Upper Critical Dimension for Wetting in Systems with Long-Range Forces

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It is shown that the upper critical dimension d^* for complete wetting is $d^*=3$ for short-range forces and $d^* < 3$ for long-range forces. The critical exponent $\nu_\parallel$ for the divergence of transverse correlations at complete wetting in three-dimensional systems is found to be $\nu_\parallel=\frac{1}{2}$ for short-range forces and $\nu_\parallel=\frac{2}{3}$ for long-range forces of van der Waals type.

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Much recent work, both theoretical[1-13] and experimental,[14-16] has been devoted to the study of wetting transitions. At such transitions, a liquid film is adsorbed on a substrate surface leading to an interface between the adsorbed liquid phase and the gas phase in the bulk. The interplay between the substrate surface and the liquid-gas interface can lead to critical phenomena since the mean distance of the interface from the surface can diverge in a continuous manner. Such interface delocalization occurs both at complete and at critical wetting as the bulk coexistence curve is approached. At critical wetting, the interface becomes also delocalized as bulk or surface parameters are varied while the system is at coexistence. Complete wetting has been observed in several experiments.[14-16] So far, there is no experimental evidence for critical wetting.

Theoretically, two types of models have been studied in order to elucidate the critical properties at the wetting transitions: (1) discrete and continuous models for the liquid-gas density,[1-4,6-8] and (2) effective solid-on-solid (SOS) models for the interface between the liquid and the gas phases.[5,9-13] In the first type of model, the density profile has been calculated by mean-field (MF) approximations which underestimate the effects of interface fluctuations, i.e., capillary waves. In the SOS model, one focuses attention on these capillary waves.

The interface fluctuations do *not* necessarily invalidate the results of MF theory. This happens only for space dimension $d \leq d^*$ where d^* is the upper-critical dimension for the transition. For $d > d^*$, MF theory should yield the correct critical singularities. It has been shown recently[7,9] that $d^*=3$ for critical wetting and short-range interactions. In this Letter, the upper critical dimension is obtained for complete wetting in systems with short-range and with long-range forces. Some remarks on critical wetting in systems with long-range forces are also included.

For temperatures above the roughening temperature, the correlation length $\xi_\parallel$ for transverse correlations diverges at complete wetting as $\xi_\parallel \propto (\delta\mu)^{-\nu_\parallel}$ where $\delta\mu$ denotes the deviation of the bulk chemical potential from its value at coexistence. It is shown below that $\nu_\parallel=\frac{1}{2}$ for three-dimensional systems with short-range forces and $\nu_\parallel=\frac{2}{3}$ for three-dimensional systems with long-range forces of van der Waals type. The correlation length $\xi_\parallel$ should show up in the diffuse scattering of light from the interfacial region. Thus, the surface exponent $\nu_\parallel$ may also be determined experimentally.

(1) *Complete wetting and short-range forces.*—In this case, the transition can be described by a Landau-Ginzburg (LG) potential $f(n)$ for the density n with two almost degenerate minima. One minimum corresponds to the gas phase with density $n=n_g$, the other to the liquid phase with $n=n_l$ The difference $f(n_l)-f(n_g)\propto\delta\mu$ which denotes the deviation of the bulk chemical potential from its value at coexistence. The mean-field (MF) approximation for the density profile $n(z)$ is obtained from $d^2n/dz^2=\partial f/\partial n$. z is the coordinate perpendicular to the surface. For special potentials $f(n)$, the MF profile $n(z)$ can be obtained analytically in closed form.[8] On the other hand, one can show that the critical properties at complete wetting do not depend on the details of $f(n)$. As long as the minima of $f(n)$ have a finite curvature corresponding to finite bulk correlation lengths, and as long as $f(n_l)-f(n_g)\propto\delta\mu$, the critical properties remain unchanged: One finds that the mean interface position $\hat{l}$ diverges as $\hat{l}\propto\ln(\delta\mu)$ and the MF surface free energy has a singular part $f_s^{\mathrm{MF}}\propto\delta\mu \times\ln(\delta\mu)$.[4,8] If the critical exponents β_s and α_s are defined via $\hat{l}\propto(\delta\mu)^{\beta_s}$ and $f_s\propto(\delta\mu)^{2-\alpha_s}$, their MF values are $\beta_s=0$ (logarithmic) and $\alpha_s=1$.[17]

