

Dynamics of roughening and complete wetting

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The kinetics of interfacial roughening, and its effect on the complete wetting of a substrate, are studied theoretically. Dynamical interface models are used to analyze the effects of fluctuations on the late stages of wetting for several different cases: at high temperatures (far from the roughening transition), near the roughening transition, in the presence of a random external field, as well as for the case where a local conservation law is present. The time dependence for the growth of the diffuse wetting layer which is predicted can be tested experimentally or by numerical simulation.

I. INTRODUCTION

Wetting has become a topic of considerable theoretical and experimental interest in recent years.¹⁻⁵ The effect of fluctuations on the kinetics of complete wetting will be the subject of this paper. Recently, the growth of wetting layers has been studied by Lipowsky.⁴ In this paper, I generalize his results to consider some of the salient features which the roughening transition, random impurities, and local conservation of the order parameter have on the dynamics of wetting.

In a liquid-vapor system, complete wetting occurs when a thin layer of liquid film is adsorbed on a substrate, at the bulk phase coexistence of the liquid and vapor. The physics is dictated by the interaction of the substrate with the liquid film's interface. That interaction causes the liquid-vapor interface to the "repelled" from the substrate, as more liquid is adsorbed. Thus, in equilibrium a length diverges, namely the thickness of the wetting layer (the distance between the substrate and the interface). During complete wetting, this length grows as time goes on.

The physics of complete wetting is somewhat analogous to that of the kinetics of a first-order phase transition, where the average size of an ordered domain grows and diverges as time proceeds.⁶ In that case, one often idealizes the situation by imagining a quench from a very high temperature, to a very low one. This gives a set of initial conditions for the interfacial configuration (i.e., a random configuration). Here, in complete wetting, a similar device is useful;⁴ one may imagine that the system can be prepared such that the deviation $\delta\mu$ of the bulk chemical potential from its value at coexistence, can be rapidly changed from some large value to zero. This has the following result. When $\delta\mu$ is large, the interface is flat and coincident with the substrate, which gives the initial conditions. When $\delta\mu$ is rapidly changed to zero, however, the interface must become *diffuse* (provided one is below the upper critical dimension for roughening) and infinitely *thick*, as it is in equilibrium, by a kinetic process.

These two effects arise from different origins; fluctua-

tions cause the film's interface to wander and become rough,⁷⁻¹⁴ while the repulsive potential of interaction between the liquid film's interface and the substrate causes the layer thickness to diverge. Explicitly, if the interface is a distance ξ from the substrate, then as time $t \rightarrow \infty$, $\langle (\xi - \langle \xi \rangle)^2 \rangle \rightarrow \infty$ due to fluctuations and $\langle \xi \rangle \rightarrow \infty$ due to the substrate interaction, where the angular brackets denote an ensemble average. Herein, I shall determine how the thickness of the diffuse wetting layer grows in the late stages of complete wetting. I shall be especially concerned with the effects of fluctuations on growth.

A brief outline follows.¹⁵ In Sec. II, I study the dynamics of roughening. I consider a single isolated interface, in the absence of a substrate, and present a theoretical analysis of the kinetics which occur as the interface roughens. First, results for the effects of fluctuations in a continuum model are obtained (which are related to earlier work of Lipowsky⁴). The effect of the roughening transition is then considered in a simplified manner. Finally, the effect of random impurities (modeled by a random external field¹⁶) is studied, and results involving a local conservation law are presented. In Sec. III, the results for the dynamics of roughening are applied to complete wetting. Lipowsky's previous results are recovered in a somewhat more transparent (but equivalent) way. New results, involving behavior near the roughening transition, random fields, and a local conservation law, are also given. Possible ways to test theory experimentally or by simulation are discussed.

II. DYNAMICS OF ROUGHENING

A. Fluctuations above the roughening transition

In this section I shall consider the kinetics by which an isolated interface roughens. In Sec. III, this will be related to complete wetting.

Consider an interface located in the $(d-1)$ -dimensional \mathbf{x} plane, which is orthogonal to the y axis. I will assume that the system can be prepared such that the interface corresponds to the $y=0$ plane, at time $t=0$.

That is, the interface is flat initially, as compared to its rough equilibrium shape. Some ways to experimentally make the interface initially flat are discussed in Sec. III. Since solutions will be presented for late times (when the thickness of the diffuse interface diverges), the details of the initial conditions are irrelevant, and simple ones may be chosen. A single-valued variables $\zeta(\mathbf{x}, t)$ gives the instantaneous position of the interface, relative to the y axis, as time goes on. Thus I neglect "overhangs" and "bubbles" (i.e., the possibility of a multivalued ζ). This assumption should be of little consequence provided ζ/L is small, where L^{d-1} is the area of a flat interface. The dynamical interface model studied in this paper is^{4, 12, 13, 17-20}

$$\frac{\partial \zeta(\mathbf{x}, t)}{\partial t} = -D \frac{\delta F}{\delta \zeta(\mathbf{x}, t)} + \eta(\mathbf{x}, t), \quad (1)$$

where F is the surface free energy, D is a constant, and η is the thermal noise. The fluctuation-dissipation relation for η is

$$\langle \eta(\mathbf{x}, t) \eta(\mathbf{x}', t') \rangle = 2k_B T D \delta^{d-1}(\mathbf{x} - \mathbf{x}') \delta(t - t'), \quad (2)$$

where k_B is Boltzmann's constant, T is temperature, and the angular brackets denote an ensemble average. Higher-order moments are assumed to be determined by a Gaussian distribution. In general, Eqs. (1) and (2) will require additional factors to ensure Euclidean invariance^{8, 18} (that is, physical invariance under rotations and translations of the prescribed coordinate system), but these are negligible to the order in which I shall work.

