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Simulated growth of wetting films with a conserved order parameter

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We have simulated the growth of saturated and unsaturated wetting films in two and three dimensions using an Ising lattice-gas model with nearest-neighbor interactions and a variety of long- and short-ranged adsorbate-substrate potentials. The Monte Carlo simulations provide a locally conserved order parameter (Kawasaki nearest-neighbor spin-exchange dynamics). Starting from a supersaturated bulk configuration, we find that the films grow as $t^{1/3}$ as predicted by Lifshitz and Slyozov. For an unsaturated bulk starting configuration, the film thickness appears to grow at intermediate times as t^{θ}, where θ is a small exponent which is determined by the substrate potential in the mean-field regime and which is universally $\frac{1}{8}$ in the fluctuation regime; at long times, the thickness approaches the equilibrium thickness as $t^{-1/2}$. These results are consistent with theoretical predictions made by Lipowsky and Huse.

I. INTRODUCTION

In a previous paper[1] we presented the results of Monte Carlo (MC) simulations, using nonconserved order-parameter (Glauber) dynamics, of the growth of wetting films on a substrate as modeled by a d-dimensional solid-on-solid (SOS) model. Emphasis in that work was placed on the rate of growth of the films as functions of time in the limit that the lateral size L of the system is large enough to play no role. The results were compared with the predictions of Lipowsky,[2] based on analysis of an effective interface model, and were found to be in agreement. A second paper[3] presented further MC studies of the SOS model with emphasis on the properties of the interface between the growing film and the bulk phase and also on the properties of an equilibrium interface between two coexisting bulk phases.

The present paper reports MC simulations of the growth of both saturated and unsaturated wetting films, using an Ising lattice-gas model and conserved order parameter (Kawasaki) dynamics. We work in both two and three dimensions, allowing nearest-neighbor adsorbate-adsorbate interactions and both long- and short-ranged adsorbate-substrate interactions. Emphasis is placed on the time dependence of the thickness of the growing film after quenching into supersaturated, unstable bulk configurations, which separate into domains of the two coexisting phases, or into metastable or stable bulk configurations, leading to the growth of an unsaturated film given appropriate interactions. In the case of an initial unstable bulk configuration, the domain growth theory of Lifshitz and Slyozov[4] predicts that at long times not only the mean domain size in the bulk will increase as $t^{1/3}$, but also the film thickness will grow with the same time dependence as a consequence of bulk domains drifting to the substrate and becoming part of the adsorbed film. As this process occurs, a depletion zone forms above the film, where there will be a relatively low density of growing bulk domains. Our simulation results are in complete agreement with this picture.

In the case of stable or metastable bulk solutions, Lipowsky and Huse[5] have given a theory, based on an effective interface model, of the rate of growth of wetting films under conditions of diffusion-limited growth and for various substrate potentials and dimensions d of the system. Our simulations are in general agreement with their theory, although we are not in every case able to make a quantitative comparison.

Section II of this paper presents our model, describes the Monte Carlo simulations, and summarizes the relevant theoretical predictions of Lifshitz and Slyozov[4] and of Lipowsky and Huse;[5] Sec. III is a compilation of the results; and Sec. IV contains a discussion and summary.

II. MODEL AND METHODS

We employ an Ising lattice-gas model on a simple cubic lattice of dimension d equal to 2 or 3 with, respectively, a [10] or [100] direction perpendicular to the surface of the substrate. A site i of the lattice is either occupied by an adsorbate atom or empty. Given neighboring occupied sites, there is an interaction energy $-J$ with $J>0$; otherwise there is no interaction energy. In addition, there is an interaction energy U_i between an adsorbate particle on site i and the substrate. Thus, the Hamiltonian is

$$\mathcal{H}=-J\sum_{\langle i,j\rangle} n_i n_j+\sum_i U_i n_i \;, \tag{1}$$

where $n_i=0$ (1) depending on whether site i is empty (occupied). The potential U_i is taken to be a function only of the distance z_i, in units of the lattice constant, of site i from the substrate; it is given by

$$U_i=\begin{cases}-5J & \text{if } z=1,\\ -3J/z^{p+1} & \text{if } z>1,\end{cases} \tag{2}$$

where in the simulations we have used $p=1$, $p=2$, and $p=\infty$ (short-ranged U_i). For $d=2$, the lattice size used in obtaining results reported here was 100×50; for $d=3$, it was $20\times 20\times 50$. Other sizes were employed to check the size dependence of various results. Run lengths were