The capillary waves show up as a soft mode in the Gaussian fluctuations around the MF profile $n(z)$ [3,7,9] In order to characterize these fluctuations, one has to consider an eigenvalue problem which has the form of a Schrödinger-type equation. The soft mode corresponds to the ground state with "energy" E_0. For a large class of LG potentials $f(n)$, upper and lower bounds for E_0 can be found[18] which show that E_0 goes continuously to zero at complete wetting as $E_0 \propto \delta\mu$. The upper bound is obtained by a variational method, the lower bound by means of Temple's inequality.[19] A detailed account of these bounds will be given elsewhere.[18]

Because of the soft mode, the Gaussian fluctuations give a singular contribution f_s^{GF} to the surface free energy. If one compares f_s^{GF} with the MF contribution f_s^{MF}, one finds[18] that f_s^{GF} is more singular than f_s^{MF} for $d < 3$, and less singular for $d > 3$. As a consequence, the upper critical dimension is $d^* = 3$ for complete wetting and short-range interactions.

Thus, for short-range forces, $d^* = 3$ both for critical and for complete wetting.[20] *A priori,* this is not to be expected since complete and critical wetting are two different types of surface criticality. At complete wetting, $\delta\mu$ is the only relevant scaling field.[4,21] In contrast, there are two such fields at critical wetting.[4,6,11] Note, for comparison, that different types of bulk criticality usually lead to different values for d^*. For instance, $d^* = 4$ for a critical bulk transition, and $d^* = 3$ for a bulk tricritical point.

The upper critical dimension $d^* = 3$ just derived can be obtained more easily in the framework of an appropriate SOS model for the local interface position $\hat{l}(\vec{\rho})$ which has the generic form

$$F\{l\} = \int d^{d-1}\rho \{\tfrac{1}{2}(\nabla l)^2 + V(l)\}, \tag{1}$$

where $\vec{\rho}$ are the $(d-1)$ coordinates parallel to the substrate surface at $l = 0$. Since the interface cannot penetrate this surface, $V(l)$ should contain a hard wall, i.e.,

$$V(l) = \begin{cases} \infty, & l < 0, \\ \bar{V}(l), & l > 0. \end{cases} \tag{2}$$

For short-range forces, the expression

$$\bar{V}(l) = Ae^{-\tau l} + \delta\mu\, l \tag{3}$$

has been obtained by field-theoretic methods starting from the above mentioned LG model for n.[7,9] As before, $\delta\mu$ measures the distance from bulk coexistence. A is proportional to the MF deviation from the critical wetting line inside the coexistence surface and τ is as parameter which contains the surface tension of the interface.

For the model described by (1)-(3), critical wetting occurs for $\delta\mu = 0$ and $A \to A_c$ from below with the critical coupling $A_c \leq 0$. Complete wetting occurs for $A > A_c$ and $\delta\mu \to 0^+$. The MF value for the critical coupling is $A_c = 0$. For $A > 0$, $V(l)$ has a minimum at a finite l value even in the presence of a hard-wall potential at $l = 0$. In MF theory, this minimum determines the mean interface position $\hat{l}$ via $\partial V(l)/\partial l|_{\hat{l}} = 0$, the correlation length $\xi_{\parallel}$ for transverse correlations parallel to the surface by $(\xi_{\parallel})^{-2} = \partial^2 V/\partial l^2|_{\hat{l}}$, and the surface free energy $f_s = V(\hat{l})$. For (3) with $A > 0$, one easily finds in this way $\hat{l} \propto \ln(\delta\mu)$, $\xi_{\parallel} \propto (\delta\mu)^{-\nu_{\parallel}}$ with $\nu_{\parallel} = \frac{1}{2}$, and $f_s \propto \delta\mu \ln(\delta\mu)$ which implies $\alpha_s = 1$. The upper critical dimension $d^* = 3$ is now obtained in the usual way[22] when the mean-field values $\nu_{\parallel} = \frac{1}{2}$ and $\alpha_s = 1$ are inserted into the hyperscaling relation $(d-1)\nu_{\parallel} = 2 - \alpha_s$