Dynamical equations of this form have been used to study the kinetics of first-order transitions,^{6, 19-22} as well as the kinetics of roughening.^{12, 13} Equation (1) can be derived from the corresponding equation of motion for the order parameter in model A (the continuum nonconserved Ising model), or it can simply be obtained from symmetry arguments. It requires modification when conservation laws are important,²³⁻²⁵ as will be discussed, or when other topological defects, such as vortex lines, vortices, or monopoles, are present.^{26, 27}

In this section, I consider a standard continuum model for F : the surface free energy is assumed to be proportional to the $(d-1)$ -dimensional area of the interface.

$$F = \sigma \int d^{d-1}x [1 + (\nabla \zeta)^2]^{1/2} \quad (3)$$

$$\approx \sigma L^{d-1} + \frac{1}{2} \sigma \int d^{d-1}x (\nabla \zeta)^2 + \dots,$$

where the proportionally constant σ is the surface tension, and the gradient is with respect to \mathbf{x} . For small deviations from $\zeta=0$ (that is, $\zeta/L \ll 1$) one obtains from Eqs. (1) and (3),

$$\frac{\partial \zeta(\mathbf{x}, t)}{\partial t} = -D \int d^{d-1}x' \frac{\delta^2 F}{\delta \zeta(\mathbf{x}) \delta \zeta(\mathbf{x}')} \zeta(\mathbf{x}', t) + \eta(\mathbf{x}, t). \quad (4)$$

The kernel is diagonal in Fourier space, so the Fourier transform

$$\zeta(\mathbf{q}) \equiv \int d^{d-1}x e^{i\mathbf{q} \cdot \mathbf{x}} \zeta(\mathbf{x})$$

is introduced. The integral has a cutoff at small x of ξ , where ξ is the thermal correlation length, and for large x of L . Likewise, then, in Fourier space there is an infrared wave-number cutoff $2\pi/L$, and an ultraviolet cutoff $2\pi/\xi$. In Eq. (4) one has

$$\frac{\partial \zeta(\mathbf{q}, t)}{\partial t} = -D \frac{\delta^2 F}{\delta \zeta^2} \zeta(\mathbf{q}, t) + \eta(\mathbf{q}, t) \quad (5)$$

so that

$$\langle \zeta(\mathbf{q}, t) \zeta(\mathbf{q}', t) \rangle = \int \int dt' dt'' \langle \eta(\mathbf{q}, t') \eta(\mathbf{q}', t'') \rangle \times e^{-D(2t - t' - t'') \delta^2 F / \delta \zeta^2},$$

where it has been assumed that the initial value of $\langle \zeta^2 \rangle$ is of negligible importance at the late time t . Using Eqs. (2) and (3) (which gives $\delta^2 F / \delta \zeta^2 = \sigma q^2$) and introducing the notation

$$\langle \zeta(\mathbf{q}, t) \zeta(\mathbf{q}', t) \rangle = (2\pi)^{d-1} \delta^{d-1}(\mathbf{q} + \mathbf{q}') \langle \zeta^2 \rangle(\mathbf{q}, t)$$

one obtains the equal-time correlation function

$$\langle \zeta^2 \rangle(\mathbf{q}, t) = \frac{k_B T}{\sigma q^2} (1 - e^{-2D\sigma q^2 t}). \quad (6)$$

The result for thermal equilibrium is found by taking the $t \rightarrow \infty$ limit of this expression, which gives $\langle \zeta^2 \rangle_{\text{eq}}(q) = k_B T / (\sigma q^2)$. It may be possible to directly observe the nonequilibrium result by elastic scattering experiments. Often, such experiments measure fluctuations in the order parameter ϕ . When the system has a single interface

$$\phi(\mathbf{x}, y; t) \approx \phi_0 + \zeta(\mathbf{x}, t) \frac{d\phi_0}{dy} + \dots, \quad (7)$$

where ϕ_0 is the bare profile.² Thus the fluctuations around ϕ_0 , $\delta\phi$, satisfy

$$\langle (\delta\phi)^2 \rangle \approx \langle \zeta^2 \rangle(\mathbf{q}, t) \left[\frac{d\phi_0}{dy} \right]^2. \quad (8)$$

The root-mean-square fluctuation of a position on the interface is given by

$$\xi_{\text{rms}} \equiv \left[\int \frac{d^{d-1}q}{(2\pi)^{d-1}} \langle \zeta^2 \rangle(q, t) \right]^{1/2}. \quad (9)$$

Before obtaining the results for the nonequilibrium behavior, I shall review the results for thermal equilibrium [which are found by taking the $t \rightarrow \infty$ limit of Eq. (6)]. One obtains, $\xi_{\text{rms}}(t \rightarrow \infty) \sim L^{(3-d)/2}$ for $d < 3$. For $d = 3$, $\xi_{\text{rms}} \sim \sqrt{\ln L}$. These are standard results for roughening in a continuum model. While they imply that interfaces are rough, and so diffuse, for $d \leq 3$, the results do not necessarily mean that phase coexistence is destroyed, since $\xi_{\text{rms}}/L \sim 1/L^{(d-1)/2}$. Thus for $d > 1$, ξ/L is small in the thermodynamic limit of $L \rightarrow \infty$, and phase coexistence and long-range order persist. The calculation is consistent with the known lower critical dimension $d_l = 1$ (that being the dimension below which there is no long-range order). It does not prove that result, since the as-

sumptions of the theory, e.g., $\zeta/L \ll 1$, break down there.