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typically 50 000 MCS (Monte Carlo steps per site). Runs were started by distributing a given number of particles $\mathcal{N}$ randomly throughout the lattice; $\mathcal{N}$ was chosen so as to produce a particular overall concentration c such as 20% or 30%. Thus the initial configuration can be thought of as a typical thermal distribution at infinite temperature. The particles were then allowed to move to nearest-neighbor sites using standard Kawasaki dynamics at temperature T. For given thermodynamic and potential parameters, runs were repeated N times with different initial configurations and random number seeds; we used values of N from 10 to 100. A variety of time-dependent quantities such as the density profile $n(z,t)$, the film thickness $l(t)$, and the coverage $\Gamma(t)$ were accumulated aged over the N runs. These quantities are given by, first,

$$n(z,t)=L^{1-d}{\sum_i}' n_i(t) , \tag{3}$$

where the prime on the sum denotes that the sites i which are summed must lie in the zth layer. Next, the film thickness $l(t)$ is defined by

$$n(l(t),t)=0.5 ; \tag{4}$$

note that it is necessary to interpolate $n(z,t)$ to nonintegral values of z to make use of this definition. Finally, the coverage $\Gamma(t)$ is taken to be

$$\Gamma(t)=\sum_{z}^{[n(z,t)\geq n_0]}[n(z,t)-n_0] , \tag{5}$$

where n_0 is the bulk density. Notice that the definition is such that the depletion layer which develops between the film and the bulk does not contribute negatively to the coverage because we do not include in the sum those z for which $n(z,t)\leq n_0$.

We turn now to a discussion of extant relevant theoretical predictions of the rates of film growth under different conditions. First, under conditions of two-phase coexistence, i.e., film formation beneath a coexisting bulk phase, Lipowsky and Huse[5] predict, on the basis of an interface model with an effective substrate-interface potential $V(l)\sim 1/l^p$ [p is the same as in Eq. (2)], that at long times the film thickness diverges as t^θ where

$$\theta=\begin{cases}\frac{1}{8} & \text{for } d=2 \text{ and } p>1,\\ \dfrac{1}{2(p+2)} & \text{otherwise (but } p>-1),\end{cases} \tag{6}$$

For a sufficiently short-ranged potential in two dimensions, fluctuations dominate the growth process, leading to a p-independent value of θ; otherwise, θ depends on the range of the potential. For $p\leq -1$, an instability develops.

It is perhaps worthwhile to point out at this juncture that our simulations cannot produce the predicted behavior at long time because we are using the canonical ensemble, i.e., the total number of particles is fixed. Consequently, as the dense film grows, the bulk is depleted and at some point ceases to be saturated or supersaturated, and the film thickness must therefore approach a finite value at long times. For "intermediate" times, however, we can attempt to verify the predictions.

In a regime where the bulk phase is stable but the system is sufficiently close to two-phase coexistence and the substrate favors the formation of a film of a phase different from the bulk phase, a film of finite thickness will grow until it reaches some equilibrium thickness. If this thickness is sufficiently large, then the film is expected[5] to grow at intermediate times in the same manner as at two-phase coexistence, and at long times it should approach the equilibrium thickness l_0 as $l_0-l(t)\sim t^{-1/2}$. Further, Lipowsky and Huse[5] suggest that in the region of metastable bulk phase, the interface between the growing film and bulk may display a Mullins-Sekerka instability.

In the regime of unstable bulk phase, the domain growth theory of Lifshitz and Slyozov[4] is appropriate. According to this theory, domains of the coexisting phases nucleate in the bulk, and at long times, these grow by coalescence of the domains into larger ones. At the same time, the presence of a nearby substrate with a potential which preferentially attracts domains of one particular phase results in the growth of a film of this phase by essentially the same mechanism which produces the domain growth in the bulk. The result is that not only the bulk domains but also the film thickness is predicted[4] to grow as $t^{1/3}$. As presented in Ref. 4, this is the process of crust sintering.

