, in the present case we know further that the eigenvalues are not degenerate. This can be seen most easily by considering (7). Let $\phi_1$ and $\phi_2$ be two eigenfunctions corresponding to an eigenvalue $B$. A straightforward calculation utilizing (6) and (7) shows that

$$\frac{d}{dx}(\phi_1' - \phi_2') = 0,$$

or equivalently $\phi_1' - \phi_2' = \text{const}$, where primes denote derivatives with respect to $x$. However, $\phi_1(1) = \phi_2(1) = 0$ so that the constant is zero. It follows that $\phi_1'$ is proportional to $\phi_2'$. For potentials asymptotically proportional to $x^{-2-a}$, the above results hold for $a > 0$. It is important that the bound leading to the requirement

$$\int_1^\infty x \left| U(x) \right| dx \text{ finite}$$

is independent of $\kappa$ since we are interested in the behavior of the spectrum in the $\kappa \rightarrow 0$ limit. In particular, since the above results hold for $\kappa = 0$, we see that the wetting transition occurs at $B = B^* = B_0$ ($\kappa = 0$). For $B < B_0$ ($\kappa = 0$) there is no bound state in the transfer-matrix spectrum for any $\kappa > 0$. At $B = B^*$ the first bound state appears, and for $B > B^*$ this state is at finite $\kappa$. Furthermore, as noted above, this state is not degenerate.

In order to determine the behavior of thermodynamic quantities at the transition, we need the dependence of $\kappa^2$ on $\delta B = B - B^*> 0$. To do this we use a perturbative approach, expanding about the $\kappa = 0$ state at $B = B^*$. For $\kappa > 0$, the solution $\phi(x)$ to Eq. (6) is proportional to $e^{-\alpha x}$ as $x \rightarrow \infty$. Writing $\phi(x) = \theta(x) e^{-\alpha x}$, $\theta(x)$ satisfies the equation

$$\frac{d^2\theta(x)}{dx^2} - 2\kappa \frac{d\theta(x)}{dx} - BU(x) \theta(x) = 0,$$

or, choosing a normalization $\theta(1) = 1$ for $x \rightarrow \infty$, the Volterra equation

$$\theta(x) = 1 - \frac{B}{2\kappa} \int_x^\infty (e^{-2\kappa(y-x)} - 1) U(y) \theta(y) dy.$$  

(11)

From the above results it follows that this eigenvalue problem has a complete set of orthonormal eigenfunctions with weight function $\left| U(x) \right|$ and corresponding eigenvalues $B_0(\kappa)$. In particular, this is true for $\kappa = 0$, and $B_0(\kappa=0)$ is the critical potential strength for the wetting transition. If $\left| U(x) \right| = x^{-2-a}$, the eigenfunctions for $\kappa=0$ can be determined explicitly. Denoting the $\kappa=0$ eigenfunctions by $\varphi_n$, $n = 0,1, \ldots, \infty$, and the $\kappa=0$ eigenvalues by $B_n$, we have

$$\varphi_n(x) \sim x^{-1/2} J_{1/4}(2 B_n^{1/2} x^{-a/2})$$

where $J_{1/4}$ is a Bessel function of order $1/4$. The eigenvalues $B_n$ are determined by $J_{1/4}(2 B_n^{1/2} x^{-a/2}) = 0$. For decreasing $a, B_0$ is a monotonically decreasing function such
that $B_0 \to \frac{1}{4}$ for $a \to 0^+$. Now let $B = B^* + \delta B \ [B^* = B_0(\kappa = 0)]$ and consider $\kappa$ and $\delta B$ infinitesimal. To lowest order in $\delta B$ and $\kappa$, (11) can be rewritten as

$$\theta(x) = 1 + B^* \int_x^\infty dy (y - x) U(y) \theta(y) + F(x), \quad (12)$$

where

$$F(x) = \frac{\delta B[\theta_0(x) - 1]/B^*}{2\kappa} \int_x^\infty dy \left[ e^{-2\kappa (y - x)} - 1 + 2\kappa (y - x) \right] \times U(y) \theta_0(y) dy,$$

and $\theta_0(x)$ is the solution of (11) for $\kappa = 0$ and $B = B_0(\kappa = 0) = B^*$. Expand $\theta(x)$ in the set of $k = 0$ eigenfunctions:

$$\theta(x) = \sum_{n=0}^\infty a_n \theta_n(x).$$

Recalling that $\theta(\infty) = 1$,

$$1 = \sum_{n=0}^\infty a_n \theta_n(\infty), \quad (13)$$

so that (12) leads to the equation

$$0 = \sum_{n=1}^\infty a_n (1 - B^*/B_n) [\theta_n(\infty) - \theta_n(x)] + F(x). \quad (14)$$

