Critical wetting: the domain of validity of mean field theory
E. Brézin, B.I. Halperin, S. Leibler

To cite this version:

HAL Id: jpa-00209658
https://hal.archives-ouvertes.fr/jpa-00209658
Submitted on 1 Jan 1983

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Critical wetting : the domain of validity of mean field theory

E. Brézin, B. I. Halperin (*) and S. Leibler

Service de Physique Théorique, Orme des Merisiers, 91191 Gif sur Yvette Cedex, France

(Reçu le 21 décembre 1982, accepté le 16 mars 1983)

Abstract. — Below the consolute point of a binary mixture, the presence of a wall which adsorbs preferentially one of the two liquids may induce a new transition, the wetting transition. Above the wetting temperature $T_w$, the phase adsorbed by the wall forms a macroscopic film. This transition has recently been analysed in the framework of mean field theory, and for a range of values of the parameters one observes a second order transition. In this work we construct a Ginzburg criterion for this transition in order to determine the upper critical dimension $d_c$ (above which mean field theory remains quantitatively correct). For that purpose we study the correlations near $T_w$; long range correlations parallel to the wall appear with an associated length which diverges near $T_w$ as $1/(T_w - T)$. The determination of the effective interactions of the modes responsible for long range correlations gives rise to delicate problems. The analysis reveals that $d_c = 3$ (i.e. three-dimension bulk, with two-dimensional surface).

1. Introduction and summary.

The physics of phase separation in a binary fluid mixture in the vicinity of an adsorbing wall is very rich. In particular for some temperature $T_w$ below the consolute point $T_c$ (i.e. in the phase-separated system) a new transition takes place : the formation of a film of one of the phases in contact with the wall. This transition from partial to complete wetting, first studied by Ebner and Saam [1] and by Cahn [1], has been observed recently in a few beautiful experiments [2].

If we use instead the equivalent magnetic language, we can say that the effect of the wall is described by the surface temperature $c$ and the surface magnetic field $h$. In particular, if the bulk boundary conditions far from the wall favour one phase (for instance down-
spins), and if $h_j$ is positive then, at sufficiently low
temperature, a layer of up-spins with a finite thickness
(determined by $h_j$, $c$ and $T$) may « partially wet »
the surface. For some value of the temperature $T_w$
the thickness of the wetting layer diverges : up-spins
« completely wet » the surface (1).

The phase diagram obtained in the mean field
approximation as a function of the physical parameters
$h_j$, $c$ and $T$ (and eventually a bulk field $h$)
is rather complicated. The (partial to complete)
wetting transition can occur as a continuous or dis-
continuous transition according to the values of the
parameters, with an even more complicated tricritical
point in between as noted recently by Pandit, Wortis
and Schick and by Nakanishi and Fisher [4]. In this
work we focus our attention on the behaviour near a
critical point $M$ of the critical wetting line OA ($h = 0$)
of figure 1.

Our main goal was the determination of the upper
critical dimension, above which mean field theory is
also quantitatively correct. The specific results of
mean field theory that we have considered are :

(i) the correlations in the directions parallel to the
wall which diverge with a characteristic length

$$\xi_\parallel \approx \frac{\zeta_0}{T - T_c},$$

(ii) the distance of the interface to the wall, which
diverges as

$$z_0 \approx \ln (T - T_c),$$

(iii) the additional surface tension of the interface
$\Delta \Sigma$, due to its binding to the wall, which behaves as

$$\Delta \Sigma(T) \approx - \sigma_0 (T - T_c)^2.$$

We show that the upper critical dimension $d_e$ is
three, i.e., a three-dimensional bulk liquid with a
two-dimensional interface. In three dimensions, there-
fore, one would expect corrections to the above mean
field theory results sufficiently close to $T_w$. The ana-
alysis for three dimensions will be presented in a sub-
sequent publication [5].

By way of comparison with the mean field formulæ,
we quote the results for a two-dimensional system
(one-dimensional interface) obtained from the « solid-
on-solid » model [6]

$$\xi_\parallel \approx \zeta_0 (T - T_c)^{-1}; \quad z_0 \approx (T - T_c)^{-1};$$

$$\Delta \Sigma \approx -(T - T_c)^2.$$

It should be emphasized that the analysis in this
paper presupposes that all interactions are short-
ranged. The van der Waals forces present in real
systems are not short-ranged in this sense. Sufficiently
close to $T_w$ the van der Waals forces will become
important, and then even the mean field behaviour
will be modified.

1.1 OUTLINE OF THE METHOD. — The procedure which
we have followed, is quite standard. We first char-
acterize the mean field correlation functions.
Specifically, we take a continuous Landau-Ginzburg-
Wilson Hamiltonian for the system; the mean field
profile is the stationary point of this Hamiltonian, and
correlations are obtained from the second variation of
the Hamiltonian at the mean field solution. The dia-
agonalization of the corresponding Green function
operator may be done explicitly. In the vicinity of the
wetting temperature $T_w$ (in the region of partial
wetting $T < T_w$) long wavelength excitations of the
interface appear (the so-called capillary waves) which
are responsible for a diverging correlation length $\xi$.
This length goes to infinity as $\xi_0 = \zeta_0 (T - T_c)^{-1}$;
this shows already that the wetting transition is
somewhat different from usual critical points, where
the correlation length diverges as $| T - T_c |^{-1/2}$,
in mean field theory.

