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E. Brézin, B.I. Halperin, S. Leibler. Critical wetting: the domain of validity of mean field theory. Journal de Physique, 1983, 44 (7), pp.775-783. 10.1051/jphys:01983004407077500 . jpa-00209658

HAL Id: jpa-00209658

<https://hal.science/jpa-00209658>

Submitted on 4 Feb 2008

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Classification
 Physics Abstracts
 64.70 — 68.10

Critical wetting : the domain of validity of mean field theory

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

Résumé. — En dessous de la température de démixion d'un mélange binaire la présence d'un mur qui adsorbe préférentiellement l'un des deux liquides peut induire une nouvelle transition, le mouillage. Aux températures supérieures à la température de mouillage T_w la phase adsorbée par la paroi forme un film macroscopique. Cette transition a été analysée récemment dans le cadre de l'approximation du champ moyen et, pour certaines valeurs des paramètres, on observe une transition continue. Nous construisons dans ce travail le critère de Ginzburg relatif à cette transition, afin d'analyser la dimension critique supérieure d_c (au-delà de laquelle le champ moyen reste quantitativement valable). A cet effet nous caractérisons les corrélations au voisinage de T_w ($T \lesssim T_w$); en particulier des corrélations à grande distance parallèles à la paroi apparaissent avec une longueur associée qui diverge à T_w comme $1/(T_w - T)$. Des problèmes délicats se présentent pour déterminer les interactions effectives des modes donnant lieu à des corrélations à longue portée. Il résulte de cette analyse que $d_c = 3$ (c'est-à-dire un volume tridimensionnel avec une paroi bidimensionnelle).

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 ($T \lesssim T_w$); 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].

The theoretical description of this transition proposed in the original article of Cahn and developed by numerous authors [3] is based upon mean field theory. The influence of the wall on the binary mixture can be

schematized in the following way : (i) the semi-infinite geometry of the system changes the interactions experienced by the molecules of the surface layer. This may be taken into account by an incremental surface temperature field c localized on the surface of the wall ; (ii) the preferential adsorption of one component of the mixture induces a difference in the chemical potential of the two components at the wall. This effect can be described by a local chemical potential h_1 on the surface. In this paper we consider only the ideal case, where the conditions far from the wall are precisely on the coexistence curve for the two fluid phases. (Hence, we neglect such effects as the gravitational potential, which complicate the situation in a real experiment.)

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_1 . In particular, if the bulk boundary conditions far from the wall favour one phase (for instance down-

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spins), and if h_1 is positive then, at sufficiently low temperature, a layer of up-spins with a finite thickness (determined by h_1 , 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_1 , c and T (and eventually a bulk field h) is rather complicated. The (partial to complete) wetting transition can occur as a continuous or discontinuous 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.

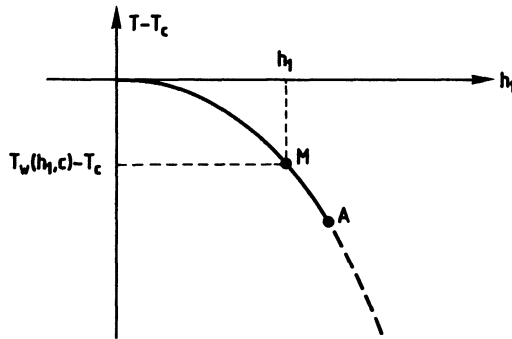


Fig. 1. — The phase diagram for a fixed given positive c and $h_{\text{bulk}} = 0_-$. The line of critical wetting OA corresponds to continuous transitions. The dotted line is the locus of first-order transitions; A is a tricritical point.

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

$$\xi_{\parallel} \approx \frac{\xi_0}{T_w - T},$$

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

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

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

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

⁽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 calculations, 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.

We show that the upper critical dimension d_c is three, i.e., a three-dimensional bulk liquid with a two-dimensional interface. In three dimensions, therefore, one would expect corrections to the above mean field theory results sufficiently close to T_w . The analysis for three dimensions will be presented in a subsequent publication [5].