The time-dependent root-mean-square fluctuation of the interface is found from Eqs. (6) and (9). If the system is sufficiently large that the limit $L \rightarrow \infty$ can be taken (so that the infrared cutoff vanishes), one obtains

$$\zeta_{\text{rms}} \sim t^{(3-d)/4}, \quad (10)$$

for "late" times in $d < 3$, which has previously been obtained by Lipowsky⁴ in a discussion of fluctuation-driven dynamics of complete wetting. For $d = 3$, $\zeta_{\text{rms}} \sim \sqrt{\ln t}$. Analogous manipulations to the above have been given by Desai and Grant,¹⁴ which involve the dynamics of capillary waves on a liquid-vapor interface in three dimensions.

The result is valid for late times in the following sense. The time t in Eq. (10) must be sufficiently large that initial conditions, and corrections to this result are negligible [e.g., $\zeta_{\text{rms}}(t=0)/\zeta_{\text{rms}}(t) \ll 1$]. (It is in anticipation of this limitation that I have chosen particularly simple initial conditions.) It may also be worth mentioning that, if the analog of Eq. (16) is required for the case with L finite, this is simply accomplished by including an infrared cutoff, as well as the usual ultraviolet one.

Finally, let me note that an experimental or numerical study of $\langle \xi^2 \rangle(q, t)$, which is predicted above by Eq. (6), could possibly test theory more severely than a determination of $\zeta_{\text{rms}}(t)$. The exponentially decaying part of Eq. (6) is the signature of a linear theory. The subsequent result Eq. (10) may, however, be slightly more general than this, in the following sense. If the exponentially decaying part is replaced by $g(q^2 t)$, where $g(\alpha \rightarrow \infty) \rightarrow 0$, then the same results are obtained for thermal equilibrium, and for $\zeta_{\text{rms}}(t)$.

B. Fluctuations near the roughening transition

The results given above apply to systems where lattice structure is unimportant. This provides a complete description of the long-time, long-wavelength properties of a system, even if there is lattice structure, provided one is above the roughening transition temperature T_R . Below T_R , however, there is no longer an infrared divergence in ζ , and interfaces are no longer rough. The underlying lattice causes facets to form on droplets.⁷ For the Ising model, $T_R = 0$ in $d = 2$, and $0 < T_R < T_c$ in $d = 3$, where T_c is the critical temperature.

Below T_R , the absence of an infrared divergence in ζ implies that dynamics is limited to large fluctuations. It is natural to expect that the rate of such fluctuations is proportional to their probability, as in nucleation theory. Thus, if the free energy of an interface is proportional to ζ^n , where n depends on the form of the free energy, then the time scale τ over which such fluctuations occur is

$$\tau \sim e^{\text{const} \times \zeta^n},$$

so that one would expect that

$$\zeta_{\text{rms}} \sim (\ln t)^{1/n} \quad (11)$$

below T_R . An exponent $n = 2$ corresponds to a quadratic

surface free-energy below T_R . Presumably the exponent would be difficult to determine numerically or experimentally, however.

At low temperatures above T_R , but close to the roughening transition, I expect crossover behavior over intermediate length scales. For the dynamics of roughening, this implies crossover behavior over intermediate times, although the $t \rightarrow \infty$ behavior studied in Sec. II C should be unchanged. A model for "lattice" effects which can be used for this purpose has been introduced by Grinstein and Ma²⁸

$$F = \sigma \int d^{d-1}x (1 + |\nabla \zeta|). \quad (12)$$

This model has limited validity, since it is not clear that a coarse graining of a lattice Hamiltonian will lead to a free energy of this form. To be explicit, while this model is plausible on intermediate length scales for $T \gtrsim T_R$, where remnants of the underlying lattice are modeled by the absolute-value signs, it is not correct on long length scales. In that case Eq. (3) above applies. Despite this drawback, this model is useful for examining *crossover* behavior near T_R . In principle, a better approach would be to use a known anisotropic surface tension like σ for the two-dimensional Ising model.⁹ However, such a calculation appears quite formidable. For our present purposes Eq. (12) provides a well-defined model from which some qualitative results concerning crossover near T_R can be obtained.

Analysis of this model is complicated because it involves the absolute value of a function. It is obvious, though, that F is minimized for $\zeta = 0$. Also analytic representations of $|\nabla \zeta|$ will lead to a free-energy quadratic in ζ , for small ζ , i.e., for small distortions of the interface). The difficulty, however, involves finding the form of the coefficient of that term, or in other words, one must obtain $(\delta^2 F / \delta \zeta^2)(q)$. I will do this by assuming that $(\delta^2 F / \delta \zeta^2)(q) \sim q^a$, for long wavelengths. Then I shall determine the exponent a self-consistently by working out $\langle \xi^2 \rangle$.

In the same manner as shown above, I obtain $\langle \xi^2 \rangle(q, t) \propto q^{-a} [1 - \exp(-Cq^a t)]$, where C is a constant. Now, to determine a I write $|\nabla \zeta| = [(\nabla \zeta)^2]^{1/2}$, and obtain²⁹

$$\frac{\delta^2 F}{\delta \zeta(\mathbf{x}) \delta \zeta(\mathbf{x}')} = -\sigma \nabla \cdot \left[\frac{1}{|\nabla \zeta|} [\bar{\mathbf{I}} - \hat{\mathbf{n}} \hat{\mathbf{n}}] \right] \cdot \nabla \delta(\mathbf{x} - \mathbf{x}'), \quad (13)$$

where $\bar{\mathbf{I}}$ is the unit tensor, and $\hat{\mathbf{n}} \equiv \nabla \zeta / |\nabla \zeta|$. By translational invariance, the Fourier transform of this will be a function of q alone. To find the wave-number dependence, I count dimensions. From the formula above $(\delta^2 F / \delta \zeta^2)(q) \sim q [\zeta^{-1}(x)]_{\text{units}}$. Thus, given the solution for $\langle \xi^2 \rangle(q, t)$ above, one obtains $[\zeta(x)]_{\text{units}} \sim q^{-(a+1-d)/2}$. Self-consistency with the assumed form of $(\delta^2 F / \delta \zeta^2)(q)$ gives $a = 3 - d$. This implies that

$$\langle \xi^2 \rangle(q, t) \sim q^{-(3-d)} (1 - e^{-Cq^{3-d}t}). \quad (14)$$

The dynamical results for roughening can now be easily

found. For $d=2$, $\xi_{\text{rms}} \sim \sqrt{\ln t}$, while for $d < 2$, $\xi_{\text{rms}}(t) \sim t^{(2-d)/(3-d)}$.