The next step consists of the use of a generalized
Ginzburg criterion which reveals the upper critical
dimension [7]. Let us review how the argument goes
for an ordinary Curie point. The first correction to
mean field theory is given by

$$\xi^{-2} = \zeta_0^{-2} |T - T_c| - u_0 \int_{\text{h.i.}} \frac{d^2q}{q^2 + T - T_c^0}. \quad (1)$$

Taking into account the shift of $T_c^0$ due to fluctuations
(i.e. we redefine $T_c$ by $\xi^{-1}(T_c) = 0$), we obtain

$$\xi^{-2} = \zeta_0^{-2} |T - T_c| + u_0 (T - T_c) \times$$

$$\times \int_{\text{h.i.}} \frac{d^2q}{q^2 + T - T_c}.$$

(1) In using the magnetic analogy, one must disregard
effects which arise from the discreteness of the underlying
lattice. Thus, for $d > 3$, there will be no capillary waves at
the interface of the discrete magnetic system, and our calcu-
lations, which depend on capillary fluctuations, would not
be applicable to that system. For $d = 3$ the discrete system
is probably equivalent to the continuum system considered
here, provided the temperature is well above the roughening
temperature of the magnetic interface.
which shows that above four dimensions \( v \) remains fixed to \( 1/2 \), since the integral in (2) converges at low wavenumber down to \( T_w \) (it also gives an estimate of the size of the critical region below four dimensions). This calculation relies on two ingredients: (a) the mean field Green’s function \([q^2 + T - T_c]^{-1}\); (b) the order-parameter self-coupling \( \omega_0 \). For the wetting problem we have determined the Green’s function, and in particular its singular long wavelength modes near \( T_w \). In addition, we had to determine the effective interaction of these singular modes. A naive calculation, which would take into account the singular modes only, would lead to conclude that the upper critical dimension is five. However, it is shown below that it is incorrect to consider only the singular modes, even near \( T_w \). The non-singular modes have the effect of modifying the self-coupling (or effective interactions) of the long-wavelength modes and these effective interactions vanish as \((T_w - T)^2\). As a consequence we obtain that the upper critical dimension is three (instead of five). Let us note that above three dimensions the interface remains smooth up to \( T_w \). Indeed the capillary waves of this interface tend to restore near \( T_w \) the translation invariance which is broken by the semi-infinite geometry: the interface becomes delocalized. However for \( d \) greater than three, these capillary waves leave this liberated interface smooth. The three-dimensional situation is more subtle. For a discrete model, or for an adsorbed solid, the wetting transition may occur above or below the roughening temperature \( T_R \) of the infinite system. In our continuum model \( T_R \) is zero: the capillary waves are always roughening the surface.

From the analysis of the effective interactions we construct an interface displacement model for a \((d - 1)\)-dimensional interface (see final section, below). This model will be further analysed in a forthcoming publication [5].

2. The model and the mean field profile.

We consider a Landau-Ginzburg-Wilson Hamiltonian \( A (= \beta H) \) in \( d \) dimensions for a one component order parameter \( \phi(z; p_1, p_2, ..., p_{d-1}) \) below the bulk miscibility temperature \( T_r \) (Curie point in the magnetic analogy), and limited to the semi-infinite half-space \( z > 0 \):

\[
A = \int_{z > 0} d^d x \left\{ \frac{1}{2} (\nabla \phi)^2 - \frac{\tau}{2} (\phi^2 - M^2) + \frac{g}{4!} (\phi^4 - M^4) \right\} + \\
+ \int d^{d-1} \rho \left\{ \frac{1}{2} c \phi^2(0, \rho) - h_1 \phi(0, \rho) - \left[ \frac{1}{2} c M^2 - h_1 M \right] \right\} \quad (3)
\]

in which the normalization is such that \( \tau = -(T - T_c)/T_c - M \) is the bulk spontaneous magnetization \( (M = (6 \tau/g)^{1/2} \) at the mean field level), \( h_1 \) is the surface field and \( c \) the surface temperature (\( c \) is assumed to be positive throughout this work; this is the normal situation for a semi-infinite magnetic model, or for a mixture in which the surface layer has less tendency to phase separate than the bulk). As usual we shall speak as if \( \tau, h_1 \) and \( c \) were the physical parameters, but the true temperature or fields are related to these effective parameters with some distortion. The partition functions, the correlation functions, etc... are defined by statistical averages with the Boltzmann weight \( \exp{-A(\phi)} \), over the order-parameter distribution. In fact the Hamiltonian (3) is still ill-defined: \( \nabla \phi \) will have in general a \( \delta \)-function at \( z = 0 \) and the product \( \theta(z) (\nabla \phi)^2 \) is not defined. We shall restrict ourselves to order parameters \( \phi(z, \rho) \) which satisfy the boundary condition

\[
\frac{\partial \phi}{\partial z}(z, \rho) \bigg|_{z=0} = c \phi(0, \rho) - h_1 . \quad (4)
\]