III. RESULTS

We present first the results for the case that the starting configuration is in the bulk unstable regime. In our simulations, the initial configuration is a homogeneous (infinite temperature) phase with 20–30 % of the sites occupied; we quench suddenly to a temperature below the critical temperature T_c so that the system is unstable; the substrate potential is such as to attract the dense phase to the substrate. Because we start from a fairly low concentration, the domains of the dense phase that form in the bulk do not percolate and so appear as isolated clusters. These diffuse toward the substrate and cause the film to grow. There also appears a "domain depletion layer" close to the film where the density of the (growing) domains of the dense phase is lower than the density far from the film-bulk interface. We have done simulations for $d=2$ and $d=3$ and have employed $p=1$, $p=2$, and short-ranged substrate potentials in both cases. A typical result well above the roughening temperature is shown in Fig. 1 where $\Gamma(t)$ and $l(t)$ are plotted against $t^{1/3}$ for $d=2$, $p=1$, $T=0.4J/k$, and $n_0=0.2$; the data are the results of ten separate runs giving, at various times, standard deviations in the coverage and thickness ranging from 3% to 7% and uncertainties in the means (the plotted values) of 1–2 %. Both sets of points fit a straight line quite well, demonstrating the predicted $t^{1/3}$ behavior even though the total coverage is not very large. One should bear in mind, however, that the growth rate of the film is determined by the influence of the potential on the material throughout the system and so is a reflection of the domain growth rate everywhere. If the same information is presented in a log-log format, the data for Γ at times larger than about 10 000 MCS are fit by a straight

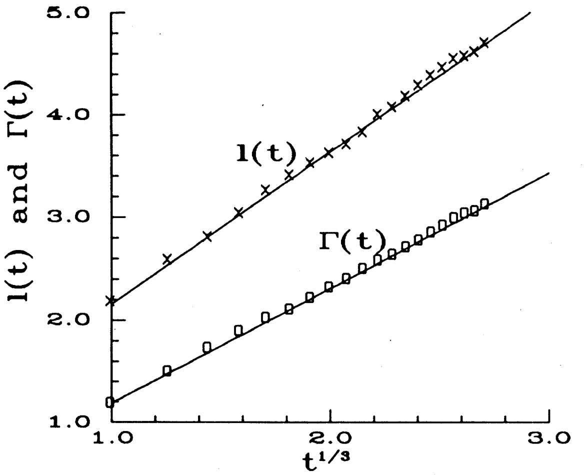

FIG. 1. The coverage (□) and thickness (×) are shown as functions of the time (in units of 2500 MCS) to the $\frac{1}{3}$ power for $d=2$, $p=1$, $n_0=0.2$, and $T=0.4J/k$. The lattice measures 100×50; ten runs have been averaged to produce these results.

line of slope 0.332±0.007, while those for the film thickness are fit by a line of slope 0.284±0.016. A nonlinear fit to the function $y=a+bt^{\theta}$ where a, b, and θ are parameters yields, for $y=\Gamma$, $\theta=0.360$ and, for $y=l$, $\theta=0.328$. The simplest interpretation of these fits is that θ is indeed $\frac{1}{3}$. Similar results are found in three dimensions and for the other substrate potentials, demonstrating consistency with the $t^{1/3}$ growth law, at least for the dimensions and substrate potentials employed here.

Figure 2 shows the domain structure in a typical run using the same parameters as above. The dots (·) represent occupied sites while empty sites are blank; the substrate is at the left of each figure. Figure 2(a) presents the structure at a "time" of 2500 MCS while Fig. 2(b) is at 50 000 MCS. The growth of both the film (at the left) and of the bulk domains is apparent, as is the appearance of a depletion zone just above the film-bulk interface where the density of domains of the dense phase is much lower than in the bulk.

For the three-dimensional systems at temperatures close to and somewhat below the roughening temperature $T_R \sim 0.6J/k$, the film growth is discernible, but very slow, and shows evidence of layering transitions. We have not succeeded in extracting any general information about the growth rate in this regime.