These results suggest that there is rich behavior near the roughening transition temperature T_R . Below T_R , I predict slow activated growth, while above that temperature, much faster growth occurs. In the vicinity of T_R , however, I predict strong crossover behavior, over intermediate time scales, due to the vicinity of the roughening transition. Of course, since the analysis is only self-consistent, and is based in part on dimensional arguments, the result is more suggestive than it is definitive. The other limitations and qualifications of this result are the same as noted above.

C. Fluctuations in the presence of a random external field

I will now study the effects of random impurities by considering a simple, but nontrivial, model of those impurities: the random-field Ising model.^{16,28,30-33} In this model, there is a random external field H in the free energy, which is linearly coupled to the order parameter ϕ . The statistics of this field are assumed to be given by $\langle H \rangle = 0$, and

$$\langle H(\mathbf{x}, y) H(\mathbf{x}', y') \rangle = h^2 \delta^d - 1 (\mathbf{x} - \mathbf{x}') \delta(y - y'), \quad (15)$$

with higher-order moments determined by a Gaussian distribution in the present treatment. The field is independent of time, if one models impurities which are fixed in position. It is a simplified model because, in many cases, impurities also cause the free energy to have a random part which is quadratically coupled to the order parameter, giving a spin glass. Nevertheless, many controlled experimental realizations of the random-field Ising model are known,³⁴⁻³⁶ such as dilute antiferromagnets in a uniform magnetic field, gels in binary fluids, and chemisorbed systems with small frozen impurities.

The equation of motion satisfied by ξ is the same as Eq. (1) above provided one adds to F a term F_h , which gives the surface free energy due to the random field.³⁷⁻³⁹ (I shall neglect thermal noise in comparison to the random field.) From the analysis of, e.g., Grinstein and Ma^{28,30,31} one has

$$F_h = 2 \int d^{d-1}x \int_0^\xi dy H(\mathbf{x}, y), \quad (16)$$

where a step-function-like profile has been assumed for the order parameter $\phi_0(y)$.

Following the same strategy as above gives,

$$\begin{aligned} \langle \xi^2 \rangle(q, t) = \int dt' \int dt'' & \left\langle \frac{\delta F_h}{\delta \xi}(t') \frac{\delta F_h}{\delta \xi}(t'') \right\rangle(q) \\ & \times e^{-D(2t - t' - t'') \delta^2 F / \delta \xi^2}, \end{aligned} \quad (17)$$

where the average is over the random field. [Recall that $(\delta^2 F / \delta \xi^2)(q) = \sigma q^2$ from above, where σ is now the bare surface tension.] It remains to evaluate $\langle (\delta F_h / \delta \xi)^2 \rangle$. I will approximate this quantity by its time-independent equilibrium value, which has been previously calculated by Grinstein and Ma,²⁸ namely

$\langle (\delta F_h / \delta \xi)^2 \rangle \approx h^{4/3} q^{(5-d)/3}$. This is justifiable because the integral's major contributions are for t' and t'' close to t . Also, the approximation is self-consistent in that the time-dependent corrections to Eq. (17) would be exponentially decaying, and so negligible in the integrand. Using this above gives the result,

$$\langle \xi^2 \rangle(q, t) \sim h^{4/3} q^{-(d+7)/3} (1 - e^{-D\sigma q^2 t})^2. \quad (18)$$

The equilibrium results are well known, and are consistent with a lower critical dimension of^{28,30,33} $d_l = 2$. Namely, by taking the $t \rightarrow \infty$ limit of the above expression, one obtains $\langle \xi^2 \rangle_{\text{eq}} \sim q^{-(d+7)/3}$, and $\xi_{\text{rms}} \sim L^{(5-d)/6}$.

The dynamical result for roughening is

$$\xi_{\text{rms}}(t) \sim h^{2/3} t^{(5-d)/6}, \quad (19)$$

for late times and $d < 5$. [For $d=5$, $\xi_{\text{rms}}(t) \sim h^{2/3} \sqrt{\ln t}$.] The analysis of Sec. II B, for roughening over intermediate length and time scales near the roughening transition, can also be generalized. I obtain $\xi_{\text{rms}} \sim t^{(3-d)/(4-d)}$ for $d < 3$, and $\xi_{\text{rms}} \sim \sqrt{\ln t}$ for $d=3$. This growth is much faster than the corresponding result for the continuum model in the absence of a random field. As in heterogeneous nucleation, where the fluctuation-limited rate of droplet formation is enhanced by impurities, the fluctuation-driven growth here is faster in the presence of impurities.

