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Coupled fluctuations near critical wetting

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Recent work on the complete wetting transition has emphasized the role played by the coupling of fluctuations of the order parameter at the wall and at the depinning fluid interface. Extending this approach to the wetting transition itself we predict decoupling of fluctuations as the temperature is lowered towards the transition temperature T_W. Using this we are able to reanalyze recent Monte Carlo simulation studies and extract a value for the wetting parameter $\omega(T_W)\simeq 0.8$ at $T_W/T_C\simeq 0.9$ in very good agreement with long-standing theoretical predictions.

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A long-standing controversy in the study of phase transitions at interfaces concerns the nature of the continuous wetting transition in three dimensional systems with short ranged forces which corresponds to the marginal dimensionality [1–3,5–8]. Renormalization group (RG) analyses of simple capillary wave models predict [1,2] strong nonuniversality for critical exponents and amplitudes dependent on the value of the "wetting parameter" $\omega(T)$ at the transition temperature T_W. However, reliable estimates for $\omega(T)$ appropriate to the Ising model are significantly larger than values fitted to extensive Monte Carlo simulation data [6] which only reveal small deviations from mean field (MF) theory [7]. Recently it has been suggested [8] that the transition in the Ising model is actually fluctuation induced (weakly) first-order hinting that the fitted values [6,7] are unreliable. However, no quantitative analysis of the simulation data was given and the question "what value of $\omega(T)$ is consistent with simulation studies of the Ising model?" remains unanswered. In addition, there are new doubts [9] that finite size (FS) effects hinder comparison of the original simulation studies with RG predictions based on a semi-infinite model.

In this paper we extend our recent analysis of fluctuation effects at the complete wetting transition based on a "two field" effective Hamiltonian $H_2[l_1,l_2]$ [10–12] to the problem of the wetting transition discussed above. We predict crossover behavior in the effective wetting parameter as the temperature is lowered towards T_W which is associated with the decoupling of fluctuations at the wall and at the fluid interface. We show that this is in qualitative agreement with more recent Monte Carlo simulation studies of FS effects in thin magnetic films [13] which have already been shown to be consistent with the two field theory deep in the complete wetting regime [10–12]. Using this prediction we are able to extract a value for the wetting parameter $\omega(T)$ at (or very close to) the transition temperature T_W while avoiding the issue of whether the transition is weakly first or second order. We find $\omega(T_W)\simeq 0.8$ at $T_W/T_C\simeq 0.9$ which is in very good agreement with the most recent series expansion estimate at this temperature [3]. This is close to the universal critical value of ω [4] which has been the long-standing expectation for the magnitude of the wetting parameter appropriate to the Ising model [1].

To begin we make some remarks about the simulation studies used to extract this value of ω. Binder, Landau, and Ferrenberg (BLF) [13] consider a thin Ising film (thickness D lattice spacings) with competing surface fields $H_1=-H_D$. For this geometry there are a number of theoretical predictions for the way in which length scales associated with wetting phenomena determine the nature of phase coexistence and criticality in the confined system [14,15]. The qualitative predictions are confirmed by the BLF simulation studies. In particular, BLF observe the predicted symmetry broken phase (in which wetting films are adsorbed at each wall) for temperatures $T<T_C(D)$ [with $T_C(D)<T_W$ [14]] and a "soft mode" phase [14] in the temperature window $T_C>T>T_W$ (with T_C the bulk critical temperature) where an up spin–down spin interface sits on average at the center of the thin film and whose fluctuations are controlled by an exponentially large correlation length [10–12,14,15]

$$\xi_\parallel \sim \exp\left(\frac{\kappa D}{4\theta}\right). \tag{1}$$

Here κ is the inverse bulk true correlation length and $\theta=\theta(T,H_1)$ is a nonuniversal critical amplitude, the temperature dependence of which plays a crucial role in our analysis. Thus the qualitative features of both theory and simulation are in good agreement.

This situation should be compared with older Ising model simulations [6] of wetting in a thin Ising film with equal surface fields $H_1=H_D$ which as mentioned above have been the source of the controversy surrounding critical wetting. Recent theory [9] has pointed out that coupling between fluctuations in the wetting layers on each side of the thin film is an important effect and may explain the discrepancy between the simulation results and the theoretical predictions for a semi-infinite system. As emphasized above the interpretation of the BLF simulations is more straightforward because the results are compared directly with predictions for the FS system and not the semi-infinite geometry.