We have studied the long-time behavior of the film growth following a quench into a regime where the bulk phase is initially stable or metastable. These are equivalent because, as the film grows, the material in the remainder of the system dilutes so that the bulk becomes stable even if initially metastable. Under these conditions we see the expected[5] long-time behavior $l(t)=l_{\infty}-At^{-1/2}$, where A is a constant and l_{∞} is the equilibrium film thickness. Figure 3 shows $l(t)$ versus $t^{-1/2}$ for $d=3$, $p=1$, $n_0=0.2$, and $T=1.4$; 36 runs were performed to achieve these results. The straight line shown is from a least-squares fit to the points. Extrapolated to $t^{-1/2}=0$, it predicts $l_{\infty}=3.02$. This prediction was

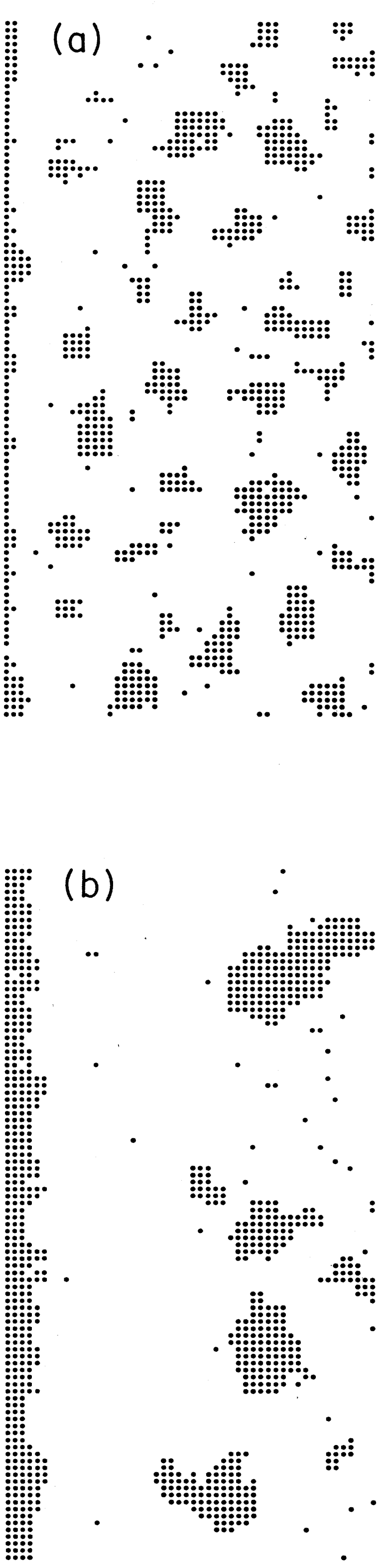

FIG. 2. The domain structure of the system is shown in one particular run for the same conditions as in Fig. 1 at times (a) 2500 MCS and (b) 50 000 MCS. Displacement parallel to the substrate is plotted along the ordinate; perpendicular to the substrate, along the abscissa. The substrate is located at the left of the figures, and a dot represents an occupied site.

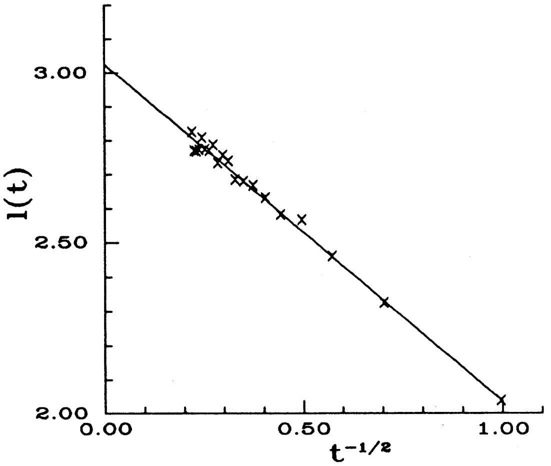

FIG. 3. The film thickness is plotted as a function of $t^{-1/2}$ for $d=3$, $p=1$, $n_0=0.2$, and $T=1.4J/k$; time is in units of 2500 MCS. The line is the result of a least-squares fit to the data.

checked by doing separate grand-canonical ensemble simulations at a number of distinct chemical potentials to infer the equilibrium film thickness as a function of the mean density of particles in the system. The result is shown in Fig. 4. For the particular case presented in Fig. 3, $n_0=0.2$ and the thickness from the grand canonical ensemble simulations is about 2.82 which is in reasonable agreement with the canonical ensemble result of 3.02.

Similar results were obtained in two dimensions and also for $p=2$ in both two and three dimensions. The fluctuations were relatively larger for $d=2$ (using a 100×50 lattice), necessitating about three times as many runs to obtain results as good as those shown in Fig. 3. In general the equilibrium thickness obtained from the grand ensemble simulations was slightly smaller than that inferred from the canonical ensemble, probably a consequence of size effects.