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

$$\xi_{\parallel} \approx \xi_0(T_w - T)^{-2}; \quad z_0 \approx (T_w - T)^{-1}; \\ \Delta\Sigma \approx -(T_w - T)^2.$$

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 characterize 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 diagonalization 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 ξ_w . This length goes to infinity as $\xi_w = \xi_0(T_w - T)^{-1}$; 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

$$\xi^{-2} = \xi_0^{-2}[T - T_c^{(0)}] - u_0 \int_{\text{B.Z.}} \frac{d^d q}{q^2 + T - T_c^{(0)}}. \quad (1)$$

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

$$\xi^{-2} = \xi_0^{-2}[T - T_c] + u_0[T - T_c] \times \\ \times \int_{\text{B.Z.}} \frac{d^d q}{q^2(q^2 + T - T_c)} \quad (2)$$

which shows that above four dimensions ν remains fixed to $1/2$, since the integral in (2) converges at low wavenumber down to T_c (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 u_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_c . 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 $A (\equiv \beta H)$ in d dimensions for a one component order parameter $\Phi(z; \rho_1, \rho_2, \dots, \rho_{d-1})$ below the bulk miscibility temperature T_c (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 τ , 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 $\exp - (A)$, over the order-parameter distribution. In fact the Hamiltonian (3) is still ill-defined : $\nabla \Phi$ will have in general a δ -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

$$\left. \frac{\partial \Phi}{\partial z}(z, \rho) \right|_{z=0+} = c \Phi(0, \rho) - h_1. \quad (4)$$

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

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

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, Φ_c is a function of the single variable z , satisfying the differential equation

$$-\frac{d^2\Phi_c}{dz^2} - \tau\Phi_c + \frac{1}{6}g\Phi_c^3 = 0. \quad (5)$$

A first integration, taking into account the asymptotic condition at z equals infinity, yields

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

We follow here Pandit and Wortis [3a] and represent graphically equation (5') with a plot of Φ_c' as a function of Φ_c (keeping in mind that $\Phi_c(z)$ 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 $(\Phi_c = M, \Phi_c' = 0)$, there is a single intersection of B with the parabolas. This occurs for

$$c > \sqrt{2\tau} \quad (6)$$

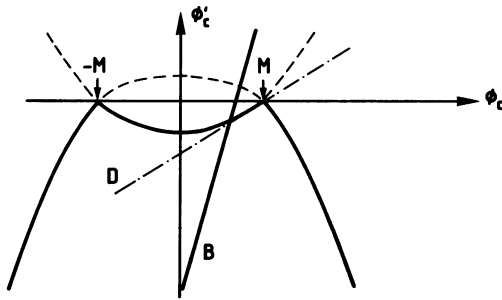


Fig. 2. — Φ_c' as a function of Φ_c . The wall boundary condition is the straight line B. The dashed line D tangent at $\Phi_c' = 0$, $\Phi_c = +M$, is the separatrix between second-order and first-order transitions.

which is the condition for having a second-order transition. We shall restrict ourselves to this case. If the temperature is increased, τ and M decrease, and, if h_1 and c remain fixed, the point $(\Phi_c = M, \Phi_c' = 0)$ will move towards the line B. When it reaches the line B the thickness of the wetting layer diverges.

This occurs when $(cM - h_1)$ vanishes, i.e. for a temperature $T_w(h_1, c)$ defined by

$$\tau_w \equiv 1 - \frac{T_w}{T_c} = \frac{gh_1^2}{6c^2}.$$

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 $T < T_w$)

$$\Phi_c(z) = -M \tanh \left[\sqrt{\frac{\tau}{2}} (z - z_0) \right] \quad (7)$$

with z_0 determined by (4) :

$$\begin{aligned} -M \sqrt{\frac{\tau}{2}} \left[1 - \tanh^2 \left(\sqrt{\frac{\tau}{2}} z_0 \right) \right] &= \\ &= cM \tanh \left(\sqrt{\frac{\tau}{2}} z_0 \right) - h_1. \end{aligned} \quad (8)$$

When T approaches T_w , $M \rightarrow M_w = h_1/c$, and z_0 diverges as

$$z_0 \sim \frac{1}{\sqrt{2\tau_w}} \ln \left[\frac{1}{T_w - T} \right]. \quad (9)$$

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).