An important qualification of the result (besides those mentioned in previous sections) concerns the possibility of anomalously slow equilibration for very late times. It is found experimentally,⁴⁰ and predicted theoretically,^{41-43,31} that a random-field system quenched from a disordered state to a low temperature (called field cooling) can get trapped in a metastable state.⁴⁴ While this is different from what is considered here (the present analysis assumes coexisting phases separated by a flat interface, and so may be more closely related to³⁴ zero-field cooling), I cannot rule out the possibility of a crossover to such slow equilibration. Thus, the present results would be valid for late times which precede that regime.⁴⁵

It should also be mentioned that the kinetics of interfacial motion in the presence of a random field is an interesting problem in its own right. A test of the predictions above could give insight into the origins of the slow equilibration which is seen experimentally in diluted antiferromagnets, and other representations of the random-field Ising model. Finally, I note that in a recent paper, which is related to the present one, those metastable states have been investigated theoretically.⁴⁶

D. Fluctuations in the presence of a local conservation law

To conclude this section, I shall briefly mention results for the case where the interfacial dynamics is constrained by a local conservation law. Kawasaki and Ohta^{24,25} have shown that model B of critical dynamics⁴⁷ (where the order parameter is conserved) implies an interface equation involving a nonlocal kernel. This kernel allows the conservation law to be satisfied by either long-range diffusion between widely separated interfaces, or short-range diffusion across parts of an interface. If, however,

there is a single interface present and the conservation law is only enforced locally, the equation simplifies significantly. It reduces to a dynamical model of sintering due to Mullins.²³ This dynamical model, which involves a local conservation law, is obtained from Eqs. (1) and (2) with the replacement $D \rightarrow -D'\nabla^2$, where D' is a constant. Additional factors are required to preserve Euclidean invariance, but to the order of the present calculations, that substitution is sufficient. The modification of the results above is that $Dt \rightarrow q^2 D' t$ in the equations for $\langle \xi^2 \rangle(q, t)$ [Eqs. (6), (14), and (18)], and the growth of the root-mean-square fluctuation obeys,

$$\xi_{\text{rms}}(t) \sim t^{\psi_{lc}}, \quad (20)$$

for late times, where ψ_{lc} is half the exponent calculated above for a given model of the free energy. The crossover results [where $\xi_{\text{rms}}(t) \sim \sqrt{\ln t}$] remain unchanged. I suspect that "late times" here is true under more restrictive qualifications than the case without the conservation law: For late times when the interface becomes extremely rough, long-range diffusion [between two neighboring peaks in $\xi(x)$], which is neglected in this model, could become comparable to short-range diffusion.⁴⁸

III. DYNAMICS OF COMPLETE WETTING

I shall now apply the results of Sec. II to the late stages of complete wetting. Of course, those results provide a description of roughening kinetics which can be tested experimentally, regardless of their relevance to wetting.

In complete wetting, the substrate on which the liquid film is absorbed plays an important role. The equation of motion is the same as Eq. (1), provided $F|\xi|$ is replaced by $F|\xi| + V|\xi|$, where V gives the interaction with the substrate. Thus the motion of the wetting layer is modeled by allowing it to minimize its surface free energy, as well as respond to the repulsive substrate interaction (which, of course, attracts the bulk liquid phase). For a short-ranged interaction with the substrate the potential can be modeled⁴ by, $V = A \exp(-\xi/\xi)$, where A is a positive constant, and ξ is the bulk correlation length. Since I will not consider temperatures close to a second-order transition, ξ will be of the order of the lattice constant. Long-ranged interactions depend on the particular system of interest. For example, long-range van der Waals interactions^{4,27} are of the form $V = A/\xi^p$, where $p = 5-d$ or $6-d$ for forces where the radiation field in the electromagnetic interaction is nonretarded or retarded,²⁷ respectively. Note that V is minimized by $\xi \rightarrow \infty$.

The mean-field results, previously given by Lipowsky,⁴ will now be recovered.⁴⁹ If $\nabla \xi = 0$, so that the effects of F can be neglected, as compared to V , then one obtains,

$$\langle \xi(t) \rangle_{\text{MF}} \sim t^{\psi_{\text{MF}}}. \quad (21)$$

The mean-field exponent is $\psi_{\text{MF}} = 1/(7-d)$, $1/(8-d)$, or $O(\log)$, if the substrate interaction is long-range retarded, long-range nonretarded, or short range, respectively. If there is a local conservation law, as in Sec. II D, there can be no mean-field growth.

On the other hand, if the substrate interaction V can be "neglected," the results involving roughening from Sec. II apply. In which case

$$\xi_{\text{rms}} \sim t^{\psi_{\text{fl}}}, \quad (22)$$

where for convenience I introduce the alternate notation $\xi_{\text{rms}}^2 \equiv \langle \xi^2 \rangle_{\text{fl}}$. From Sec. II, the exponent for growth due to fluctuations is $\psi_{\text{fl}} = (3-d)/4$ or $(5-d)/6$, above a roughening transition, where the second exponent applies to the case of a random external field.⁵⁰ Below a roughening transition, growth due to fluctuations is limited by large fluctuations, which leads to logarithmic growth (or powers of logarithms). For temperatures above, but close to the roughening transition T_R , I expect crossover for intermediate length and time scales (but not for the limits $q \rightarrow 0$ and $t \rightarrow \infty$). The exponent which characterizes that crossover is $\psi_{\text{fl}} = (2-d)/(3-d)$ or $(3-d)/(4-d)$, where the second exponent again applies to the case of a random external field. It is worth emphasizing again, however, that these results only apply to intermediate times for $T \gtrsim T_R$. For $t \rightarrow \infty$ the previously mentioned results apply. If there is a local conservation law, then all ψ_{fl} 's are halved, and at the crossover dimensions where the ψ_{fl} 's vanish, $\xi_{\text{rms}} \sim \sqrt{\ln t}$.