This has the effect to make \( \frac{\delta A}{\delta \phi(z, \rho)} \) well defined down to \( z = 0 \) since

\[
A(\phi + \delta \phi) - A(\phi) = \int_{z > 0} d^d x \, \delta \phi \left( - \nabla^2 \phi - \tau \phi + \frac{1}{6} g \phi^3 \right) + \\
+ \int d^{d-1} \rho \, \delta \phi \left( - \frac{\partial \phi}{\partial z} \bigg|_{0} + c \phi(0, \rho) - h_1 \right) + O(\delta \phi^2)
\]

and the surface variation term disappears if (4) is used.

Within the mean field approximation we look for a fluctuationless solution, i.e. a minimum \( \phi_c(z, \rho) \) of \( A \) which satisfies the boundary condition (4) and approaches the bulk magnetization \( -M \) far from the wall. It is the solution of the equation \( \delta A/\delta \phi = 0 \),
and since there is a translation invariance in the
directions parallel to the wall, \( \Phi_e \) is a function of the
single variable z, satisfying the differential equation

\[
- \frac{d^2 \Phi_e}{dz^2} - \tau \Phi_e + \frac{1}{6} g \Phi_e^3 = 0. \tag{5}
\]

A first integration, taking into account the asymptotic
condition at \( z = \infty \), yields

\[
\left[ \frac{d\Phi_e}{dz} \right]^2 = \frac{1}{12} g (\Phi_e^2 - M^2)^2. \tag{5'}
\]

We follow here Pandit and Wortis \cite{3a} and represent
graphically equation (5') with a plot of \( \Phi_e' \) as a function
of \( \Phi_e \) (keeping in mind that \( \Phi_e(z) \) is decreasing from
the wall to infinity). On figure 2 one can see the two
parabolas corresponding to equation (5') and the
straight line B which is the image on this plot of the
boundary condition (4). If the slope of B is larger than
the slope of D, the tangent at the point \( (\Phi_e = M, \Phi_e' = 0) \), there is a single intersection of B with the
parabolas. This occurs for

\[
c > \sqrt{2 \tau}
\]

which is the condition for having a second-order
transition. We shall restrict ourselves to this case.
If the temperature is increased, \( \tau \) and \( M \) decrease,
and, if \( h_i \) and \( c \) remain fixed, the point \( (\Phi_e = M, \Phi_e' = 0) \) will move towards the line B. When it reaches
the line B the thickness of the wetting layer diverges.

This occurs when \( (cM - h_i) \) vanishes, i.e. for a tem-
perature \( T_w(h_i, c) \) defined by

\[
T_w = 1 - \frac{T_w}{T_c} = \frac{gh_i^2}{6c^2}.
\]

For temperatures in-between \( T_w \) and \( T_c \) the
thickness of the up-spin layer remains infinite and a
finite negative magnetic field \( h \) bulk is necessary to keep
the interface within any specified finite distance
of the wall. The profile is depicted on figure 3.

The explicit solution to (5) is of course (for \( T < T_w \))

\[
\Phi_e(z) = -M \tanh \left[ \frac{\tau}{\sqrt{2}} (z - z_0) \right]
\]

with \( z_0 \) determined by (4):

\[
\left[ \frac{\tau}{\sqrt{2}} \right] \left[ 1 - \tanh \left( \frac{\tau}{\sqrt{2} z_0} \right) \right] = cM \tanh \left( \frac{\tau}{\sqrt{2} z_0} \right) - h_i. \tag{8}
\]

When \( T \) approaches \( T_w \), \( M \rightarrow M_w = h_i/c \), and \( z_0 \)
diverges as

\[
z_0 \sim \frac{1}{\sqrt{2 \tau}} \ln \left[ \frac{1}{T_w - T} \right]. \tag{9}
\]

Finally we can compute the surface tension which is
the free energy per unit area. (Note that we have
subtracted from our definition (3) of the free energy
the (constant) contribution of a free interface).

\[
\Delta \Sigma = \frac{A}{T^2-1} = \int_0^\infty dz \left\{ \frac{1}{2} \left( \frac{d\Phi_e}{dz} \right)^2 - \frac{\tau}{2} (\Phi_e^2 - M^2)^2 + \right. \]

\[
\left. + \frac{\tau}{4} (\Phi_e^4 - M^4) \right\} + \frac{1}{2} c (\Phi_e^2 - M^2) - h_i (\Phi_e - M)
\]

in which \( \Phi_e = M \tanh \sqrt{\pi/2} z_0 \) is the magnetization
on the wall. It is then elementary using (5) and (8), to
derive

\[
\Delta \Sigma = \left[ \frac{\tau}{12} (\Phi_e^3 - 3 M^2 \Phi_e + 2 M^3) + \right. \]

\[
\left. + \frac{1}{2} c (\Phi_e^2 - M^2) - h_i (\Phi_e - M) \right] \tag{10a}
\]