$$\begin{aligned} \Delta\Sigma = \frac{A}{L^{d-1}} &= \int_0^\infty dz \left\{ \frac{1}{2} \left(\frac{d\Phi_c}{dz} \right)^2 - \frac{\tau}{2} (\Phi_c^2 - M^2) + \right. \\ &+ \frac{g}{4!} (\Phi_c^4 - M^4) \left. \right\} + \frac{1}{2} c (\Phi_s^2 - M^2) - h_1 (\Phi_s - M) \end{aligned} \quad (10a)$$

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

$$\begin{aligned} \Delta\Sigma = -\frac{1}{3} \sqrt{\frac{g}{12}} (\Phi_s^3 - 3M^2\Phi_s + 2M^3) &+ \\ + \frac{1}{2} c (\Phi_s^2 - M^2) - h_1 (\Phi_s - M) \end{aligned} \quad (10b)$$

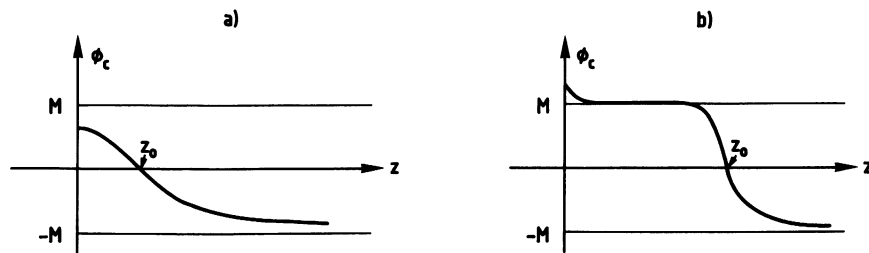


Fig. 3. — The mean field profile. (a) $T < T_w$; (b) $T_c > T > T_w$: the thickness z_0 is proportional to $\log 1/h_{\text{bulk}}$.

and to verify that equation (9) for z_0 is nothing but $\partial\Sigma/\partial\Phi_s = 0$. Expanding $\Delta\Sigma$ near T_w we obtain

$$\Delta\Sigma(T) \approx -\frac{3}{2g} \left(\frac{T_w - T}{T_c} \right)^2 \frac{1}{c - \sqrt{2}\tau_w}.$$

If we define the exponents ν and α in the usual way, as governing $\xi_{||}$ and the surface tension, mean field yields $\nu = 1$, $\alpha = 0$; hyperscaling is satisfied for an (interface) 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 Φ_c have to be considered. Let us write

$$\Phi(z, \rho) = \Phi_c(z) + \chi(z, \rho) \quad (11)$$

and the boundary condition (4) imposes upon χ the condition

$$\left. \frac{\partial\chi}{\partial z}(z, \rho) \right|_{z=0+} - c\chi(0, \rho) = 0. \quad (12)$$

We expand the Hamiltonian A to second order in χ

$$A = A_c + \frac{1}{2} \int \chi(z_1, \rho_1) \chi(z_2, \rho_2) \times \\ \times A^{(2)}(z_1, z_2; \rho_1 - \rho_2) + O(\chi^3) \quad (13)$$

in which

$$A^{(2)} = \frac{\delta^2 A}{\delta\Phi\delta\Phi} = \delta(z_1 - z_2) \delta^{d-1}(\rho_1 - \rho_2) \times \\ \times \left[-\frac{\partial^2}{\partial z_1^2} - \nabla_{||}^2 - \frac{3\tau}{\cosh^2\left(\sqrt{\frac{\tau}{2}}(z - z_0)\right)} + 2\tau \right]. \quad (14)$$

The Green function $G(x_1, x_2)$ is given by

$$G(x_1, x_2) = \langle \Phi(x_1) \Phi(x_2) \rangle - \langle \Phi(x_1) \rangle \langle \Phi(x_2) \rangle \\ = [A^{(2)}]^{-1} \quad (15)$$