During complete wetting in real systems, both the substrate interaction and the surface free energy play important roles. In the late stages, however, these effects can be separated, as will now be shown. First, I shall inquire as to where the predictions for $\xi_{\text{rms}}(t)$ are relevant to wetting. Clearly, the corrections to this result will be due to the neglected substrate interaction. Dimensional analysis implies that the leading order correction to the root-mean-square result for ξ is

$$\begin{aligned} \langle (\xi - \langle \xi \rangle)^2 \rangle &= \langle \xi^2 \rangle_{\text{fl}} + O(\langle \xi \rangle_{\text{MF}}^2) \\ &\sim t^{2\psi_{\text{fl}}} [1 + O(t^{-2(\psi_{\text{fl}} - \psi_{\text{MF}})})], \end{aligned} \quad (23)$$

as $t \rightarrow \infty$. Thus, provided that $(\psi_{\text{fl}} - \psi_{\text{MF}})$ is positive, the root-mean-square value of ξ can be consistently calculated to leading order, in the late-time limit, from the results involving roughening. Alternatively, the leading-order correction to the mean-field result for $\langle \xi \rangle$ will be

$$\begin{aligned} \langle \xi \rangle &= \langle \xi \rangle_{\text{MF}} + O[(\langle \xi^2 \rangle_{\text{fl}})^{1/2}] \\ &\sim t^{\psi_{\text{MF}}} [1 + O(t^{-(\psi_{\text{MF}} - \psi_{\text{fl}})})]. \end{aligned} \quad (24)$$

Thus, depending on the sign of $(\psi_{\text{fl}} - \psi_{\text{MF}})$ (i.e., the Ginzburg criterion), one may obtain either $\langle (\xi - \langle \xi \rangle)^2 \rangle$ or $\langle \xi \rangle$ in the late-time limit, from the results summarized above.⁵⁰

Note, though, that there is a qualitative difference depending on whether the late-stage dynamics is dominated by the substrate interaction or fluctuations. In the mean-field limit, growth by layers ($\langle \xi \rangle$ increasing) takes place, with negligible inhomogeneity in that growth. On the other hand, growth by fluctuations implies that the time dependence due to the increase of $\langle (\xi - \langle \xi \rangle)^2 \rangle$ is stronger than that due to $\langle \xi \rangle^2$, for late times. This corresponds to the rather different physical picture of an interface becoming rougher and more diffuse. Also, note

that, since I have presented solutions for late times, I have excluded the possibility of early time depinning.⁵¹ In that case, the amplitude of ζ , due to roughening, would be of the order of the distance of the interface from the substrate. This could occur for early times if the substrate interaction is weak in absolute value, and of exceedingly short range.

The most interesting predictions involve the rich behavior near T_R . For example, in two dimensions, for all $T > T_R$ (where $T_R = 0$ for the Ising model), Lipowsky's result⁴ $\zeta_{\text{rms}} \sim t^{1/4}$, should be true as $t \rightarrow \infty$. However, for intermediate times and $T \gtrsim T_R$, I expect crossover behavior due to the proximity of the roughening transition; my analysis gives $\zeta_{\text{rms}} \sim \sqrt{\ln t}$. This would lead to an effectively temperature-dependent ψ , with ψ close to 0 for low T , rising to $\frac{1}{4}$ for high T , for analysis over a limited time regime.

A test of this, and the other predictions requires a system prepared with a flat interface of large extent separating coexisting phases, as in the late stages of complete wetting. By flat, I mean in comparison to its rough equilibrium shape. The difficulty then, in simulation or experiment, is to prepare the system in this fashion. In complete wetting this is accomplished by rapidly changing the chemical potential from a value far from bulk coexistence, to its value at coexistence, as discussed above. I will now briefly describe some other ways to do this, which directly test the results for ψ_R .

Numerical simulation of these initial conditions is straightforwardly accomplished by pinning the system at the boundaries of the y axis. The main drawback to numerical studies is that the finite size of L can be important, although the results above can be straightforwardly modified to account for non-negligible $1/L$. A Monte Carlo study of the kinetics of complete wetting in the two-dimensional chiral Potts model has already been done by Grant, Kaski, and Kankaala¹⁵ (a short discussion of the theory given here was also presented in that paper). The results found there are in qualitative agreement with the predictions of this study for two-dimensional lattice systems. The data showed a pronounced crossover, from slow late-time growth at low temperatures, to faster growth at high temperatures. For $T \gtrsim 0.6T_c$, the effective growth exponent was approximately independent of temperature, being $\psi = 0.25 \pm 0.03$ (where T_c is the critical temperature), which is in agreement with

Lipowsky's prediction of $\psi = \frac{1}{4}$ [Eq. (10) in $d = 2$]. Below this temperature, however, the effective ψ becomes smaller as the temperature is decreased, as is predicted by the above analysis. [For example, $\psi(T = 0.4T_c) \approx 0.12$, and $\psi(T = 0.3T_c) \lesssim 0.05$.] It should be emphasized, however, that this temperature dependence of ζ_{rms} was due to the limited time regime over which simulations were done; for $t \rightarrow \infty$, I expect this crossover to only take place at the roughening transition $T_R = 0$.

Many experimental systems will have no significant finite-size effects. However, it will be more difficult to prepare them with a flat interface to test the results involving roughening kinetics. (Complete wetting will involve a flat interface, but in many cases the late-stage growth will be determined by the mean-field results). One possible method of preparation would be to "quench" from a small value of ψ_R to a larger one. For example, one could prepare a system in $d = 3$ with a flat interface at a low temperature below T_R , and then suddenly quench it to a significantly higher temperature T' , where $T_R < T' < T_c$. Alternatively, one could suddenly turn on a random field in a system which has been prepared with a flat interface. For example, a three-dimensional diluted antiferromagnet could be prepared in a state of two-phase coexistence,⁵² and then a uniform magnetic field applied (which acts as a random field for this system³⁴). This is somewhat analogous to zero-field cooling. It is worth noting that such an experiment may provide further insight into the kinetics of the random-field Ising model, which is of current interest. Finally, it may be worth repeating that an experimental test of $\langle \zeta^2 \rangle(q, t)$ would test theory more stringently than a test of its integral $\zeta_{\text{rms}}(t)$.