\[
\Delta \Sigma = \left[ \frac{\tau}{12} (\Phi_e^3 - 3 M^2 \Phi_e + 2 M^3) + \right. \]

\[
\left. + \frac{1}{2} c (\Phi_e^2 - M^2) - h_i (\Phi_e - M) \right] \tag{10b}
\]
and to verify that equation (9) for \( z_0 \) is nothing but
\[
\frac{\partial \Sigma}{\partial \Phi} = 0. 
\]
Expanding \( \Sigma \) near \( T_w \) we obtain
\[
\Delta \Sigma(T) \approx -\frac{3}{2 g} T_w^2 \left( \frac{T_w}{T_c} \right)^2 \frac{1}{c - \sqrt{2} \tau_w}. 
\]
If we define the exponents \( \nu \) and \( \alpha \) in the usual way, as
regulating \( \zeta_\perp \) and the surface tension, mean field yields
\( \nu = 1, \alpha = 0 \); hyperscaling is satisfied for an (interface)
\( \text{dimension 2, i.e. a bulk dimension three. It}
\]
is thus not surprising that we shall obtain in the following
sections \( d_c = 3 \).

3. Mean field correlation functions.

In order to characterize the correlations, we have to go
beyond the single saddle-point approximation which
we used at the mean field level. Gaussian fluctuations
of the order parameter around the profile \( \Phi_e \) have
to be considered. Let us write
\[
\Phi(z, \rho) = \Phi_e(z) + \chi(z, \rho) 
\]
and the boundary condition (4) imposes upon \( \chi \) the condition
\[
\frac{\partial \chi}{\partial z}(z, \rho) \bigg|_{z=0^+} = c \chi(0, \rho) = 0. 
\]
We expand the Hamiltonian \( A \) to second order in \( \chi \)
\[
A = A_e + \frac{1}{2} \int \chi(z_1, \rho_1) \chi(z_2, \rho_2) \times 
A^{(2)}(z_1, z_2; \rho_1 - \rho_2) + O(\chi^3) 
\]
in which
\[
A^{(2)} = \frac{\delta^2 A}{\delta \Phi \delta \Phi} = \delta(z_1 - z_2) \delta^{d-1}(\rho_1 - \rho_2) \times 
\#
- \frac{\partial^2}{\partial z_1^2} - V_\perp^2 \frac{3 \tau}{\cosh^2 \left( \frac{\sqrt{2}}{2} (z - z_0) \right)} + 2 \tau. 
\]
The Green function \( G(x_1, x_2) \) is given by
\[
G(x_1, x_2) = \langle \Phi(x_1) \Phi(x_2) \rangle - \langle \Phi(x_1) \rangle \langle \Phi(x_2) \rangle = [A^{(2)}]^{-1} 
\]
an operator kernel inverse being meant of course in the last equation. We shall give explicitly below the
result for \( G \), but it is helpful to characterize the eigenmodes of \( G \), or of \( A^{(2)} \). A Fourier transform on the
\( (d - 1) \) variables \( \rho \) parallel to the surface is naturally
performed first and we then look for eigenmodes of \( A^{(2)} \)
\[
- \frac{d^2}{d z^2} - \frac{3 \tau}{\cosh^2 \left( \frac{\sqrt{2}}{2} (z - z_0) \right)} + q_\parallel^2 + 2 \tau \times 
\]
\[
\varphi_n(z) = \varphi_n(q_\parallel) \varphi_n(z) 
\]
with \( \varphi_n \) regular at infinity, and constrained by (12)
at the origin. With the notations
\[
y = \sqrt{2} (z - z_0) 
\]
we have
\[
\varphi_n = q_\parallel^2 + 2 \tau \left( 1 + \frac{\omega_n}{4} \right) 
\]
and the excited states \( \varphi_n(z) \exp(iq_\parallel \cdot \rho) \)
with eigenvalues \( \epsilon_n \):
\[
\epsilon_n = q_\parallel^2 + 2 \tau \left( 1 - \frac{\omega_n}{4} \right) 
\]
In addition there is a continuous spectrum \( \omega_n > 0 \).
Therefore the spectrum of \( A^{(2)} \) consists of the lowest
states \( \varphi_0(z) \exp(q_\parallel \cdot \rho) \) with eigenvalue
\( \epsilon_0 = q_\parallel^2 + 2 \tau \left( 1 - \frac{\omega_0}{4} \right) \) and the excited states \( \varphi_n(z) \exp(iq_\parallel \cdot \rho) \)
with eigenvalues \( \epsilon_n = q_\parallel^2 + 2 \tau \left( 1 - \frac{\omega_n}{4} \right) \). In the vicinity of \( T_w \) (large \( z_0 \)):
\[
\kappa_0 \tau \sim - \frac{3}{4} \left( \frac{c^2}{2 \tau_w} \right)^2 \left( \frac{T_w - T_c}{T_c - T_w} \right)^2 
\]
and thus
\[ \varepsilon_0(q_{\parallel}) \sim q_{\parallel}^2 + \frac{c^2}{2} \left( \frac{1}{1 - T_w/T_c} \right) \left( \frac{T_w - T}{T_c} \right)^2 \]