To continue we recall some pertinent ideas in the development of effective Hamiltonian models of wetting transitions. The standard capillary wave model $H[l(\mathbf{y})]$ has the form [1,2]

$$H[l(\mathbf{y})]=\int d\mathbf{y}\left[\frac{\Sigma_{\alpha\beta}(T)}{2}(\nabla l)^2+W(l(\mathbf{y}))\right] \tag{2}$$

where $\Sigma_{\alpha\beta}(T)$ is the stiffness coefficient of the fluid interface (separating bulk α and β phases) which unbinds from the wall and whose position is described by the collective coordinate $l(\mathbf{y})$. For systems with short ranged forces the binding potential $W(l)$ is taken to have the form [1,2]

$$W(l)=\bar{h}l+ae^{-\kappa l}+be^{-2\kappa l}, \tag{3}$$

where $\bar{h}$ is proportional to the bulk ordering field. At mean field level *critical wetting* occurs at $\bar{h}=a(T_W^{\rm MF})=0$ provided $b>0$. Similarly the *complete wetting* transition occurs in the limit of vanishing bulk field $\bar{h}\rightarrow 0^+$ for $T_C>T>T_W^{\rm MF}$ where $a(T)>0$. RG theory based on (2) and (3) predicts critical exponents and amplitudes which are sensitive to the wetting parameter

$$\omega(T)=\frac{k_BT\kappa^2}{4\pi\Sigma_{\alpha\beta}}. \tag{4}$$

For values $\omega<2$ the phase boundary for critical wetting remains $a(T_W)=0$, i.e., $T_W=T_W^{\rm MF}$ but the critical exponents are very different from MF theory. For example, along the isobar $\bar{h}=0^+$ the transverse correlation length diverges (as $T\rightarrow T_W^-$) with an exponent $\nu_\parallel=(\sqrt{2}-\sqrt{\omega})^{-2}$ for $\frac{1}{2}<\omega<2$ [1,2]. The implications for complete wetting are less dramatic—only critical amplitudes are sensitive to ω while exponents retain their MF values [2].

The discrepancy between these predictions and the older Monte Carlo simulations [6,7] led Fisher and Jin [8,16] to reassess previous derivations of $H[l(\mathbf{y})]$ concluding that the stiffness coefficient should be replaced with a position dependent term

$$\Sigma_{\rm FJ}(l;T,\dots)=\Sigma_{\alpha\beta}(T)+ae^{-\kappa l}-qle^{-2\kappa l}+\cdots \tag{5}$$

although the binding potential $W(l)$ is essentially correct. The important term in (5) is the next to leading order exponential decay which is negative ($q>0$) at the MF phase boundary $\bar{h}=a(T_W^{\rm MF})=0$. When this position dependence is taken into account in RG calculations the wetting transition is driven first order for sufficiently small values of $\omega<\omega^*$ where the tricritical value ω^* is expected to be of order unity. Fisher and Jin estimate that the transition appropriate to the Ising model is very weakly first order (the correlation length is enormous at the transition) and that T_W is very close to $T_W^{\rm MF}$.

The concept of a position dependent stiffness coefficient was forwarded independently by Parry and Evans [17], who pointed out that Hamiltonians of the form (2) could not describe next to leading order singularities of correlation functions at the complete wetting transition (which are known to exist from exact statistical mechanical sum rules). Unfortunately the position dependence of $\Sigma(l)$ explicitly derived by Fisher and Jin using crossing and integral criteria is not of the type required by Parry and Evans [17] to satisfy full thermodynamic consistency. One way around this is to introduce a two field effective Hamiltonian $H_2[l_1,l_2]$ [10–12]

$$H_2[l_1,l_2]=\int d\mathbf{y}[\tfrac{1}{2}\Sigma_{\mu\nu}(l_1,l_2)\nabla l_\mu\cdot\nabla l_\nu+U(l_1)+W_{(2)}(l_2-l_1)], \tag{6}$$