We have also studied film growth under the same conditions but at intermediate times. In at least some runs it is possible to interpret the observed growth rate before saturation begins to set in as $l(t)\sim t^{\theta}$ with θ given by Eq. (6); however, θ is so small that a quantitative determination is not easy. As an example, consider Fig. 5 which displays $l(t)$ versus $t^{1/6}$ for $d=3$, $n_0=0.22$, $p=1$, and $T=1.12J/k$. Sixteen runs were done, producing distributions at various times with standard deviations of typically 4% of the mean value and an uncertainty in the mean of about 1%. A least-squares fit to a log-log plot of the same data produces a line of slope 0.18 ± 0.02. The predicted[5] value of θ for this case is $\frac{1}{6}$. The simulation results are certainly not inconsistent with the prediction but neither is there quantitative agreement of a fully satisfactory sort. Figure 6 shows the thickness as a function of $t^{1/8}$ for a case which differs from the preceding one in that $p=2$ and eighteen runs were performed; the standard deviations of the distributions at various times were typically around 5% of the mean, leading to uncertainties in the mean of slightly more than 1%. For this case θ is predicted to be $\frac{1}{8}$. A least-squares fit to a log-log plot of the data yields $\theta=0.14\pm0.03$. An alternative fitting procedure is to write $l(t)=l_0+bt^{\theta}$ with l_0, b, and θ as variable parameters. This method results in the data of Fig. 5 being best fit by $\theta=0.161$ and those from Fig. 6, by $\theta=0.131$. On the basis of these results, we feel that we cannot claim unambiguous verification of the predictions for θ in Ref. 5, but the simulations are certainly qualitatively consistent with them.

IV. SUMMARY AND DISCUSSION

In this paper we have presented results of film-growth simulations of an Ising model using conserved order-

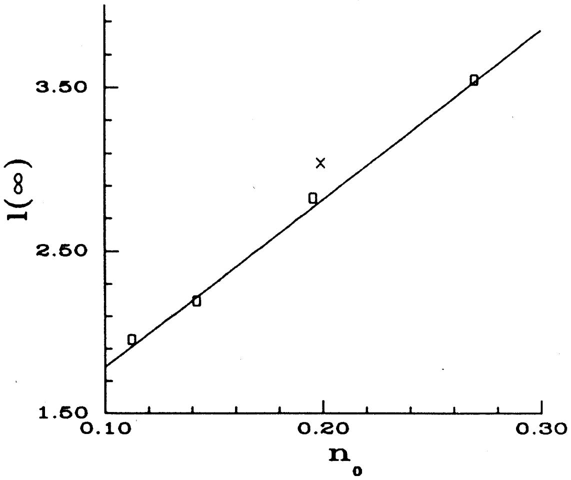

FIG. 4. The equilibrium film thickness l_∞ (□), found from grand-canonical ensemble simulations, is plotted against the mean density of particles in the system n_0 for $d=3$, $p=2$, and $T=1.4J/k$; the value of l_∞ inferred from canonical ensemble simulations (see Fig. 3) is shown (×) for the particular case of $n_0=0.2$. The line is included to guide the eye.

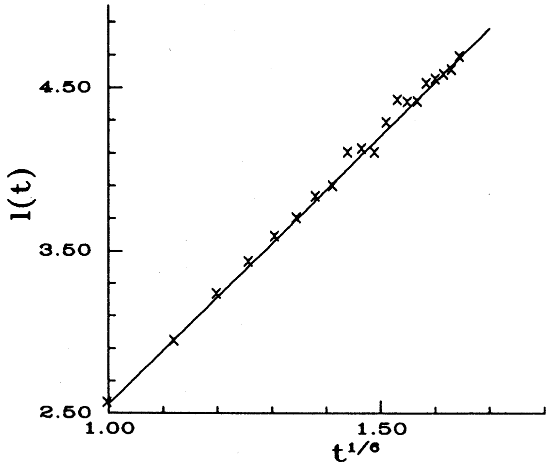

FIG. 5. The thickness $l(t)$ at intermediate times is plotted as a function of $t^{1/6}$ for $d=3$, $p=1$, $n_0=0.22$, and $T=1.12J/k$. The time is in units of 2500 MCS and a straight line is included to guide the eye.