(22)

whereas \( \varepsilon_n(q_{\parallel}) \) remains larger than \( q_{\parallel}^2 + \frac{3\tau}{2} \) for \( n > 1 \). Let us note that the « mass » term of \( \varepsilon_0(q) \) is small near \( T_w \) provided (i) \( c^2 \) remains much greater than \( 2\tau_w \), i.e. we are not looking at the vicinity of the tricritical point A of figure 1, (ii) \( T_w \) remains well below \( T_\ast \), i.e. \( h_1 \) is not too small and we are not looking at the vicinity of the Curie point 0 of figure 1. Therefore long-range correlations are induced by this \( n = 0 \) mode for \( q_{\parallel} \) small and \( T \) close to \( T_w \). They correspond to the propagation of long wavelength excitations along the interface (capillary modes). At long distance the Green's function, i.e. the correlations are dominated by this lowest mode
\[ G(z, z'; q_{\parallel}) \approx \frac{\varphi_0(z) \varphi_0(z')}{\varepsilon_0(q_{\parallel})}. \]

(23)

Thus if we study the correlations between two points at fixed distance from the wall but at large separation in the direction parallel to the wall we obtain, in the vicinity of \( T_w \)
\[ \langle \Phi(z; \mathbf{p}_1) \Phi(z; \mathbf{p}_2) \rangle_c \approx \varphi_0(z) \varphi_0(z') \int_{\text{B.Z.}} d^{d-1}q \left[ \frac{\exp iq_{\parallel} \cdot (\mathbf{p}_2 - \mathbf{p}_1)}{q_{\parallel}^2} + \text{const.} \right] \frac{(T_w - T)^2}{\rho^{d-2}}. \]

(24)

These long wavelength modes give a correlation length in directions parallel to the wall
\[ \xi_w = \varepsilon_0(T_w - T)^{-1}. \]

(25)

This is in contrast to the usual \( v = 1/2 \) mean field law, \( \xi \propto |T - T_c|^{-1/2} \) that one finds for a conventional critical point.

This wetting transition corresponds to a restoration of a broken symmetry : in the infinite system translation invariance would leave the location of the interface undetermined (the parameter \( z_0 \) of Eq. (8) would be arbitrary). The low \( q_{\parallel} \) modes which translate and distort the interface would thus be gapless. In the semi-infinite geometry, the wall breaks translation invariance : long wavelength fluctuations of the interface are suppressed at low temperature by the wall. However at \( T_w \), the energy-entropy balance for the interface favours a liberation of the interface ; \( z_0 \) becomes arbitrary and translation invariance is restored.

Before we leave the subject of correlation functions we note here the exact solution for the Green's function and not simply its leading mode approximation (23) (indeed we shall see later on that we need to go beyond this approximation). The result of a straightforward calculation which consists of inverting \( A^{(2)} \) given by equation (14) in the space of functions satisfying the boundary condition (12) yields
\[ G(z, z'; q_{\parallel}) = aF_+(y) F_+(y') + bF_+(y) F_-(y') \]

(26a)
with
\[ F_\pm(y) = e^{\text{cosh}} \left[ \frac{\text{tanh}^2 y}{2} + \hbar \text{tanh} y + \frac{1}{3} (\hbar^2 - 1) \right] \]

(26b)
\[ y = \sqrt{\frac{\tau}{2}} (x - z_0), \quad \omega = \left( 4 + \frac{2\tau}{3} \right)^{1/2} \]
\[ b = \sqrt{\frac{2}{\tau}} \left[ 2 \omega (1 - \omega^2)(4 - \omega^2) \right] \]
\[ a = -c \sqrt{\frac{2}{\tau}} F_+ - (\partial F_+/\partial y) \]
\[ = -c \sqrt{\frac{2}{\tau}} F_+ (\partial F_+/\partial y) \]

(26c) \quad (26d) \quad (26e)

This representation is not well adapted to the \( q_{\parallel} = 0 \) (\( \omega = 2 \)) Green's function. It does have a limit, but it is more convenient to use for \( q_{\parallel} = 0 \) the alternative form :
\[ G(z, z'; q_{\parallel} = 0) = \frac{1}{\sqrt{\tau}} [Au(y) \psi(y') + v(y) u(y')] \]

(27a)
with
\[ u(y) = \frac{1}{\cosh^2 y} \]
\[ v(y) = \frac{1}{\cosh^2 y} \int_{-\sqrt{10} z_0}^{\sqrt{10} z_0} dw \cosh^4 w \]
\[ A = \frac{\cosh^4 \left( \sqrt{10} z_0 \right)}{c \sqrt{\tau}/2 - 2 \tanh \left( \sqrt{10} z_0 \right)}. \]

(27b) \quad (27c)

