Corrections to late-stage behavior in spinodal decomposition: Lifshitz-Slyozov scaling and Monte Carlo simulations

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The Lifshitz-Slyozov theory of the late stages of diffusion-limited spinodal decomposition (Ostwald ripening) is generalized to apply for arbitrary volume fractions of the two phases. Corrections to the asymptotic $R(t)\sim t^{1/3}$ scaling are considered; they are due to excess transport in interfaces and are therefore of relative order $R^{-1}(t)$, where $R(t)$ is the average domain size. That the asymptotic exponent $\frac{1}{3}$ has not been observed in Monte Carlo simulations of Ising models can be attributed to such corrections. Further simulations of the square-lattice Ising model are performed: The results are consistent with the generalization of the Lifshitz-Slyozov theory. The recent work of Mazenko *et al.* that proposes instead $R(t)\sim\log t$ is criticized.

I. INTRODUCTION

The kinetics of domain growth in the late stages of diffusion-limited spinodal decomposition (Ostwald ripening) have been studied by a variety of methods.[1-6] However, disagreement remains as to the asymptotic time dependence of the average linear domain size, $R(t)$, for long times, t. The classic paper of Lifshitz and Slyozov[1] examined the case of widely spaced domains of one phase growing and shrinking in a matrix (one large domain) of the second phase. They found that the domain growth at long times is limited by diffusion through the matrix; the asymptotic long-time form they obtained is a power-law growth,

$$R(t)\sim t^{n}\ , \tag{1}$$

with exponent $n=\frac{1}{3}$. More recent work that considers interactions between domains finds no change in this asymptotic growth law (see, for example, Ref. 4). The analysis in Refs. 1 and 4 applies when the volume fraction of the first phase forming isolated domains is much smaller than that of the second phase forming the matrix. When the total volumes of the two phases are comparable, as in a near critical quench, the geometry of the resulting domains is quite different, but one can still argue (see below) that $R(t)\sim t^{1/3}$ at long times.[7]

Simulations of spinodal decomposition at zero total magnetization after cooling below the critical temperature, T_c, in spin-exchange Ising models[2,3,5] have found exponents n in the range 0.17—0.25 when fitting the domain size to the power-law form (1). Lebowitz *et al.*[3] suggest that the asymptotic time dependence of $R(t)$ probably does have exponent $n=\frac{1}{3}$ and the lower observed exponents are due to insufficiently long simulation times. This view will be argued for in this paper, also. Mazenko *et al.*,[6] on the other hand, have argued that $R(t)\sim\ln t$ at long times. Their conclusions are based on analysis of data for the square lattice Ising model at temperatures $T<0.6T_c$ and times $t\leq 2000$ attempted exchanges per spin. Criticism of their approach is offered at the end of this paper.

In this paper I argue that the Lifshitz-Slyozov growth law, $n=\frac{1}{3}$, should apply even for a critical quench with equal volume fractions for the two phases. Similar arguments have recently been made by Glicksman and Voorhees[7] for the coarsening of dendrites. At finite times an effective exponent

$$n_{\rm eff}(t)=\frac{d[\ln R(t)]}{d[\ln t]} \tag{2}$$

can be defined. It is argued below that this effective exponent should behave at long times as

$$n_{\rm eff}(t)=\frac{1}{3}\left[1-\frac{R_0}{R(t)}+O(R^{-2}(t))\right]\ , \tag{3}$$

where the length R_0 depends on the temperature and relative volumes of the two phases and is positive for near critical quenches when the diffusion constants in the two phases are approximately equal. Simulations of the two-dimensional spin-exchange Ising model are then performed for times up to 40 000 attempted exchanges per spin (Metropolis algorithm). The results are consistent with (3), with $n_{\rm eff}(t)$ definitely increasing with time, in contrast to the decrease with time if $R(t)\sim\ln t$. However, the simulation times are fairly short and an extrapolation of $n_{\rm eff}(t)$ for $t\to\infty$ [assuming it is a smooth function of $1/R(t)$] yields $n=0.29\pm0.04$ for the asymptotic exponent. Thus the uncertainty in the numerically measured exponent n is still disappointingly large.