which models the coupling of fluctuations at the wall and $\alpha\beta$ interface. The binding potential $W_{(2)}$ is essentially the same as the expression (5) while U simply binds the lower surface to the wall. The Hamiltonian (6) may be derived from an underlying "microscopic" Landau-Ginzburg-Wilson functional using a double crossing criterion in which $l_1(\mathbf{y})$ and $l_2(\mathbf{y})$ are collective coordinates denoting surfaces of fixed magnetization m_1^X and m_2^X, respectively. In the approach to the complete wetting transition the collective coordinate l_2 unbinds from the wall while l_1 remains bound. The position dependence of the stiffness elements $\Sigma_{\mu\nu}(l_1,l_2)$ provides a very elegant explanation of the correlation function singularities which single field Hamiltonians fail to describe. In particular, it is the off diagonal elements which provide the dominant exponential decay essential for thermodynamic consistency in the correlation function theory. The term Σ_{11} is essentially position independent and may be identified with the stiffness of the wall-β interface $\Sigma_{w\beta}$ while $\Sigma_{22}(l_{21})$ is very similar to the Fisher-Jin stiffness (5). The presence of coupled fluctuations has a rather profound effect on the critical behavior at complete wetting. Assuming that $U(l_1)$ may be approximated by a Gaussain $U(l_1)=rl_1^2/2$ RG calculations [10,12] predict that critical amplitudes are no longer determined by ω but by the renormalized quantity

$$\bar{\omega}=\omega+\frac{\omega_\beta}{1+(\Lambda_1\xi_{w\beta})^{-2}}, \tag{7}$$

where $\omega_\beta=k_BT\kappa^2/4\pi\Sigma_{w\beta}$ and $\xi_{w\beta}\equiv\sqrt{r/\Sigma_{11}}$ is the (finite) correlation length at the $w\beta$ interface. Λ_1 is the momentum cutoff for the bound surface l_1. The distinction between momentum cutoffs for the surfaces of fixed magnetization m_1^X and m_2^X was not addressed in our earlier discussion of coupling effects deep in the complete wetting regime. This will play an important role in our treatment of the crossover to critical wetting.

Consider for example the effective Hamiltonian (2) with cutoff Λ. In standard interpretation the range of wave vectors allowed in the Fourier decomposition of $l(\mathbf{y})$ is $0\leq Q<\Lambda$ where $\Lambda\ll\sqrt{\Sigma_{\alpha\beta}/k_BT}$ corresponding to length scales much greater than the bulk correlation length [18]. The same idea applies to the two field Hamiltonian. In fact, it is easy to establish [19] that the local cutoff Λ_1 must satisfy $\Lambda_1\ll\sqrt{\Sigma_{w\beta}/k_BT}$ otherwise this picture of fluctuations breaks down. Of course this does not mean that fluctuations of the underlying order parameter $m(\mathbf{r})$ with wave vectors greater than Λ_1 do not exist, rather that only for sufficiently small wave vectors are they well described by an interfacial-like collective coordinate $l_1(\mathbf{y})$ which couples to $l_2(\mathbf{y})$. Fluctuations in $m(\mathbf{r})$ with wave vectors greater than Λ_1 are not interfacial-like and have to be added to the model in some other way [19]. Coupling between these modes and $l_2(\mathbf{y})$ does not lead to renormalization of the wetting parameter.

We now apply these ideas to the wetting transition starting in the complete wetting regime and ask how the critical amplitudes describing the transition vary as the temperature is lowered towards $T_W^{\rm MF}$. The important features of the Hamiltonian in this limit are as follows.

(i) The cancellation of the leading order exponential decay in $W_{(2)}(l_{21})$ and $\Sigma_{22}(l_{21})$ similar to that indicated in (3) and (5). Such behavior could have been anticipated from the simpler capillary wave model and the Fisher-Jin theory.

(ii) The vanishing of the local stiffness $\Sigma_{w\beta}\sim a^2$ and hence the momentum cutoff Λ_1. These effects are specific to the two field model.

The important behavior related to (ii) corresponds to a decoupling of fluctuations in the order parameter $m(\mathbf{r})$ at the wall and $\alpha\beta$ interface. Within our theory all these features, (i) and (ii), are associated with the flattening of the magnetization profile near the wall as $T\rightarrow T_W^{\rm MF}$. While we were initially worried that this was an artifact of our model, inspection of the simulation results for the magnetization [13] appears to confirm this very close to the observed T_W. Exactly at $T=T_W^{\rm MF}$ the two field model is essentially identical to that of Fisher and Jin so repeating their argument [8] we predict that the wetting transition is fluctuation induced (very weakly) first order provided ω is not too big. However, because the tricritical value ω^* is not known very accurately the transition in the Ising model may still be second order. Even if the transition was first order it is very unlikely that this could be seen directly in simulations [12].