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 ρ parallel to the surface is naturally performed first and we then look for eigenmodes of $A^{(2)}$

$$\left[-\frac{d^2}{dz^2} - \frac{3\tau}{\cosh^2\left(\sqrt{\frac{\tau}{2}}(z - z_0)\right)} + q_{||}^2 + 2\tau \right] \times \\ \times \varphi_n(z) = \varepsilon_n(q_{||}) \varphi_n(z) \quad (16)$$

with φ_n regular at infinity, and constrained by (12) at the origin. With the notations

$$y = \sqrt{\frac{\tau}{2}}(z - z_0) \\ \varepsilon_n = q_{||}^2 + 2\tau \left(1 + \frac{\omega_n}{4} \right) \quad (17)$$

we have

$$\left(-\frac{d^2}{dy^2} - \frac{6}{\cosh^2 y} \right) \varphi_n = \omega_n \varphi_n \quad (18a)$$

$$\left(c\varphi_n - \sqrt{\frac{\tau}{2}} \frac{d\varphi_n}{dy} \right) \Big|_{y_0 = -\sqrt{\tau/2} z_0} = 0. \quad (18b)$$

The potential $-6/\cosh^2 y$, limited to the half-space $y > -\sqrt{\tau/2} z_0$ (see Fig. 4), has two bound states $\omega_n = -\kappa_n^2$, $n = 0, 1$; for large z_0 $\kappa_0 \approx 2$ and $\kappa_1 \approx 1$. The wave-functions are

$$\varphi_n = N_n e^{-\kappa_n y} \left(\tanh^2 y + \kappa_n \tanh y + \frac{1}{3}(\kappa_n^2 - 1) \right) \quad (19)$$

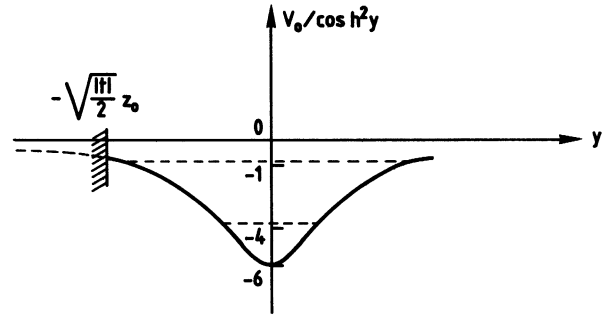


Fig. 4. — The potential which gives the eigenmodes of the Green's function (Eq. (18)), and its two bound states.

with κ_n determined as the positive roots of the equation

$$\left(c + \kappa_n \sqrt{\frac{\tau}{2}} \right) \left[u_0^2 - \kappa_n u_0 + \frac{1}{3}(\kappa_n^2 - 1) \right] - \\ - \sqrt{\frac{\tau}{2}} (1 - u_0^2) (\kappa_n - 2u_0) = 0 \quad (20) \\ u_0 \equiv \tanh \left(\sqrt{\frac{\tau}{2}} z_0 \right).$$

In addition there is a continuous spectrum $\omega_n > 0$. Therefore the spectrum of $A^{(2)}$ consists of the lowest states $\varphi_0(z) \exp i q_{||} \cdot \rho$ with eigenvalue $\varepsilon_0 = q_{||}^2 + 2\tau \left(1 - \frac{\kappa_0^2}{4} \right)$ and the excited states $\varphi_n(z) \exp(i q_{||} \cdot x_{||})$ with eigenvalues $\varepsilon_n = q_{||}^2 + 2\tau \left(1 - \frac{\omega_n}{4} \right)$. In the vicinity of T_w (large z_0):

$$\kappa_0 \underset{T \rightarrow T_w}{\sim} 2 - \frac{3}{4} \frac{c^2}{(c^2 - 2\tau_w)} \left(\frac{T_w - T}{T_c - T_w} \right)^2 \quad (21)$$

and thus

$$\varepsilon_0(q_{\parallel}) \sim q_{\parallel}^2 + \frac{3}{2} \frac{c^2}{c^2 - 2\tau_w} \frac{1}{(1 - T_w/T_c)} \left(\frac{T_w - T}{T_c} \right)^2 \quad (22)$$

whereas $\varepsilon_n(q_{\parallel})$ remains larger than $q_{\parallel}^2 + \frac{3}{2}\tau$ 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_c 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

$$G(z, z'; q_{\parallel}) \approx \frac{\varphi_0(z) \varphi_0(z')}{\varepsilon_0(q_{\parallel})}. \quad (23)$$