In a recent experiment, Marsh and Glicksman[8] have studied the coarsening of dendrites of succinonitrile immersed in liquid succinonitrile. On short length scales, before gravitational effects enter, this process is limited by heat diffusion. They measure the depression ΔT of the temperature below the melting temperature; ΔT is proportional to the average interface curvature and therefore to the inverse of the average domain size. They find the Lifshitz-Slyozov growth law $\Delta T\sim t^{-1/3}$ over a range of a factor of 50 in time, from a few minutes to a few hours.

II. LIFSHITZ-SLYOZOV ARGUMENT GENERALIZED

The coarsening of isolated, widely spaced domains of one phase in a matrix of a second phase occurs by the shrinking due to evaporation of the smaller domains and the growth by condensation of the larger domains.[1,4] The rates of both processes are limited by the rate at which diffusion into and out of the matrix can occur. On length scales small compared to the domain size each neighborhood is near to local equilibrium and the local field conjugate to the diffusing density (of atoms, molecules, spins, energy, etc.) varies slowly with position. The time necessary to approach local equilibrium on length scale L is proportional to L^2/D, where D is the diffusion constant. If the domain size is growing according to $R(t)\sim(Dt)^n$ then the system can be near local equilibrium on scales $L \ll R(t)$ if $R^2 \ll Dt$. This will occur at long times whenever $n < \frac{1}{2}$.

Mazenko *et al.*[6] have suggested that local equilibrium near the interfaces is never approached at low temperatures in spin-exchange Ising models because diffusion across the interface is activated. However, the activation energy is finite, leading to a nonzero diffusion constant for transport across the interface. At low temperatures this transport is slow, so local equilibrium will not be approached at early times, but provided $n < \frac{1}{2}$ the diffusion must eventually catch up with the domain growth and cause an approach to local equilibrium at sufficiently long times. Therefore the Lifshitz-Slyozov argument as generalized below should work at long times for any nonzero temperature.

Let us then consider a near critical quench, where the volume fractions of the two phases are comparable and we do not at all have isolated domains, but instead highly connected interpenetrating domains of a complicated and random geometry. An example is shown in Fig. 1 of the pattern obtained after 16000 attempted exchanges per spin (Metropolis algorithm) on a square lattice spin-exchange Ising model quenched instantly from infinite temperature to $T=0.9T_c$. This is a lattice of size 108×108 with periodic boundary conditions and zero total magnetization. Similar pictures with a 400×400 triangular lattice at $T=0.6T_c$ and comparable times are given in Ref. 5. For such complicated patterns one can still define a typical or average linear domain size, $R(t)$: The order parameter correlation function, $G(\mathbf{r},t)$, which for the Ising model is

$$G(\mathbf{r},t)=\langle S(\mathbf{0},t)S(\mathbf{r},t)\rangle-\langle S\rangle^2\,, \tag{4}$$

where $S(\mathbf{r},t)$ is the spin at position $\mathbf{r}$ and time t, falls off with r in an oscillatory fashion, as is illustrated in Fig. 2. Here we define $R(t)$ as the position of the first zero of $G(r,t)$, which is one measure of the typical domain size.

Let us assume that our system is near local equilibrium on length scales small compared to $R(t)$, as should be the case at long times when $n < \frac{1}{2}$. For the Ising model it is the up and down spins that are the diffusing species and the local relative "chemical potential" for these two species is simply a local magnetic field h. For the remainder of this paper the language appropriate for the Ising model will be used. The interfaces between domains