Multiplying (14) by $|U(x)| \theta_0(x)$ and integrating from 1 to $\infty$ we obtain

$$\gamma \int_1^\infty dx |U(x)| \theta_0(x) + \int_1^\infty dx |U(x)| \theta_0(x) F(x) = 0, \quad (15a)$$

where

$$\gamma = \sum_{n=1}^\infty a_n (1 - B^*/B_n) \theta_n(\infty).$$

Multiplying (14) by $|U(x)| \theta_k(x), k \neq 0$, and integrating we get

$$\gamma \int_1^\infty dx |U(x)| \theta_k(x) - a_k (1 - B^*/B_k)$$

$$\quad + \int_1^\infty dx |U(x)| \theta_k(x) F(x) = 0 \quad (15b)$$

Since $\theta_n(1) = 0$, (14) implies $\gamma + F(1) = 0$. Equation (15a) therefore becomes

$$\int_1^\infty dx |U(x)| \theta_0(x) [F(x) - F(1)] = 0, \quad (15a')$$

and (15b),

$$a_k (1 - B^*/B_k) = \int_1^\infty dx |U(x)| \theta_k(x) [F(x) - F(1)], \quad k \neq 0. \quad (15b')$$

We use (15a') to determine $\kappa(\delta B)$. Equation (15b') can then be used to determine $\theta_k$ for $k \geq 1$, and $a_0$ can then be determined from (13).

Integrating by parts, (15a') reduces to

$$\int_1^\infty dx \theta_0(x) F'(x) = 0,$$

where

$$F'(x) = \frac{\delta B}{B^*} \theta_0(x)$$

$$- B^* \int_x^\infty (e^{-2\kappa (y - x)} - 1) U(y) \theta_0(y) dy.$$ This implies

$$\delta B / \theta_0(\infty) = B^* \int_1^\infty dx \theta_0'(x) \int_x^\infty (e^{-2\kappa (y - x)} - 1) U(y)$$

$$\quad \times \theta_0(y) dy. \quad (16)$$

First assume that

$$\int_1^\infty e^{ax} |U(x)| \ dx < \infty \quad (17)$$

for some $a > 0$. This implies that $U(x)$ goes to zero at least exponentially fast for $x \to \infty$. In this case the exponential $e^{-2\kappa (y - x)}$ can be expanded and all resulting integrals (to all orders in $\kappa$) converge because of the cutoff provided by $U(x)$. It follows that

$$\delta B = \sum_{n=1}^\infty b_n \kappa^n$$

or, inverting,

$$\kappa = \sum_{n=1}^\infty c_n \delta B^n$$

so that $\kappa$ and therefore $F_1$ is analytic in $\delta B$ (or the thermal scaling field $t$). Assume now that

$$\int_1^\infty x^n |U(x)| \ dx \ < \infty$$

but

$$\int_1^\infty x^{n+1} |U(x)| \ dx = \infty$$

for some $n \geq 1$. Restricting attention to the class of potentials for which $|U(x)| \sim x^{-2-a}$ for large $x$, the above assumption implies $n - 1 < a \leq n$. To see what happens in this case consider first $n = 1, 0 < a \leq 1$ and rewrite the right-hand side of (16) as

$$\kappa U_0(\infty) + B^* \int_1^\infty dx \theta_0'(x) \int_x^\infty dy [e^{-2\kappa (x-y)} + 2\kappa (y-x) - 1] \times U(y) \theta_0(y).$$

We break up the remaining integral into parts by choosing a constant $c$, independent of $\kappa$, such that $\theta_0(x) \sim \theta_0(\infty) = 1$ for $x > c$. Defining

$$Y(x, y) = e^{-2\kappa (x-y)} + 2\kappa (y-x) - 1,$$

we write the integral as

$$\int_1^c dx \theta_0'(x) \left[ \int_x^c Y(x, y) U(y) \theta_0(y) dy + \int_x^\infty Y(x, y) U(y) dy \right] + \int_c^\infty dx \theta_0'(x) \int_x^\infty Y(x, y) U(y) dy.$$