Note that $\xi_{\parallel}$ is predicted to diverge at complete wetting with the critical exponent $\nu_{\parallel}$. The MF value $\nu_{\parallel} = \frac{1}{2}$ found above should be correct for $d > d^* = 3$. On the other hand, if one includes the effect of capillary waves by the methods described in Refs. 5, 9, and 10, one finds that $\nu_{\parallel} = \frac{1}{2}$ holds also for $d = 3$

It has been realized before by numerical investigations of the van der Waals integral theory for fluids that the transverse correlations diverge at complete wetting.[2,3] However, the nature of this divergence has not been determined. In Fig. 11 of Ref. 3, $\xi_{\parallel}$ as obtained from the numerical work was plotted as a function of $\ln(\delta\mu)$ Presumably, this was motivated by the logarithmic divergence of $\hat{l}$. However, this plot clearly shows that $\xi_{\parallel}$ does not diverge logarithmically. On the other hand, if one takes these numerical data and plots $\ln(\xi_{\parallel})$ as a function of $\ln(\delta\mu)$, one finds a straight line with a slope $\cong -\frac{1}{2}$. Thus, the numerical investigations of the van der Waals integral theory yield $\nu_{\parallel} \cong \frac{1}{2}$ in accordance with the MF result derived above from the SOS model, Eqs. (1)-(3).

(2) *Complete wetting and long-range forces.*—In this case, an appropriate SOS mode is defined by (1), (2), and[11,13]

$$\bar{V}(l) = Bl^{-r} + \delta\mu\, l, \tag{4}$$

with $0 < r < \infty$. For $B > 0$ and $\delta\mu \to 0^+$, the MF approximation gives

$$\hat{l} \propto (\delta\mu)^{\beta_s}, \quad \beta_s = -1/(r+1), \tag{5a}$$

$$\xi_{\parallel} \propto (\delta\mu)^{-\nu_{\parallel}}, \quad \nu_{\parallel} = (r+2)/(2r+2), \tag{5b}$$

$$f_s \propto (\delta\mu)^{2-\alpha_s}, \quad \alpha_s = (r+2)/(r+1), \tag{5c}$$

at complete wetting. The divergence (5a) of the mean interface position has been obtained previously in the context of lattice gas models.[1] As far as I know, (5b) and (5c) have not been derived before. Note that the scaling relation $\beta_s = 1 - \alpha_s$ which is valid for short-range forces[4] also holds in this case for arbitrary r. If one inserts the mean-field values for $\nu_{\parallel}$ and α_s as given by (5b) and (5c) into the hyperscaling relation, one obtains the upper critical dimension

$$d^*(r) = (3r+2)/(r+2) \tag{6}$$

for complete wetting in systems with long-range forces. Note that $d^* = 3$ for short-range forces is recovered from (6) in the limit $r \to \infty$. For finite r, $d^*(r) < 3$, i.e., the upper critical dimension is *reduced* by longer-ranged forces. Such a reduction is well known in the context of bulk critical phenomena. In addition, a nontrivial test of (6) can be obtained for $d = 2$. In this case, the field theory defined by (1), (2), and (4) can be solved exactly by transfer-matrix methods. One finds[23] that $f_s \propto (\delta\mu)^{r/(r+1)}$ for $0 < r < 2$, and $f_s \propto (\delta\mu)^{2/3}$ for $r > 2$. Thus, the MF result for α_s is recovered for $0 < r < 2$ in $d = 2$ as predicted by (6).[24]

From a physical point of view, the most interesting case is $r = 2$ which corresponds to three-dimensional systems with van der Waals forces.[1,13] From (6), one finds $d^*(r=2) = 2$. Thus, MF theory should be valid for $r = 2$ and $d = 3$. As a consequence, such systems should exhibit a diverging correlation length $\xi_{\parallel} \propto (\delta\mu)^{-\nu_{\parallel}}$ at complete wetting with $\nu_{\parallel} = \frac{2}{3}$ from (5b). It would be interesting to see whether this value for $\nu_{\parallel}$ can also be obtained by the van der Waals integral theory for fluids.