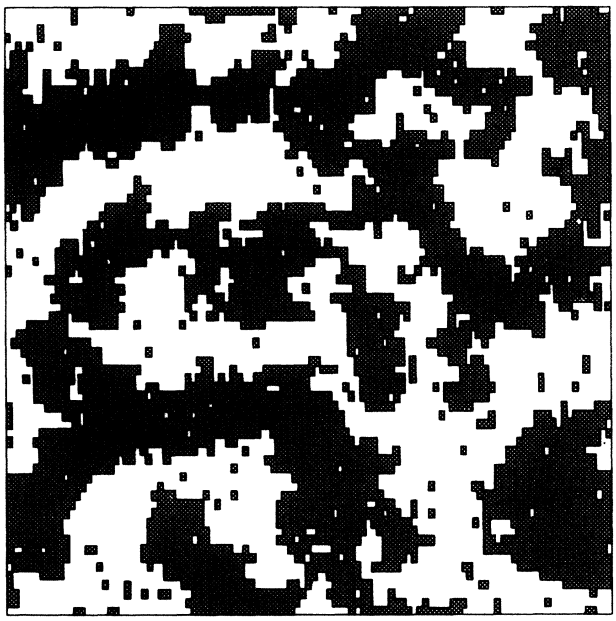

FIG. 1. Domain configuration obtained after quenching a square lattice spin-exchange Ising model with zero total magnetization instantly from infinite temperature to $0.9T_c$ and then annealing for 16000 Monte Carlo steps per spin. The spin-up phase is dark and the spin-down phase white. The sample consists of 108^2 spins. See Ref. 5 for similar pictures of larger samples.

of the two phases have local radii of curvature of order $R(t)$ or greater. For a portion of such a curved interface to be in local equilibrium requires that the pressure due to its tension cancel that due to the local field h. If the interfacial tension is Σ, then the former pressure is of order $\Sigma/R(t)$, while the latter is of order hM, where M is the order parameter. Therefore the local field is of order $\Sigma/MR(t)$ and the variations in this field from place to place are of the same order. These variations occur over distances of order $R(t)$, resulting in field gradients of order $\Sigma/MR^2(t)$. In response to these gradients there are currents of order $\lambda\Sigma/MR^2(t)$, where $\lambda=D\chi$ is the spin conductivity[9] and $\chi=\partial M/\partial h$ is the susceptibility. Due to these currents, interfaces are moving with velocities of order $\lambda\Sigma/M^2R^2(t)$. It is due to this interface motion that the domain structure coarsens and $R(t)$ increases. Thus we expect

$$\frac{dR(t)}{dt}\sim\frac{\lambda\Sigma}{M^2R^2(t)} \tag{5}$$

for large $R(t)$. This simple equation is the result of two reasonable assumptions: (1) the usual scaling assumption that the domain pattern can be characterized by a single length scale $R(t)$; (2) that the rate of evolution of the pattern is limited by diffusion through the domains. The resulting growth law $R(t)\sim t^{1/3}$ is the same as obtained by Lifshitz and Slyozov.[1] Their approach has been generalized in the reasoning leading to Eq. (5) to apply to a near critical quench, in a fashion that is very much in the spirit

of Lifshitz' later paper[10] on domain growth *without* order-parameter conservation. Glicksman and Voorhees[7] have recently formulated a very similar argument.

Now let us consider what sort of finite-time corrections to (5) we should expect. One correction is due to transport in the interfaces. The local conductivity will be enhanced in the interface for many systems[11] because there are more low-energy processes available to cause transport. This is certainly the case for lattice Ising models. For the square lattice spin-exchange Ising model with nearest-neighbor couplings J only, the bulk conductivity λ in a pure phase vanishes as $\exp(-8J/T)$ as $T\rightarrow 0$, because the transport is carried out by overturned spins in the ordered phase that cost energy $8J$ to create. An overturned spin in contact with an interface, on the other hand, costs only energy $4J$, so the excess conductivity along an interface running parallel to a nearest-neighbor direction vanishes as $\exp(-4J/T)$ for $T\rightarrow 0$. Thus transport along the interfaces can dominate at low temperatures. I have measured the local conductivity along an interface in Monte Carlo simulations of the square lattice Ising model and find that this enhanced interface conductivity persists up to $0.9T_c$. Presumably it is always present for $T<T_c$; it would be interesting to know its critical behavior.