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¹(a) M. Wortis, R. Pandit, and M. Schick, in *Melting, Localization and Chaos*, edited by R. Kalia and P. D. Vashishta (North-Holland, Amsterdam, 1982); (b) R. Pandit, M. Schick, and M. Wortis, Phys. Rev. B **26**, 5112 (1982).

²J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon, Oxford, 1982).

³D. Jasnow, Rep. Prog. Phys. **47**, 1059 (1984).

⁴(a) R. Lipowsky, J. Phys. A **18**, L585 (1985); (b) Phys. Rev. B **32**, 1731 (1985), and references therein; (c) the same results have been derived and numerically tested by F. Family, J.

Phys. A **19**, L441 (1986), in another context.

⁵The kinetics of wetting and prewetting have been discussed in a review by P. G. de Gennes, Rev. Mod. Phys. **57**, 827 (1985). D. J. Srolovitz and S. A. Safran, J. Appl. Phys. **60**, 247 (1986), have discussed the dynamics of beading. The kinetics of critical wetting have been studied by G. Forgacs, H. Orland, and M. Schick, Phys. Rev. B **31**, 7434 (1985).

⁶(a) J. D. Gunton, M. San Miguel, and P. S. Sahni (a) in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1983), Vol. 8; (b) J. D. Gunton, J. Stat. Phys. **34**, 1019 (1984).