(3) *Critical wetting and long-range forces.*—In order to apply MF theory to the SOS model (1), (2), and (4) with $\delta\mu = 0$, one has to replace the hard wall at $l = 0$ in (2) by a smooth repulsive potential. *A priori* it is not clear what l dependence such a repulsive potential should have. For short-range forces, an exponential l dependence has been derived in a systematic way starting from the LG model for the fluid density.[7,9] For long-range forces, an exponential l dependence can also be obtained if one starts from a LG model for the density where the long-range interactions in the fluid enter only indirectly via a contribution to the effective substrate potential [cf. Eq. (10) of Ref. 1]. This approximation leads to[23]

$$V(l) = Ae^{-\tau l} + Bl^{-r} \tag{7}$$

at bulk coexistence. In MF theory, a critical transition can only occur for $B \to B_c = 0^-$. As $B \to B_c$, the MF singularities obtained from (7) are $\hat{l} \propto \ln(1/b)$ $\xi_{\parallel} \propto b^{-1/2}$, and $f_s \propto b\ln(b)$ with $b = |B||\ln|B||^{-(1+r)}$. This implies the upper critical dimension

$$\bar{d}^*(r) = 3 \tag{8}$$

for the critical transition of (7).

Note that (3), (4), and (7) may be combined in order to study wetting in the extended (t,A,B) phase diagram. It then becomes apparent that, within MF theory, the critical transition in systems with long-range substrate potentials corresponds to the complete transition in systems with short-range potentials.[23]

In $d = 2$, exact results show that $r = 2$ is a boundary value also for the critical transition: For $r < 2$, the critical coupling has its MF value $B_c = 0$, whereas $B_c < 0$ for $r > 2$.[11] $r = 2$ is rather special since the surface free energy has an essential singularity.[11,13] Although these results have been obtained for a hard wall they should also hold for (7). This seems to indicate that the critical transition is described by MF theory for $r < 2$ in $d = 2$. On the other hand, the hyperscaling relation holds for all values of r since $\alpha_s = \frac{4}{3}$ and $\nu_{\parallel} = \frac{2}{3}$. This implies $\bar{d}^*(r) \geqslant 2$. In addition, the scaling dimension Δ_b of $\delta B = B_c - B$ is $\Delta_b = (2-r)/3$ and $\frac{1}{3}$ in $d = 2$ for $r < 2$ and $r > 2$, respectively, whereas $\Delta_b = 1$ from MF theory applied to (7). Thus, the exact results in $d = 2$ imply $\bar{d}^*(r) > 2$ which is consistent with (8).

As long as $B_c = 0$, a critical wetting transition cannot occur at a finite temperature.[13] For short-range forces $(B = 0)$, capillary waves can shift the phase boundary in $d = 3$ from its MF value $A_c = 0^-$ to $A_c < 0$ as shown in Ref. 9. For long-range forces and (7) with $r < 2$, such a shift is not to be expected since $B_c = 0$ even in $d = 2$. In addition, the results of Ref. 13 indicate that capillary waves do not change $B_c = 0$ for the SOS model (7) and arbitrary r in $d = 3$. On the other hand, it is not known how (7) is modified if one starts from a more realistic model for the fluid density. More work in this direction seems to be called for. This may also shed some light on the contradictory results for critical wetting obtained by Teletzke, Scriven, and Davis[25] and Tarazona and Evans[26] for $d = 3$

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