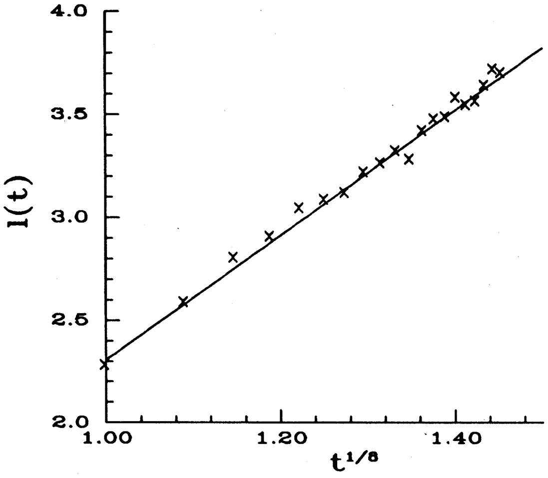

FIG. 6. The same as Fig. 5 except that $p=2$ and $T^{1/8}$ is plotted along the abscissa.

parameter dynamics. We include nearest-neighbor interactions between adsorbate particles and both short- and long-ranged (algebraic) interactions between the substrate and adsorbate; the latter do not depend on displacement lateral to the substrate surface. Both two- and three-dimensional lattices were used. Temperatures (after quenching from very high T) and mean particle concentrations were chosen to produce initially either an unstable uniform bulk phase or a stable or metastable uniform bulk phase in order to examine the growth rate of the films under a variety of conditions.

In the case of starting in an unstable uniform bulk phase, the film thickness or coverage appears to grow at long times as $t^{1/3}$ in agreement with the theory of domain growth and sintering developed by Lifshitz and Slyozov.[4] The mechanism producing this behavior, the validity of the theory, and numerical simulations of domain growth in the bulk have been much discussed of late.[6] The mechanism involves the evaporation and coalescence of individual domains in the bulk; these domains initially nucleate spontaneously as a consequence of having an unstable system. In the bulk, the average domain size, according to the theory, increases as $t^{1/3}$; further, given appropriate substrate potentials, domains of one phase drift to the substrate and cause a film of this phase to grow there. As discussed in Ref. 4, the same mechanism is responsible for crust sintering. We have studied only the film growth and find surprisingly clear evidence, considering the film thicknesses we were able to achieve and the apparent difficulty in obtaining unequivocal results in the case of bulk domains,[6] for an exponent of $\frac{1}{3}$ in both two and three dimensions and for both short- and long-ranged [$p=1$ and $p=2$ in Eq. (2)] substrate potentials.

Under conditions of a metastable initial configuration so that domains of a second phase do not nucleate in the bulk, the theory of Lipowsky and Huse[5] is applicable. They find that the film coverage or thickness should grow as t^{θ} where θ is a small exponent that will depend on the range of the substrate potential if it is sufficiently long-ranged. In $d=3$ and for any algebraically decaying substrate potential, $U(z)\sim z^{p+1}$, $\theta=1/2(p+2)$; this relation also holds in $d=2$ and for $p<1$, but for $p>1$, $\theta=\frac{1}{8}$, independent of p.

It is difficult to do simulations of sufficient length in this regime to see the expected power law dependence of $l(t)$ very clearly in most cases, although our results are always consistent with the predictions. The reasons for the difficulty are, first, that the exponent θ is small and it is not easy to determine a small exponent accurately. Also, the film will not grow with this time dependence forever in the simulations because the number of particles is fixed and the total system size is quite limited (50 layers in the direction normal to the substrate). Consequently, as the film grows, the bulk phase is depleted and ceases at some point to be metastable or to be on the two-phase coexistence curve. Under these conditions the film thickness approaches some limiting value rather than continuing to grow. In order to maintain the appropriate conditions as long as possible, we did runs using a quite large initial uniform density, $n_0=0.2$ to 0.3; it was therefore necessary to run at temperatures not far below the bulk critical temperature, giving rise to rather large fluctuation effects, thereby further increasing the difficulty of obtaining clear-cut results. We have presented here results for the particular case of $d=3$ with $p=1$ and $p=2$; they are qualitatively consistent with the predictions. We achieved similar results in two dimensions, but with rather more difficulty because of the larger influence of fluctuations.

Finally, at longer times under the conditions just described, we were able to study the approach of the film thickness to the saturated, equilibrium value. Lipowsky and Huse[5] predict that the thickness should approach this value as $t^{-1/2}$; our simulations support this prediction unequivocably.

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