The first integral has an analytic expansion in $\kappa$, starting with $\kappa^2$. The second and third integrals are not analytic in $\kappa$. The leading $\kappa$ dependence in these two integrals is the same and can be determined as follows. Taking $|U(x)| \sim x^{-2-a}$
for \( x > c \) and defining \( z = \kappa(y - x) \),

\[
\int_1^\infty dx u_0(x) \int_e^\infty dy Y(x,y)U(y) = -\kappa^{1+a} \int_1^\infty dx u_0(x) \int_{\kappa(x-c)}^\infty dz \left( e^{-2z} + 2z - 1 \right) \frac{1}{(z + \kappa x)^{2+a}}.
\]

For \( 0 < a < 1 \) we can take the limit \( \kappa \to 0 \) in the integral. The resulting contribution is proportional to \( \kappa^{1+a} \). The third integral can be handled in a similar fashion. Collecting results we have

\[
\delta \varphi_B = b_1 \kappa - b_2 \kappa^{1+a} + O(\kappa^2)
\]
or, inverting,

\[
\kappa = c_1 \delta \varphi_B + c_2 (\delta \varphi_B)^{1+a} + \cdots,
\]

implying

\[
F_s \sim t^2 + \alpha t^{2+a} + \cdots.
\]

The leading term in \( F_s \) is still \( t^2 \), but the next-to-leading term, \( t^{1+a} \), is not analytic in \( t \). For \( a = 1 \), a similar analysis yields

\[
\delta \varphi_B = b_1 \kappa - b_2 \kappa^2 \ln | \kappa | + \cdots
\]
or

\[
\kappa = c_1 \delta \varphi_B + c_2 (\delta \varphi_B)^2 \ln | \delta \varphi_B | + \cdots,
\]

and a free energy

\[
F_s \sim t^2 + \alpha t^3 | \ln t | + \cdots,
\]

so that the next-to-leading term contains a logarithmic correction.

For general \( a > 0 \) the analysis is similar and one finds

\[
F_s = \sum_{n=0}^a d_n t^{2+n} + d_n t^{2+a} + \cdots
\]

for noninteger \( a \), where \( [n] \) is the largest integer smaller than \( a \), and

\[
F_s = \sum_{n=0}^{a-1} d_n t^{2+n} + d_n t^{2+a} | \ln t | + \cdots
\]

for integer \( a \).

The leading term in the free-energy density \( F_s \) is therefore \( t^2 \) for all potentials \( U(x) \leq 0 \) such that (10) is fulfilled.\(^{14}\) Furthermore, for potentials such that (17) holds, \( F_s \) is analytic in \( t \), while if (17) is not fulfilled, \( F_s \) is not analytic in \( t \) and some derivatives of \( F_s \) will diverge at the wetting transition. In particular, for the physically relevant class of potentials \( | U(x) | \sim x^{-2-a}, x \to \infty \), \( F_s \) is given by (18) or (19) depending upon whether \( a > 0 \) is an integer or not.

Since the ground-state wave function is proportional to \( e^{-\kappa x} \) for \( x \to \infty \) for all potentials satisfying (10), the leading divergence of \( m_1 \) is given by \( \kappa^{-1} \). \( m_1 \) therefore has the asymptotic divergence \( t^{-1} \) for all potentials in this class, but there exist in general nonanalytic correction terms given by the above analysis.

Finally, we note that at and above the wetting transition \( F_s \sim t^{2/a} \) for all \( a > 0 \). This is understandable since in this case the asymptotic behavior of the wave function is determined by the magnetic field term, regardless of the form of the substrate potential.

These results characterize the wetting transition for potentials which drop off faster than \( x^{-2} \) at large distances. In the next section it is shown that there is no wetting transition for potentials which drop off more slowly than \( x^{-2} \). In this case the interface remains pinned to the substrate at all finite temperatures. Potentials asymptotically proportional to \( x^{-2} \) are a borderline case. There is also a wetting transition, but of a very different nature than that described above.

C. \( U(x) = -x^{-2} \)

For \( U(x) = -x^{-2} \), Eq. (6) can be solved explicitly.\(^{15}\) A bound-state solution

\[
\phi(x) \sim x^{1/2} K_{i\lambda}(\kappa x)
\]

exists for \( B > B^* = \frac{1}{4} \), where \( K_{i\lambda} \) is a modified Bessel function of imaginary order \( i\lambda \) and \( \lambda = (B - B^*)^{1/2} \). For small argument,

\[
K_{i\lambda}(\kappa x) \sim \sin[\lambda \ln(\kappa x/2)]
\]

so that the boundary condition \( \phi(1) = 0 \) implies

\[
\lambda \ln(\kappa/2) = -n \pi
\]

or

\[
\kappa = 2 \exp(-n \pi / \lambda),
\]

where \( n \) is a positive integer. In contrast to the previously studied cases, infinitely-many bound states break off from the continuum simultaneously at the wetting transition. These bound states form a point spectrum with a point of accumulation at zero. The interface free energy \( F_s \) now has an essential singularity\(^{16}\)

\[
F_s \sim \exp(-t^{-1/2})
\]
at the wetting transition and since \( \phi(x) \sim e^{-\kappa x} \) for \( x \to \infty \), \( m_1 \) diverges as

\[
m_1 \sim \exp(t^{-1/2}).
\]