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

$$\langle \Phi(z; \rho_1) \Phi(z; \rho_2) \rangle_c \underset{T \lesssim T_w}{\approx} \varphi_0(z) \varphi_0(z') \int_{B.Z.} d^{d-1} q \frac{\exp i q_{\parallel} \cdot (\rho_2 - \rho_1)}{q_{\parallel}^2 + \text{const.} (T_w - T)^2} \quad (24)$$

$$\underset{\rho = |\rho_2 - \rho_1| \rightarrow \infty}{\approx} \varphi_0(z) \varphi_0(z') \frac{\exp - c\rho(T_w - T)}{\rho^{(d-2)/2}}.$$

These long wavelength modes give a correlation length in directions parallel to the wall

$$\xi_w = \xi_0(T_w - T)^{-1}. \quad (25)$$

This is in contrast to the usual $\nu = 1/2$ 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

$$G(z, z'; q_{\parallel}) = aF_+(y)F_+(y') + bF_+(y_>)F_-(y_<) \quad (26a)$$

with

$$F_{\pm}(y) = e^{\omega y} \left[\tanh^2 y \pm \omega \tanh y + \frac{1}{3}(\omega^2 - 1) \right] \quad (26b)$$

$$y = \sqrt{\frac{\tau}{2}}(z - z_0), \quad \omega = \left(4 + \frac{2}{\tau} q_{\parallel}^2 \right)^{1/2} \quad (26c)$$

$$b = \sqrt{\frac{2}{\tau}} \frac{9}{[2\omega(1 - \omega^2)(4 - \omega^2)]} \quad (26d)$$

$$\frac{a}{b} = - \frac{c\sqrt{2/\tau} F_- - (\partial F_-/\partial y)}{c\sqrt{2/\tau} F_+ - (\partial F_+/\partial y)} \Big|_{y = -\sqrt{\tau/2} z_0}. \quad (26e)$$

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 :

$$G(z, z'; q_{\parallel} = 0) = \sqrt{\frac{2}{\tau}} [Au(y_>)v(y_<) + u(y)u(y')] \quad (27a)$$

with

$$u(y) = \frac{1}{\cosh^2 y}$$

$$v(y) = \frac{1}{\cosh^2 y} \int_{-\sqrt{\tau/2} z_0}^y dw \cosh^4 w \quad (27b)$$

$$A = \frac{\cosh^4(\sqrt{\tau/2} z_0)}{c\sqrt{\tau/2} - 2 \tanh(\sqrt{\tau/2} z_0)}. \quad (27c)$$

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 $\chi(z; \rho)$ (see Eq. (11)) in terms of the eigenvalues φ_n of the Green functions

$$\chi(z; \rho) = \sum_{n=0}^{\infty} \varphi_n(z) \lambda_n(\rho) \quad (28)$$

we would keep the $n = 0$ mode alone for χ . If we wrote a Taylor expansion for the Hamiltonian

$$A(\Phi) = A(\Phi_c) + \frac{1}{2} A^{(2)} \chi \cdot \chi + \frac{1}{3!} A^{(3)} \chi \cdot \chi \cdot \chi + \frac{1}{4!} A^{(4)} \chi \cdot \chi \cdot \chi \cdot \chi \quad (29)$$

and if we kept only the singular mode

$$\chi(z, \rho) \sim \varphi_0(z) \lambda_0(\rho) \quad (30)$$

we would obtain

$$A_{\text{eff}}(\lambda_0) = A(\Phi_c) + \int d^{d-1} \rho \left\{ \frac{1}{2} \left[(\nabla_{\parallel} \lambda_0)^2 + 2 \tau \left(1 - \frac{\kappa_0^2}{4} \right) \lambda_0^2 \right] + \frac{1}{3!} u_3 \lambda_0^3 + \frac{1}{4!} u_4 \lambda_0^4 \right\} \quad (31)$$

in which

$$u_3 = g \int_0^{\infty} dz \Phi_c(z) \varphi_0^3(z) \quad (32)$$

$$u_4 = g \int_0^{\infty} dz \varphi_0^4(z). \quad (33)$$

$$A \{ \lambda_n \} = A_c + \int d^{d-1} \rho \left\{ \sum_{n=0}^{\infty} \frac{1}{2} [(\nabla_{\parallel} \lambda_n)^2 + 2 \tau (1 - \kappa_n^2/4) \lambda_n^2] + \frac{1}{3!} \sum u_3^{(n_1, n_2, n_3)} \lambda_{n_1} \lambda_{n_2} \lambda_{n_3} + \frac{1}{4!} \sum u_4^{(n_1, n_2, n_3, n_4)} \lambda_{n_1} \lambda_{n_2} \lambda_{n_3} \lambda_{n_4} \right\}. \quad (34)$$