- ⁷(a) S. T. Chui and J. D. Weeks, *Phys. Rev. B* **14**, 4978 (1976); (b) J. D. Weeks, in *Ordering in Strongly Fluctuating Condensed Matter Systems*, edited by T. Riste (Plenum, New York, 1980).
- ⁸D. J. Wallace, in *Gauge Theories and Experiments at High Energies*, edited by K. C. Bowler and D. G. Sutherland (SUSSP, Edinburgh, 1983).
- ⁹R. K. P. Zia, in *Statistical and Particle Physics, Common Problems and Techniques*, edited by K. C. Bowler and A. J. McKane (SUSSP, Edinburgh, 1984).
- ¹⁰(a) T. W. Burkhardt, *J. Phys. A* **14**, 63 (1981); (b) T. W. Burkhardt, in *Proceedings of the Winter School, Karpacz, Poland, 1984*, Phase Transitions in Disordered Systems (Springer, Berlin, 1985).
- ¹¹S. T. Chui and K. B. Ma, *Phys. Rev. B* **28**, 2555 (1983).
- ¹²S. T. Chui and J. D. Weeks, *Phys. Rev. Lett.* **40**, 733 (1978).
- ¹³(a) Y. Saito, *Z. Phys. B* **32**, 75 (1978); (b) *Ordering in Strongly Fluctuating Condensed Matter Systems*, edited by T. Riste (Plenum, New York, 1980).
- ¹⁴R. C. Desai and M. Grant, in *Fluid Interfacial Phenomena*, edited by C. A. Croxton (Wiley, New York, 1985).
- ¹⁵Some of the results given here, as well as numerical simulations of interfacial wetting, are presented in a short paper: M. Grant, K. Kaski, and K. Kankaala, *J. Phys. A* **20**, L571 (1987).
- ¹⁶(a) Y. Imry and S.-K. Ma, *Phys. Rev. Lett.* **35**, 1399 (1975); (b) A review is given by Y. Imry, *J. Stat. Phys.* **34**, 849 (1984).
- ¹⁷S. M. Allen and J. W. Cahn, *Acta Metall.* **27**, 1085 (1979).
- ¹⁸R. Bausch, V. Dohm, H. K. Janssen, and R. K. P. Zia, *Phys. Rev. Lett.* **47**, 1837 (1981).
- ¹⁹(a) K. Kawasaki and T. Ohta, *Prog. Theor. Phys.* **67**, 147 (1982); (b) K. Kawasaki and T. Ohta, *ibid.* **68**, 129 (1982).
- ²⁰(a) S. A. Safran, P. S. Sahni, and G. S. Grest, *Phys. Rev. B* **28**, 2693 (1983); (b) M. Grant and J. D. Gunton, *ibid.* **28**, 5496 (1983); (c) T. Ohta, *Ann. Phys. (N.Y.)* **158**, 31 (1984).
- ²¹K. Binder and D. W. Heermann, in *Scaling Phenomena in Disordered Systems*, edited by R. Pynn and A. Skjeltorp, *NATO Advanced Study Institute* (Plenum, New York, 1986), p. 237.
- ²²K. Kawasaki, *Phys. Rev. A* **31**, 3880 (1985).
- ²³W. W. Mullins, *J. Appl. Phys.* **28**, 333 (1957).
- ²⁴K. Kawasaki and T. Ohta, *Physica (Utrecht)* **118A**, 175 (1983).
- ²⁵T. Ohta, *Prog. Theor. Phys. (Suppl.)* **79**, 141 (1984); and Ref. 20(c).
- ²⁶K. Kawasaki, *Ann. Phys. (N.Y.)* **154**, 319 (1984); *Prog. Theor. Phys. (Suppl.)* **79**, 161 (1984).
- ²⁷H. B. G. Casimir and D. Polder, *Phys. Rev.* **73**, 360 (1948); E. M. Lifshitz, *Zh. Eksp. Teor. Fiz.* **29**, 94 (1955) [*Sov. Phys. JETP* **2**, 73 (1956)]; I. E. Dzyaloshinskii, E. M. Lifshitz, and L. P. Pitaevskii, *Adv. Phys.* **10**, 165 (1961).
- ²⁸G. Grinstein and S.-K. Ma, *Phys. Rev. B* **28**, 2588 (1983).
- ²⁹G. Arfken, *Mathematical Methods for Physicists* (Academic, New York, 1970).
- ³⁰J. Villain, *J. Phys. (Paris)* **43**, L551 (1982).
- ³¹T. Natterman, *Z. Phys. B* **54**, 247 (1984); *Phys. Status Solidi B* **131**, 563 (1985); **132**, 125 (1985).
- ³²K. Binder, *Z. Phys. B* **50**, 343 (1983).
- ³³(a) J. Z. Imbrie, *Phys. Rev. Lett.* **53**, 1747 (1984); (b) *Commun. Math. Phys.* **98**, 145 (1985).
- ³⁴(a) A review is given by R. J. Birgeneau, R. A. Cowley, G. Shirane, and H. Yoshizawa, *J. Stat. Phys.* **34**, 817 (1984); (b) S. Fishman and A. Aharony, *J. Phys. C* **12**, L729 (1979).
- ³⁵Two experimental studies of chemisorbed Ising-like systems are (a) A. Glachant, M. Jaubert, M. Bienfait, and G. Boato, *Surf. Sci.* **115**, 219 (1981) and (b) G.-C. Wang and T.-M. Lu, *Phys. Rev. Lett.* **50**, 2014 (1983).
- ³⁶W. I. Goldburg, University of Pittsburgh, 1985 (unpublished) and references therein.
- ³⁷D. Boyanovsky and J. L. Cardy, *Phys. Rev. B* **27**, 557 (1983).
- ³⁸M. Grant and J. D. Gunton, *Phys. Rev. B* **29**, 1521 (1984); **29**, 6266 (1984).
- ³⁹R. Bruinsma and G. Aeppli, *Phys. Rev. Lett.* **52**, 1547 (1984).
- ⁴⁰(a) D. P. Belanger, A. R. King, and V. Jaccarino, *Phys. Rev. B* **31**, 4538 (1985); (b) H. Yoshizawa, R. A. Cowley, G. Shirane, and R. Birgeneau, *ibid.* **31**, 4548 (1985), and references in these papers.
- ⁴¹J. Villain, *Phys. Rev. Lett.* **52**, 1543 (1984); *J. Phys. (Paris)* **46**, 1843 (1985). See also D. S. Fisher, *Phys. Rev. Lett.* **56**, 416 (1986).
- ⁴²G. Grinstein and J. F. Fernandez, *Phys. Rev. B* **29**, 6389 (1984).
- ⁴³D. Andelman and J. F. Joanny, *Phys. Rev. B* **33**, 1111 (1986).
- ⁴⁴In this footnote I differentiate between theories for the kinetics of the random-field Ising model, including the one presented here. The present theory corresponds to a special case of zero-field cooling (here, a system with coexisting phases, in low-temperature equilibrium, has a random-field suddenly applied). Other theories correspond to temperature quenches from the disordered state, which is called field cooling. Reference 38 is intended to describe the early to intermediate time regime following an instantaneous temperature quench, while my understanding of Refs. 41, 42, and 39 (and extensions in Refs. 31 and 43) is that they apply to a late time regime, when domains are in local equilibrium. See also Ref. 46.
- ⁴⁵Note that, in spin glasses, the order of the limits $t \rightarrow \infty$ and $L \rightarrow \infty$ can give rise to subtleties: A. Houghton, S. Jain, and A. P. Young, *Phys. Rev. B* **28**, 2630 (1983), and references therein. Note also that, at d_l , the results can only apply for late times, but for times sufficiently early that $\xi_{rms}(t)/L \ll 1$, since $\xi_{rms}(t \rightarrow \infty) \sim L$. The lower critical dimension here is $d_l = 1$, unless there is a random-field present, in which case $d_l = 2$.
- ⁴⁶M. Grant and J. D. Gunton, *Phys. Rev. B* **35**, 4922 (1987).
- ⁴⁷P. C. Hohenberg and B. I. Halperin, *Rev. Mod. Phys.* **49**, 435 (1977).
- ⁴⁸A study of wetting in the presence of a conservation law which involves long-range, as well as short-range, diffusion has been done by R. Lipowsky and D. A. Huse, *Phys. Rev. Lett.* **57**, 353 (1986). They obtain the same exponent for the dynamics of roughening, i.e., $\psi_{lc} = (3-d)/8$.
- ⁴⁹The mean-field results may be related to Frank-van der Merwe growth by layers in thin films [see for example J. A. Venables, G. D. T. Spiller, and M. Hanbücken, *Rep. Prog. Phys.* **47**, 399 (1984)], as has been noted by Lipowsky (Ref. 4).
- ⁵⁰This is equivalent to a distinction made by Lipowsky (Ref. 4). He first determines an "upper critical dimension" through a Ginzburg criterion. The mean-field results thus apply above that dimension, while those due to fluctuations apply below it. That upper critical dimension depends upon dimensionality and the form of the substrate interaction, however. Thus, rather than introduce a similar upper critical dimension in this paper, I am using a Ginzburg criterion to determine the late-stage growth directly. The Ginzburg criterion here simply involves $(\psi_R - \psi_{MF})$.
- ⁵¹See, for example, the paper by D. B. Abraham, *Phys. Rev. Lett.* **51**, 1279 (1983), and references within.
- ⁵²One could also prepare a two-dimensional chemisorbed sys-

tem (see Ref. 35) with coexisting phases. The system could then be quenched to a low temperature where it is immobile, and small impurities added. [Small impurities cause a random field (Ref. 30) while large ones would give a random in-

teraction.] Raising the temperature again, assuming that the impurities are immobile there, would give the initial conditions considered here.