When the domain size is $R(t)$, the amount of interface present per unit volume is of order $1/R(t)$. The excess conductivity in the interfaces will enhance the ripening process at this order. At intermediate volume fractions where both phases have large tortuous domains, like in Fig. 1, transport both along and across interfaces is important. In the dilute limit of isolated domains, only transport across interfaces plays a role in ripening. There do not appear to be any physical processes available that could generate corrections to the Lifshitz-Slyozov growth law (5) at lower relative order than $1/R$. Including this enhanced interface conductivity in (5) yields

$$\frac{\partial R(t)}{\partial t}=\frac{C_2}{R^2(t)}+\frac{C_3}{R^3(t)}+O(R^{-4}) , \tag{6}$$

where $C_2>O$. Note that when the correction speeds ripening, $C_3>0$. Solving (6) for large R,t, yields

$$R(t)=(3C_2t)^{1/3}+C_3/2C_2+O(t^{-1/3}) . \tag{7}$$

This results in an effective exponent (2) of

$$n_{\rm eff}(t)=\frac{1}{3}-\frac{C_3}{6C_2R(t)}+O(R^{-2}) . \tag{8}$$

For $C_3>O$ we therefore should expect to find that the effective exponent is less than $\frac{1}{3}$ and for $t\rightarrow\infty$ approaches $\frac{1}{3}$ linearly in $R^{-1}(t)$. We may write (8) as

$$3n_{\rm eff}(t)=1-R_0/R(t)+O(R^{-2}(t)) , \tag{9}$$

where R_0 is a length which should be microscopic, except for near T_c where, by scaling, we expect it is proportional to the correlation length and for $T\rightarrow 0$, where for fully connected geometries it might diverge due to excess transport along the interfaces.

III. SIMULATIONS

I have performed extensive Monte Carlo simulations of the square lattice spin-exchange Ising model with isotropic nearest-neighbor couplings J in order to test the ideas presented in the preceding section of this paper. The Metropolis algorithm was used; a pair of nearest-neighbor spins being selected randomly and exchanged (a) with probability one if there is no increase in energy; (b) with probability $\exp(-\Delta E/T)$ if the exchange increases the energy by ΔE. Since the bulk conductivity λ is activated, the domain growth process goes faster as temperature is increased, even very near $T_c=2J/\ln(1+\sqrt{2})$ where the driving force Σ/M^2 is decreasing. In order to get to the largest domain size in a given time, most of the simulations were performed at temperature $T=0.9T_c$. At this temperature, the correlation length is still less than two lattice spacings so critical phenomena are not playing an important role for the domain sizes studied. At low temperatures the domain growth is slower, see, e.g., $T=0.5T_c$ in Fig. 3. The simulations were always started at time $t=0$ with a completely random initial configuration. The unit of time is one attempted exchange per spin.

The correlation function $G(\mathbf{r},t)$, Eq. (4), was recorded for spacings $\mathbf{r}$ parallel to the lattice axes, results are shown in Fig. 2. The domain size $R(t)$ was calculated by fitting the three points in $G(r,t)$ closest to its first zero

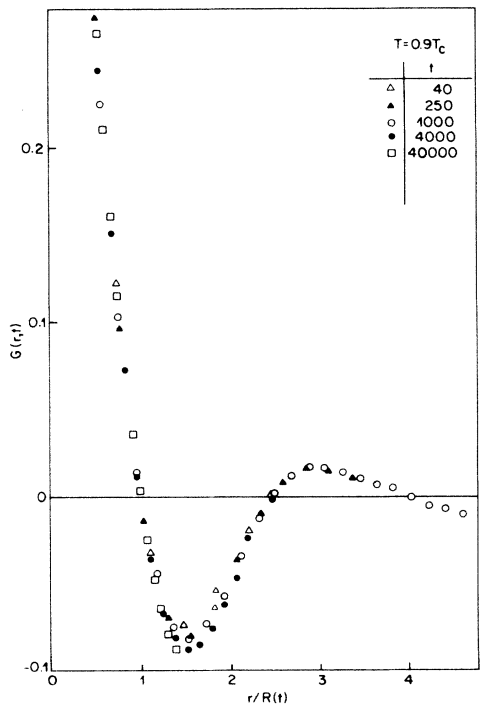

FIG. 2. Correlation function $G(r,t)$ [Eq. (4)] at various times t after a quench to $0.9T_c$ from infinite temperature. The domain size $R(t)$ is defined so the first zero crossing is at $r=R(t)$. The data are plotted versus scaled distance $r/R(t)$ to show that they are well represented by one scaling function [see Eq. (11)].