The vertices are given by similar formulae

$$u_3^{(n_1, n_2, n_3)} = g \int dz \Phi_c(z) \varphi_{n_1}(z) \varphi_{n_2}(z) \varphi_{n_3}(z) \quad (35)$$

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 $u_3^{(0,0,0)}$ vanishes near T_w because for large z_0 , $\varphi_0(z)$ is even whereas Φ_c is odd; therefore if we take an excited state such as $\varphi_1(z)$ (which is odd for large z_0) $u_3^{(0,0,1)}$ 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 λ_0 -mode, we have to take the trace over the λ_n -modes with $n \geq 1$, in the partition function

$$e^{-A_{\text{eff}}(\lambda_0)} = \int \prod_1^{\infty} D\lambda_n(\rho) e^{-A(\lambda_n)} \quad (36)$$

Near T_w , $1 - \kappa_0^2/4$ vanishes as $(T_w - T)^2$ (Eq. (21)), and since $z_0 \rightarrow \infty$, $\Phi_c(z)$ 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 u_3 vanishes near T_w (in fact as $(T_w - T)^2$) and u_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 $(T - T_c)$ by $(T_w - T)^2$; hence the upper critical domain would be $d_c - 1 = 4$, with the usual Ising-like ε -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 $z_0 \rightarrow z_0 + \delta z_0$ of the profile $\Phi_c(z - z_0)$ 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 ($\varphi_0(z) \underset{z_0 \text{ large}}{\sim} \Phi_c'(z - z_0)$). Consequently a constant change in λ_0 should not cost any energy and therefore we expect that all the vertices of the effective Hamiltonian for λ_0 should vanish for constant λ_0 ; therefore u_4^{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 :

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

$$(u_4)_{\text{eff}} = \begin{array}{c} 0 \quad 0 \\ \diagdown \quad \diagup \\ 0 \quad 0 \end{array} - \begin{array}{c} 0 \quad 0 \\ \diagdown \quad \diagup \\ 0 \quad n \quad 0 \\ \diagup \quad \diagdown \\ 0 \quad 0 \end{array} \quad (37)$$

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

$$(u_4)_{\text{eff}} = u_4^{(0,0,0,0)} - 3 \sum_{n=0}^{\infty} \frac{[u_3^{(0,0,n)}]^2}{\varepsilon_n(q_{\parallel} = 0)}. \quad (38)$$

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

$$G(z, z'; q_{\parallel}) = \sum_{n=0}^{\infty} \frac{\varphi_n(z) \varphi_n(z')}{\varepsilon_n(q_{\parallel})} \quad (39)$$

we obtain

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

The functions Φ_c , φ_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 $\nabla\lambda_0$ should vanish). An extremely tedious calculation leads to

$$(u_4)_{\text{eff}} \approx_{T \rightarrow T_w} -27g \left(\frac{4}{3} \frac{1}{c + \sqrt{2}\tau_w} + \frac{2}{5} \frac{1}{\sqrt{2}\tau_w} \right) \times \\ \times \frac{c^2}{c^2 - 2\tau_w} \left(\frac{T_w - T}{T_c - T_w} \right)^2. \quad (41)$$

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

$$\varphi_0(y) \approx_{T \rightarrow T_w} \frac{N_0}{\cosh^2 y} \times \\ \times \left[1 + \text{const.} (T_w - T)^2 \left(y - \frac{\frac{4}{3} + \tanh y}{(1 + \tanh y)^2} \right) \right] \quad (42)$$

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 $\nabla\lambda_0$ only. The effective action should thus look like

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

in which $F(\lambda_0)$ is some power series in λ_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 ξ_w at first order in $(u_4)_{\text{eff}}$; we obtain

$$\xi_w^{-2} = \xi_0^{-2} (T_w - T)^2 + \\ + (u_4)_{\text{eff}} \int_{\text{B.Z.}} \frac{d^{d-1} q}{q_{\parallel}^2 + \text{const.} (T_w - T)^2}. \quad (44)$$