4. The upper critical dimension.
In order to complete our program, we have now to determine the effective interactions of the singular mode \( n = 0, q_{\parallel} \) small, \( T \) near \( T_w \). At first sight one could conclude that a replacement in all diagrams of the full Green function by its leading form (23) is
legitimate. Specifically this would mean that if we expanded \( x(z ; \rho) \) (see Eq. (11)) in terms of the eigenvalues \( \varphi_n \) of the Green functions

\[
\chi(z ; \rho) = \sum_{n=0}^{\infty} \varphi_n(z) \lambda_n(\rho)
\]  

(28)

we would keep the \( n = 0 \) mode alone for \( \chi \). If we wrote a Taylor expansion for the Hamiltonian

\[
A(\Phi) = A(\Phi_e) + \frac{1}{2} A(\Phi_e^2) + \frac{1}{3} A(\Phi_e^3) + \frac{1}{4} A(\Phi_e^4) + \chi(\chi \cdot \chi)
\]

(29)

and if we kept only the singular mode

\[
\chi(z, \rho) \sim \varphi_0(z) \lambda_0(\rho)
\]  

(30)

we would obtain

\[
A_{\text{eff}}(\lambda_0) = A(\Phi_e) + \int \text{d}^d \rho \left\{ \varphi_0^2 + \frac{1}{2} \left[ (\nabla \lambda_0)^2 + 2 \tau \left( 1 - \frac{\kappa_0^2}{4} \right) \lambda_0^2 \right] + \frac{1}{3} \sigma_3 \lambda_0 \lambda_2 + \frac{1}{4} \sigma_4 \lambda_4 \right\}
\]  

(31)

in which

\[
u_3 = g \int_0^{\infty} \text{d} z \Phi_e(z) \varphi_0^3(z)
\]  

(32)

\[
u_4 = g \int_0^{\infty} \text{d} z \Phi_e(z) \varphi_0^4(z)
\]  

(33)

Near \( T_w \), \( 1 - \frac{\kappa_0^2}{4} \) vanishes as \((T_w - T)^2\) (Eq. (21)), and since \( z_0 \to \infty \), \( \Phi_e(z) \) is close to an odd function, whereas the limit of \( \varphi_0(z) \) is even (for \( \kappa_0 = 2 \) Eq. (19) gives \( \varphi_0 \approx 1/\cosh^2(z - z_0) \)). Therefore \( \nu_3 \) vanishes near \( T_w \) (in fact as \((T_w - T)^2\)) and \( \nu_4 \) remains finite. A conclusion on the basis of this computation would be that we have recovered for the \( \lambda_0(\rho) \)-mode an ordinary critical model with \( d \) replaced by \((d - 1) \) and \((T - T_w) \) by \((T_w - T)^2 \); hence the upper critical domain would be \( d_{c - 1} = 4 \), with the usual Ising-like \( e \)-expansion below four dimensions.

However this whole line of argumentation (which was our first reaction) is wrong. The first reason is that near \( T_w \) we expect translation invariance to be restored; a simple translation \( z_0 \to z_0 + \delta z_0 \) of the profile \( \Phi_e(z - z_0) \) should not cost any energy. But the mode \( \varphi_0(z) \), in the large \( z_0 \) limit, is precisely this « zero mode » of the profile for the infinite volume geometry \((\varphi_0(z) \sim \Phi_e(z - z_0)) \). Consequently a constant change in \( \lambda_0 \) should not cost any energy and therefore we expect that all the vertices of the effective Hamiltonian for \( \lambda_0 \) should vanish for constant \( \lambda_0 \); therefore \( u^{\text{eff}} \) should also vanish at \( T_w \) and it should not be given by (33). A more technical reason explaining why the consideration of the singular mode alone is not sufficient, may be based upon a study of the structure of the full Hamiltonian (29), keeping now all the modes:

\[
A \{ \lambda_n \} = A_e + \int \text{d}^d \rho \left\{ \sum_{n=0}^{\infty} \frac{1}{2} [(\nabla \lambda_n)^2 + 2 \tau (1 - \frac{\kappa_0^2}{4}) \lambda_n^2] + \frac{1}{3} \sum u_{(1,2,3)} \lambda_1 \lambda_2 \lambda_3 + \frac{1}{4} \sum u_{(1,2,3,4)} \lambda_1 \lambda_2 \lambda_3 \lambda_4 \right\}.
\]  

(34)

The vertices are given by similar formulae

\[
u_{(1,2,3)} = g \int \text{d} z \Phi_e(z) \varphi_{n_1}(z) \varphi_{n_2}(z) \varphi_{n_3}(z)
\]  

(35)

etc... The leading diagrams which control the singularities near \( T_w \) are obtained by exchanging the \( n = 0 \) propagator, provided the corresponding vertex does not vanish near \( T_w \). For instance we have seen that \( u_{(0,0,0)}^{(0,0,0,0)} \) vanishes near \( T_w \) because for large \( z_0 \), \( \varphi_0(z) \) is even whereas \( \Phi_e \) is odd; therefore if we take an excited state such as \( \varphi_1(z) \) (which is odd for large \( z_0 \)) \( u_{(2,0,0,0)}^{(0,0,0,0)} \) does not vanish and the massive modes are as important as the massless ones. Therefore in order to derive the correct effective Hamiltonian for the \( \lambda_0 \)-mode, we have to take the trace over the \( \lambda_n \)-modes with \( n \geq 1 \), in the partition function

\[
e^{-A_{\text{eff}}(\lambda_0)} = \int \prod_1^{\infty} D\lambda_n(\rho) e^{-A(\lambda_n)}
\]  