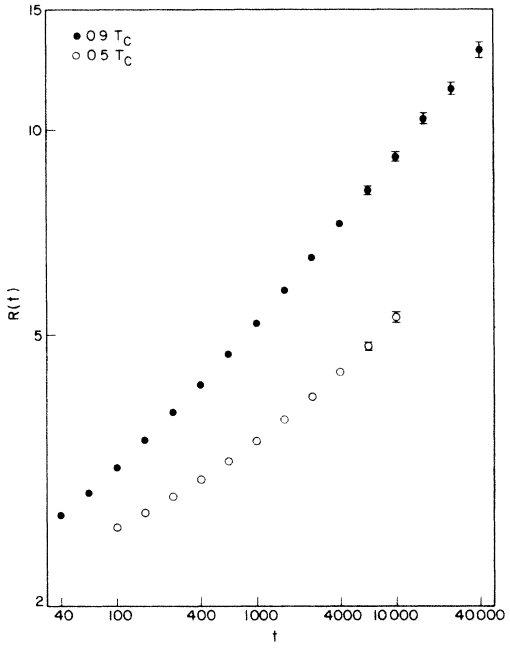

FIG. 3. Domain size $R(t)$ as a function of time for quenches to $0.9T_c$ (solid points) and $0.5T_c$ (open circles).

crossing to a quadratic function of r and defining $R(t)$ as the value of r where this function vanishes. The results for $R(t)$ are shown in Fig. 3. All data shown here were taken on square or rectangular lattices with periodic boundary conditions and both linear dimensions greater than or equal to 192 lattice spacings. Runs on smaller lattices showed that finite-size effects did not alter $R(t)$ by more than 1% until it reached approximately one-third of the lattice size. Therefore with the lattices of size greater than or equal to 192 the error in $R(t)$ due to finite-size effects must be much smaller than the statistical error in all data shown here. The error bars shown are $\pm\Delta R(t)$, where

$$\Delta R(t)=R^2(t)/N^{1/2}\ , \tag{10}$$

and N is the total number of spins in the simulation. This is chosen so that the relative error in $R(t)$ is equal to the inverse of the square root of the total number of correlation volumes in the sample. The statistical error as calculated from the variation between different runs was approximately equal to that given by (10). The total area simulated (using various lattices of size $192\times M$, $192\le M\le 2304$) for $T=0.9T_c$ was $N=21\times 192^2=774\,144$ for $t\le 4000$ and one-third of that for $t>4000$. For $T=0.5T_c$ one run of a sample size $192\times 960=184\,320$ was performed.

The standard scaling ansatz for the correlation function is that

$$G(r,t)\approx f(r/R(t))\ , \tag{11}$$

for large $R(t)$, where f is the scaling function. The results in Fig. 2 show that such a scaling ansatz works reasonably well in the regime studied here. The only deviation from this simple scaling (11) that can be discerned is in the first minimum of $G(r,t)$, which deepens slightly as time progresses. This correction to scaling is too weak to measure with any useful accuracy. That the Fourier transform of $G(\mathbf{r},t)$ scales in a similar fashion was shown in Refs. 2 and 3, so this is not a new result. The fact that the scaling form (11) works well at times when the effective growth exponent (see below) far from its asymptotic value says that the geometry of the domains is not very sensitive to the excess transport in the interfaces.

What has not been done in previous simulation studies is to measure $R(t)$ with sufficient accuracy and over enough of a time range to measure the time variation of the effective exponent $n_{\rm eff}(t)$ as defined in Eq. (2). It is clear from the upwards curvature of the data in the log-log graph of Fig. 3 that $n_{\rm eff}$ is increasing with time. A numerically measured effective exponent is extracted from this data using the simple definition

$$n_{\rm eff}(t)=\log_{10}[R(10t)/R(t)]\ . \tag{12}$$

The results are shown in Fig. 4. The generalized Lifshitz-Slyozov theory [Eqs. (8) and (9) above] says that $n_{\rm eff}(t)$ should approach $\frac{1}{3}$ as $1/R\to 0$ with a finite slope on the graph in Fig. 4. Unfortunately, only a rather small range of $1/R$ was accessible, due to the slowness of the domain growth. However, the results are certainly consistent with the theory, and the length R_0 needed to fit the data to (9) is of order 1 or 2 lattice spacings at the temperatures studied, which does not seem unreasonable.[12] The results are clearly inconsistent with the prediction of Ref. 6 that $R(t)\sim\ln t$, since this gives an $n_{\rm eff}(t)$ that decreases with time, vanishing as $n_{\rm eff}(t)\sim 1/R(t)$ for $t\to\infty$.