A prediction of this analysis is a crossover effect associated with the decoupling of fluctuations. Deep in the complete wetting regime the coupling of fluctuations described by (6) increases the effective value of the wetting parameter [as given in Eq. (7)] but this effect vanishes as the temperature is lowered to the wetting temperature (or more accurately $T_W^{\rm MF}$). In other words, the effective wetting parameter $\bar{\omega}$ displays the limiting behavior

$$\lim_{T\rightarrow T_W^{\rm MF^+}} \bar{\omega}(T,\ldots)=\omega(T_W^{\rm MF}), \tag{8}$$

which is our central result. This has important consequences for the temperature dependence of critical amplitudes. For example, in [10] we showed that the critical amplitude θ defined in (1) is related to the effective wetting parameter by $\theta=1+\bar{\omega}/2$. The decoupling of fluctuations thus implies that θ should decrease as T is reduced to T_W and that the extrapolated value at the wetting temperature (or more accurately $T_W^{\rm MF}$) is $\theta^+(T_W)=1+\omega(T_W)/2$. (Recall that T_W and $T_W^{\rm MF}$ are extremely close together and it is unlikely that they can be distinguished.) In Fig. 1 we plot values of the critical amplitude θ taken from the susceptibility measurements of BLF. Using linear and cubic fits to extrapolate to the wetting temperature $T_W/T_C\simeq 0.9$ we obtain $\theta^+\sim 1.4$ which implies that $\omega(T)\sim 0.8$ at this temperature. This is very close to the series expansion result of Fisher and Wen [3]. Importantly there is no indication that that "old" fitted values $\omega_{\rm fit}\simeq 0.3$ [7] and

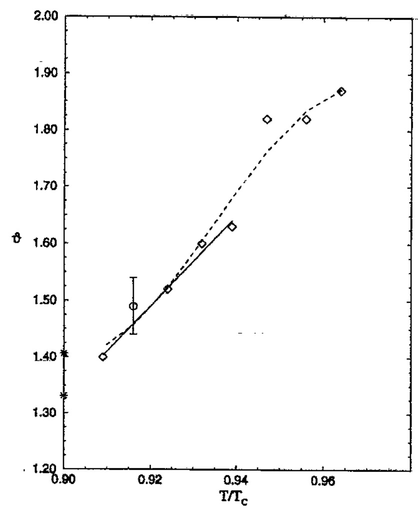

FIG. 1. A cubic fit of the simulation results for $\theta(T,\ldots)$. A linear fit to the lower four diamonds is also shown. The extrpolated values θ^+ at $T_W/T_C\sim 0.9$ are indicated by stars. Apart from the data point at $T/T_C=0.916$ the error is within the symbol. As the temperature rises from T_W the value of θ increases.

$\omega_{\rm fit}\sim 0$ [6] are appropriate. Such values of the wetting parameter would imply $\theta^+\sim 1.15$ or $\theta^+\sim 1$ (corresponding to MF theory) which are totally inconsistent with the new BLF data.

Four points that are worth emphasizing are as follows.

(a) The method avoids the issue of whether the transition is first or second order. Even if the transition is fluctuation induced first order the wetting temperature T_W is very close to $T_W^{\rm MF}$ and coupling effects may be ignored when θ is extrapolated to T_W.

(b) In contrast to the original simulations [6] the FS effects for the BLF studies are well understood and thus we are confident that the simulations are probing equilibrium behavior. Problems encountered with the $H_1=H_D$ parallel plate geometry do not arise [9].

(c) The data used to extract the critical amplitude θ are taken from the susceptibility measurements of BLF which are local to the fluctuating interface. Specifically they involve the susceptibilities χ_n and χ_{nn} centered at the middle of the thin film geometry where the interface lies on average. Older simulations [6] had relied on measurements of the wall susceptibilities χ_1 and χ_{11} which require assumption of scaling methods to analyze.

(d) The correlation length $\xi_\parallel$ in the soft mode phase is very large and easily satisfies the Ginzburg criteria [20].

In summary, we have used a two field Hamiltonian model to predict a decoupling effect at the three dimensional wetting transition which has implications for the temperature dependence of critical amplitudes. On the basis of this we have reanalyzed recent Monte Carlo simulations and extracted a value of the wetting parameter which is very close to long-standing theoretical predictions.

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