III. LONG-RANGE POTENTIALS

AND PINNING FIELDS

Potentials which drop off more slowly than \( x^{-2} \) for large \( x \) have sufficiently long tails to pin the interface for all finite values of \( B \). This is proven below for the restricted class of potentials asymptotically proportional to \( x^{-2-a}, a < 0 \). It is also shown that

\[
F_s \sim B^{2/a} | a |
\]

for \( B \to 0^+ \) in this case. This restriction on the form of the potential is in no way necessary; however, the physically interesting potentials are of this form and it is straightforward to extend the analysis to other potentials.
First, we consider potentials with \(-2 < a < 0\) so that 
\[ U(x) \rightarrow 0 \] 
for \( x \rightarrow \infty \). Both upper and lower bounds are constructed which show that the ground-state energy \( \kappa^2 \) satisfies

\[ \kappa^2 \geq B^{2/|a|} \]

in this case. Next we consider pinning fields 
\[ U(x) \sim x |a|^{-2} \] 
with \(|a| > 2\). In this case the bound-state energy eigenvalues \( E \) are positive, and using similar methods we again find that the ground-energy eigenvalue

\[ E_0 \sim B^{2/|a|} \]

In both cases the coverage \( m_4 \) diverges as

\[ m_4 \sim B^{-1/|a|} \]

for \( B \rightarrow 0^+ \).

A. \( U(x) \sim -x^{-2-a}, \quad -2 < a < 0 \)

In order to obtain an upper bound on the ground-state energy (a lower bound on \( \kappa^2 \)), we consider the mini-max problem equivalent to (6) (Refs. 8, and 11)

\[ \kappa^2 = \max \int_1^\infty dx [-(\phi')^2 + B\phi^2x^{-2-a}] \]

where \( \phi(x) \) belongs to the space of continuous functions such that \( \phi(1) = 0 \) and \( \phi(x) \rightarrow 0 \) for \( x \rightarrow \infty \). Since \( \phi(x) \sim e^{-ax} \) for \( x \rightarrow \infty \), a suitable choice of trial wave function for (20) is

\[ \phi(x) = e^{\kappa(1-x)} + e^{2\kappa(1-x)} \]

Utilizing \( \phi(x) \) in (20) we have

\[ \kappa^2 \geq \frac{-\langle (\phi')^2 \rangle + B\int_1^\infty dx \phi^2x^{-2-a}}{\langle \phi^2 \rangle} \]

where \( \langle \phi^2 \rangle = \int_1^\infty dx \phi^2 \).

To leading order in \( \kappa \), the ground-state energy, can be obtained using the mini-max principle based on (23).

\[ E = \int_1^\infty dx \phi^2 \]

for solutions \( \phi(x) \) of (22). An upper bound on \( E_0 \), the ground-state energy, can be obtained using the mini-max principle based on (23). Thus

\[ E_0 = \min \int_1^\infty dx \phi^2 \]

for general continuous functions \( \phi(x) \) such that \( \phi(1) = 0 \) and \( \phi(x) \rightarrow 0 \) for \( x \rightarrow \infty \). Noting that the asymptotic behavior of a solution \( \phi(x) \) to (22) is

\[ \phi(x) \sim \exp(-\gamma x|a|^{-1/2}), \]

where \( \gamma \approx \sqrt{B} \), a suitable choice of trial wave function is

\[ \phi(x) \sim \exp(-\gamma x|a|^{-1/2} - 1) - \exp(-2\gamma x|a|^{-1/2} - 1) \]

Employing this choice with \( \gamma \approx \sqrt{B} \), we find to leading order in \( \gamma \)

\[ E_0 \leq C_5 B^{2/|a|} \]

where \( C_5 \) is a positive constant.

Similarly, a lower bound can be obtained utilizing (21) and (23) as in the previous section (IIIA). One finds that the functional dependence of the upper bound is again
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