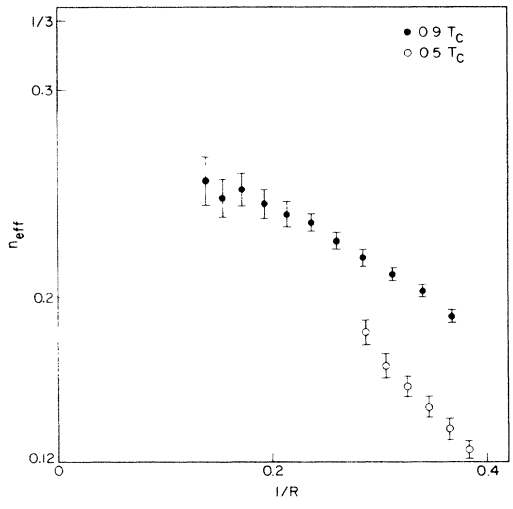

FIG. 4. Effective exponent $n_{\rm eff}(t)$ as a function of $1/R(t)$ for the quenches to $0.9T_c$ and $0.5T_c$ shown in Fig. 3. The exponent is obtained from the ratio of $R(t)$ to $R(10t)$; see Eq. (12).

The reader may find it disturbing that the last few points for $T=0.9T_c$ are all lower than expected, but this may be a statistical fluctuation. The errors on these points are highly correlated because they are all obtained from the same runs. If we do not assume that we know the exponent n in (1), but do make the reasonable assumption that the leading corrections are of order $1/R(t)$, then we obtain $n=0.29\pm0.04$ by allowing any reasonably smooth extrapolation of the data in Fig. 4 for $T=0.9T_c$. I must admit that this uncertainty in n is rather disappointing, but to improve it requires significantly more computer time; to go to twice the $R(t)$ with comparable accuracy will require approximately fifty times as many attempted exchanges. This work took approximately 6 CPU hours on a Cray I.

A possibility for future simulations is to attempt to independently adjust the interfacial and bulk conductivities in order to reduce the magnitude of the leading correction to scaling R_0. This could be done by making the exchange probability smaller in interfacial regions than it is in the model simulated here. If successful, this might yield a more accurate estimate of the asymptotic exponent, n, as well as more information about the corrections to scaling.

IV. DISCUSSION

It is worth noting why the data used by Mazenko *et al.*[6] in their Monte Carlo renormalization-group analysis are not relevant for the long-time behavior. Since there are processes with different activation energies in this square lattice spin-exchange Ising model, there are probably three different time regimes in the growth process at low temperatures. First, for times $t \ll \exp(4J/T)$ only nonactivated processes occur and the domains grow to a finite size of order unity and then stop, as is seen in zero-temperature simulations.[6] Then, for $\exp(4J/T) \ll t \ll \exp(8J/T)$, the processes with activation energy $4J$ are occurring, but not those with activation energy $8J$. It is not clear what growth law holds in this regime; probably the domains just grow a little larger and then stop again because to go to large domains appears to require processes with activation energy $8J$. Finally, for long times, $t \gg \exp(8J/T)$, significant conduction through the bulk domains finally can occur and the Lifshitz-Slyozov growth law holds, with the finite-time corrections discussed above. In Ref. 6 they worked at low temperatures and such short times that they never entered the last regime. Therefore their data has nothing to do with the long-time growth behavior. The simulations reported in this paper, on the other hand, are performed at high enough temperatures and for long enough times that plenty of time is available for the activated conduction to occur and most of the data is in the long-time regime.