(36)

This is clearly a difficult task but we may proceed through a loop-wise equation. At the tree level we would have

\[
(u^{\text{eff}})_{\text{tree}} = 0 \begin{array}{cccc}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{array}
\]

(37)

in which the index on the line refers to the eigenmode of the Green's functions. This graphical equation means that

\[
(u^{\text{eff}})_{\text{eff}} = u_{(0,0,0,0)}^{(0,0,0,0)} - 3 \sum_{n=0}^{\infty} \frac{[u_{(3,0,0,0)}^{(0,0,0,0)}]^2}{\varepsilon_n(\Omega)}
\]  

(38)

Using (38), and the spectral decomposition of the Green functions

\[
G(z, z'; q_{\parallel}) = \sum_{n=0}^{\infty} \frac{\varphi_n(z) \varphi_n(z')}{\varepsilon_n(q_{\parallel})}
\]  

(39)
we obtain

$$ (u_4)_{\text{eff}} = g \int_0^\infty \varphi_0^4 \, dz - 3 \, g^2 \int_0^\infty dz \, \varphi_0^2(z) \, \Phi_c(z) \times $$
$$ \times \int_0^\infty dz' \, \varphi_0^2(z') \, \Phi_c(z') \, G(z, z'; q|| = 0). \quad (40) $$

The functions $\Phi_c, \varphi_0, G$ are given explicitly by the equations (8)-(9), (19)-(20), (27). Therefore the calculation is reduced to quadratures. In the limit of $T$ approaching $T_w$ the difference between the two terms in (40) vanishes as expected (again because at $T_w$ the interface becomes free, and for an infinite geometry all the terms generated by (36) without powers of $V\lambda_0$ should vanish). An extremely tedious calculation leads to

$$ (u_4)_{\text{eff}} \approx \frac{27g}{T - T_w} \left[ \frac{4}{3} \frac{1}{c + \sqrt{2} \tau_w} + \frac{2}{3} \frac{1}{\sqrt{2} \tau_w} \right] \times $$
$$ \times \frac{c^2}{c^2 - 2 \tau_w (T - T_w)^2}. \quad (41) $$

Similarly all the higher effective interactions $(u_5)_{\text{eff}}, (u_6)_{\text{eff}}, \ldots$ generated by the partial sum (36) over the massive modes will vanish at $T_w$ as $(T - T_w)^2$; (it is clear from the previous arguments that they have to vanish; they vanish as $(T - T_w)^2$ because the differences between the semi-infinite geometry and the infinite one are proportional to $(T - T_w)^2$; for instance

$$ \varphi_0(y) \approx \frac{N_0}{T - T_w} \cosh^2 y \times $$
$$ \times \left[ 1 + \text{const.} \, (T - T_w)^2 \left( y - \frac{1}{3} \tanh y \right) \left( y - (1 + \tanh y)^2 \right) \right]. \quad (42) $$

and $1/\cosh^2 y$ is the « zero-mode » of the free interface problem).

In fact we expect a cross-over near $T_w$ between our model and interface model of the Wallace-Zia [9] type which involves powers of $V\lambda_0$ only. The effective action should thus look like

$$ A_{\text{eff}} \{ \lambda_0 \} = $$
$$ = \int d^{d-1} \rho \left\{ [1 + (V\lambda_0)^2]^{1/2} + (T - T_w)^2 F(\lambda_0) \right\} \quad (43) $$

in which $F(\lambda_0)$ is some power series in $\lambda_0$.

Consequently corrections to mean field theory for the critical wetting problem will be drastically modified by the vanishing of the effective interactions at $T_w$. For instance let us consider the correction to the mean field correlation length $\xi_w$ at first order in $(u_4)_{\text{eff}}$; we obtain

$$ \xi_w^{-2} = \xi_0^{-2} (T_w - T)^2 + $$
$$ + (u_4)_{\text{eff}} \int \frac{d^{d-1}d}{B. Z.} \left[ \frac{q^2}{q|| + \text{const.} \, (T_w - T)^2} \right]. \quad (44) $$

Since $(u_4)_{\text{eff}}$ vanishes at $T_w$ there is no shift of $T_w$ due to the fluctuations. Furthermore, for $(d - 1) > 2$ the integral over $q||$ converges for small $q||$ even for $T = T_w$. Therefore since $(u_4)_{\text{eff}}$ vanishes as $(T_w - T)^2$ the only effect of the fluctuations is a modification of the amplitude $\xi_0$ of the singularity. Any interaction term $(u_5)_{\text{eff}}, (u_6)_{\text{eff}}, \ldots$ vanishing as $(T_w - T)^2$ leads to the same analysis in perturbation theory they yield integrals such as the one in equation (44) which have no effect on the mean field behaviour above three dimensions. Similarly a different choice of the initial Landau Hamiltonian (3) with higher powers of the order parameter would not change our result.