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_{\parallel} converges for small q_{\parallel} 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 ξ_0 of the singularity. Any interaction term $(u_5)_{\text{eff}}$, $(u_6)_{\text{eff}}$, etc..., 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 $\int d^2 q / [q_{\parallel}^2 + \text{const.} (T_w - T)^2] \ll 1 \dots$

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

(ii) Higher order interactions $(u_5)_{\text{eff}}$, $(u_6)_{\text{eff}}$, ... 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

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

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

Indeed we have already noted that the location of the interface is given by the minimization of this surface tension with respect to Φ_s , with $\Phi_s = M \tanh \zeta \sqrt{\tau/2}$. Near T_w , the interface is far away

from the wall and an expansion of $\Delta\Sigma(\Phi_s)$ for large ζ yields

$$V(\zeta) = -A e^{-\beta\zeta} + B e^{-2\beta\zeta} + C e^{-3\beta\zeta} + \dots \quad (46)$$

with

$$\begin{aligned} A &= 2 M(cM - h_1) \\ B &= 2 M^2(c - \sqrt{2\tau}) \quad \text{and} \quad \beta = \sqrt{2\tau} \quad (47) \\ C &= 2 M(\frac{4}{3}M^3 - cM + h_1). \end{aligned}$$

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

$$V(\zeta) = -A e^{-\beta\zeta} + B e^{-2\beta\zeta}. \quad (48)$$

This potential is very repulsive for negative ζ ; 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

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

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 $m^2 = V''(z_0) = \frac{A^2}{2B} \beta^2$ vanishes as $(T_w - T)^2$ in agreement with (25). The effective interactions $V^{(n)}(z_0)$ 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 $\xi_{||} \sim (T_w - T)^{-2}$, $z_0 \sim (T_w - T)^{-1}$, 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. Beysens, 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

- [1] CAHN, J. W., *J. Chem. Phys.* **66** (1977) 3667;
EBNER, C. and SAAM, W. F., *Phys. Rev. Lett.* **38** (1977) 1486.
- [2] MOLDOVER, M. R. and CAHN, J. W., *Science* **207** (1980) 1073.
KWON, O'D. *et al.*, *Phys. Rev. Lett.* **48** (1982) 185.
POHL, D. W. and GOLDBURG, W. J., *Phys. Rev. Lett.* **48** (1982) 1111.
- [3] See for instance :
(a) PANDIT, R. and WORTIS, M., *Phys. Rev. B* **25** (1982) 3226;
PANDIT, R., SCHICK, M. and WORTIS, M., *Phys. Rev. B* **26** (1983) 5112;
(b) SULLIVAN, D. E., *J. Chem. Phys.* **74** (1981) 2604;
(c) HAUGE, E. H. and SCHICK, M., to be published;
(d) TELO DA-GAMA, M. M. and EVANS, R., to be published in *Mol. Phys.* and references therein.
- [4] See reference [3a], and NAKANISHI, H. and FISHER, M., *Phys. Rev. Lett.* **49** (1982) 1565.
- [5] BRÉZIN, E., HALPERIN, B. I. and LEIBLER, S., to be published.
- [6] ABRAHAM, D. B., *Phys. Rev. Lett.* **44** (1980) 1165;
- BURKHARDT, T. W., *J. Phys. A* **14** (1981) L-63;
- CHALKER, J. T., *J. Phys. A* **14** (1981) 2431;
- CHUI, S. T. and WEEKS, J. D., *Phys. Rev. B* **23** (1981) 2438;
- HILHORST, H. and VAN LEEUWEN, J. M. J., *Physica A* **107** (1981) 319;
- KROLL, D. M., *Z. Phys. B* **41** (1981) 345;
- VALLADE, M. and LAJZEROWICZ, J., *J. Physique* **42** (1981) 1505.
- [7] See for instance :
BRÉZIN, E., LE GUILLLOU, J. C. and ZINN-JUSTIN, J. in *Phase Transitions and Critical Phenomena*, vol. VI, eds. C. Domb and M. S. Green (Academic Press, London) 1976.
- [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.
- [9] WALLACE, D. J. and ZIA, R. K. P., *Phys. Rev. Lett.* **43** (1979) 808.