The renormalization-group analysis of Mazenko *et al.*[6] that leads to their conclusion $R \sim \ln t$ assumes that the same zero-temperature fixed point governs the long-time behavior at $T=0$ and $T>0$. It is this assumption that is the source of their disagreement with Lifshitz-Slyozov. What long-distance or long-time properties does an ordered phase have that must be properties of the zero-temperature fixed point governing it? One is the dependence on interfacial orientation of the interfacial tension: For two-dimensional Ising models on regular lattices the interfacial tension is an analytic function of interfacial orientation for $T>0$, while at $T=0$ it develops singularities at certain orientations.[13] In this respect the fixed point governing $T=0$ is very different from those governing $T>0$. Another property of the ordered phase is the bulk spin conductivity λ. This is strictly zero for $T=0$, while for $T>0$ it is nonzero. This again makes the fixed point governing $T=0$ special. I argue that the fixed point governing the $T=0$ behavior governs the $T>0$ behavior only for times $t \ll \exp(8J/T)$, when activated conduction is not occurring. At later times the behavior is governed by a very different fixed point which allows conduction and ripening and yields the Lifshitz-Slyozov growth law.[14] Therefore, it appears that a proper renormalization-group treatment of this problem must allow for both fixed points, unlike Ref. 6 where only one fixed point was permitted.

ACKNOWLEDGMENT

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[10] I. M. Lifshitz, Zh. Eksp. Teor. Fiz. **42**, 1354 (1962) [Sov. Phys.—JETP **15**, 939 (1962)].

[11] In systems where one phase has significantly larger conductivity than the other, the conductivity in the interface might be reduced from that of the more conducting phase and therefore serve to reduce the average conductivity (which is predominantly due to one phase) for small $R(t)$.

[12] From Eqs. (6)–(9) we see that R_0 is proportional to the ratio of the total excess conductivity in the interface to the bulk conductivity. Because the interfacial conductivity has a lower

activation energy than the bulk conductivity, this ratio should increase as temperature decreases. Such behavior is indeed seen in Fig. 4, where the data for $T=0.5T_c$ fall well below those for $T=0.9T_c$.

[13]See, for example, C. Rottman and M. Wortis, Phys. Rev. B **24**, 6274 (1981).

[14]J. Vinals and J. D. Gunton [Phys. Rev. B **33**, 7795 (1986)] have suggested that there are two different fixed points, one for $T=0$ and one for $T>0$, governing domain growth in an eight-state Potts model with no conservation laws (model A dynamics).

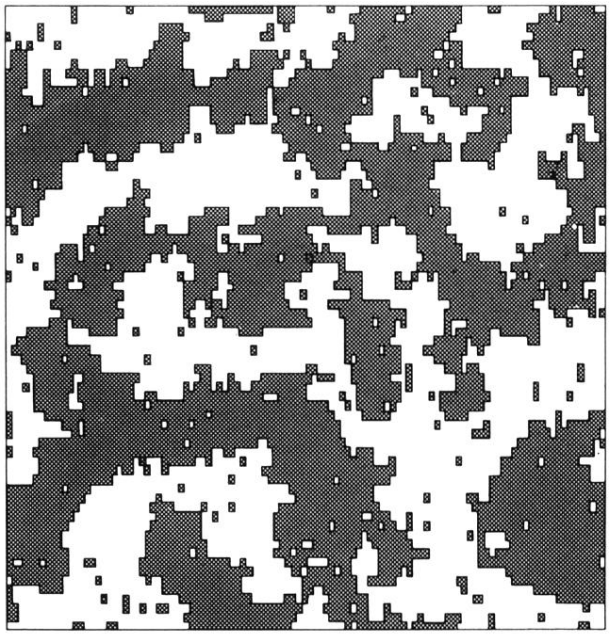

FIG. 1. Domain configuration obtained after quenching a square lattice spin-exchange Ising model with zero total magnetization instantly from infinite temperature to $0.9\,T_c$ and then annealing for 16000 Monte Carlo steps per spin. The spin-up phase is dark and the spin-down phase white. The sample consists of 108^2 spins. See Ref. 5 for similar pictures of larger samples.