5. Three dimensions.

If $d = 3$ the integral in equation (44) diverges logarithmically near $T_w$. This has two effects:

(i) Mean field theory is not valid when the temperature is too close to $T_w$. There is a critical region in which fluctuations break the mean field behaviour and mean field theory is applicable only if $(T_w - T)$ is large so that \[ \int d^2 q ([q_\parallel^2 + \text{const.} \, (T_w - T)^2] [A^2]) \ll 1 \ldots \]

The scale of $(T_w - T)$ is given by equation (22) for $\varepsilon_0(q||)$; the integral is cut off at large $q||$ by $\Lambda$, the inverse of a typical interatomic distance. This condition implies that $\ln [ \text{const.} \, (T_w - T)^2 / \Lambda^2 ]$ remains small.

(ii) Higher order interactions $(u_5)_{\text{eff}}, (u_6)_{\text{eff}}, \ldots$ will contribute higher powers of logarithms; from this infinite sequence of logarithms many behaviours may be generated and this approach does not allow us to control the nature of the three-dimensional singularities.

6. Interface displacement model.

In order to make more explicit the previous results we can construct directly a displacement model in which the dynamical variable is the position $\zeta(\rho)$ of the interface. The effective Hamiltonian

$$ A(\zeta) = \int d^{d-1} \rho [(V\zeta)^2 + V(\zeta)] \quad (45) $$

reduces, for a uniform $\zeta(\rho)$, to the free energy of the interface, i.e. the surface tension $\Delta \Sigma(\Phi_c)$.

Indeed we have already noted that the location of the interface is given by the minimization of this surface tension with respect to $\Phi_c$ with $\Phi_c = M \tanh \zeta(\rho)$ near $T_w$, the interface is far away
from the wall and an expansion of $\Delta \Sigma(\Phi)$ for large $\zeta$ yields

$$V(\zeta) = -Ae^{-\beta \zeta} + Be^{-2\beta \zeta} + C e^{-3\beta \zeta} + \ldots$$

(46)

with

$$A = 2M(cM - h_0)$$
$$B = 2M^2(c - \sqrt{2} \tau) \quad \text{and} \quad \beta = \sqrt{2} \tau$$

(47)

The mean field phase diagram is easily reproduced from this potential $V(\zeta)$ [8]. The critical wetting line is $A = 0$, $B > 0$, and $T < T_w$ corresponds to $A > 0$. The first order line corresponds to $B < 0$, $B^2 = 4AC$. In order to study the critical wetting transition we can take the simplified form

$$V(\zeta) = -Ae^{-\beta \zeta} + Be^{-2\beta \zeta}.$$  (48)

This potential is very repulsive for negative $\zeta$; this is a reminder of the impenetrability of the wall. As long as $A$ is positive the interface remains attracted by the wall.

The minimum of the potential occurs for a value $z_0$ determined by the equation

$$e^{-\beta z_0} = \frac{A}{2B}.$$  (49)

$z_0$ goes to infinity at fixed $B$, when $A$ vanishes; this result coincides with our previous mean field treatment (9) since $A$ vanishes linearly as $(T_w - T)$. Similarly the « mass » term $m^2 = V''(0) = \frac{A^2}{2B} \beta^2$ vanishes as $(T_w - T)^2$ in agreement with (25). The effective interactions $V(0)(z_0)$ that one would encounter in a systematic expansion about the mean field solution $\zeta = z_0$ are all proportional to $A^2$, i.e. to $(T_w - T)^2$; this was indeed expected on the basis of our previous analysis. It is much easier now to understand why $d_c = 3$. Furthermore this model may be solved exactly [5] for the case $d = 2$ (one-dimensional interface) and one obtains $\xi \sim (T_w - T)^{-\frac{1}{2}}$, $z_0 \sim (T_w - T)^{-1}$, in agreement with the results [6] of discrete solid-on-solid models. The analysis of the three-dimensional situation is more delicate and it will be reported in a subsequent publication.

Acknowledgments.

It is a pleasure to thank for numerous helpful discussions D. B. Yeomans, B. Derrida, E. Fradkin, C. Itzykson, J. M. Luck, L. Peliti, M. Wortis and J. Zinn-Justin. One of us (S. L.) also wishes to thank D. M. Kroll for a useful discussion. The work of B. I. Halperin has been supported in part by the NSF through grant # DMR 82-07431.

References

[3] See for instance :
(c) Haug, E. H. and Schick, M., to be published;
(d) Teo da Gama, M. M. and Evans, R., to be published in Mol. Phys. and references therein.
[7] See for instance:
[8] Kroll and Lipowsky have studied the effective Hamiltonian built by two Gaussian functions in the problem of pinning transition. (Kroll, D. M. and Lipowsky, R., Phys. Rev. B 26 (1982) 5289). We shall discuss the applicability of that model to critical wetting in the subsequent publication.