Kinetics of the order-disorder herringbone transition

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(Received 7 November 1983)

The development of orientational order in an anisotropic planar rotor model has been studied by Monte Carlo methods. The order develops following an instantaneous quench from a high-temperature, disordered phase to an unstable low-temperature state in which a threefold-degenerate herringbone phase is the equilibrium state. The model describes the orientational properties of N_2 molecules physisorbed on graphite. Both the dynamical structure factor and average domain size have been determined. The structure factor is shown to satisfy dynamical scaling. The growth laws for three different measures of a "domain size" are all shown to obey the Allen-Cahn law. This is in disagreement with the interpretation of an earlier Monte Carlo study of the same model.

INTRODUCTION

Recently, considerable theoretical and experimental attention has been given to the dynamics of order-disorder transitions in physisorbed and chemisorbed overlayer systems.[1,2] Indeed, very recently the dynamics of ordering in the oxygen on tungsten [O/W(112)] system was studied experimentally by means of low-energy electron diffraction (LEED).[2] This is the first study of submonolayer systems which confirms the theoretical prediction of the Allen-Cahn domain growth law.[3] Many other physisorbed and chemisorbed systems are excellent candidates for the study of domain growth kinetics. Often a reasonably realistic model Hamiltonian for such systems can be constructed using the results of spectroscopic studies such as LEED. Such Hamiltonians can then be used in Monte Carlo simulations to study the kinetics of domain growth. The actual experiments are done with heterogeneous substrates, so that the typical system sizes are less than about 500 lattice constants. Thus the computer simulations can be adjusted to actual system sizes. It should also be mentioned that the model simulations give information about the "pure" system, whereas impurities are often present in experimental systems. Such impurities could affect the dynamics of the order-disorder transition.

In this paper we have studied the dynamics of the order-disorder transition of an anisotropic-planar-rotor Hamiltonian[4,5] with nearest-neighbor interactions on a triangular lattice

$$\mathcal{H}=J\sum_{\langle ij\rangle}\cos(2\phi_i+2\phi_j-4\theta_{ij}),\quad J>0\,. \tag{1}$$

Here ϕ_i is the polar angle of the ith rotor and θ_{ij} is the directional angle of the line joining the centers of rotors on sites i and j. This Hamiltonian has been shown to model reasonably well N_2 molecules physisorbed on the hexagonal graphite surface. It has been proposed that this Hamiltonian in a generalized form could also model certain smectic phases in liquid crystals.[4,6] At low temperatures the registered $(\sqrt{3}\times\sqrt{3})R\,30°$ commensurate phase of N_2 molecules orders orientationally in a (2×1) herringbone structure.[4] There are three equivalent orientations in which this (2×1) structure can be placed on the graphite lattice at angles 120° apart. Thus the order parameter has three components. The Hamiltonian is predicted to lie in the universality class of the three-component Heisenberg model with face-type cubic anisotropy.[4] It has been shown recently that the anisotropic planar rotor model Eq. (1) undergoes a fluctuation-induced first-order phase transition.[4] The ground state of this Hamiltonian is sixfold degenerate and the herringbone structure has three equivalent orientations. Thus the order parameter has three degenerate components

$$\psi_\alpha=M^{-1}\left\langle\sum_{i=1}^{M}\sin(2\phi_i-2\theta_\alpha)\exp(i\vec{Q}_\alpha\cdot\vec{r})\right\rangle,\quad \alpha=1,2,3 \tag{2}$$

where M is the number of sites, ϕ_i describes the orientation of the rotor i, and $\theta_1=0$, $\theta_2=\pi/3$, and $\theta_3=2\pi/3$. The wave vectors $\vec{Q}_\alpha$ which describe the three states are

$$\vec{Q}_1=\left[\frac{\pi}{a}\right]\left[0,\frac{2}{\sqrt{3}}\right],$$

$$\vec{Q}_2=\left[\frac{\pi}{a}\right]\left[-1,\frac{1}{\sqrt{3}}\right],$$

and

$$\vec{Q}_3=\left[\frac{\pi}{a}\right]\left[-1,\frac{-1}{\sqrt{3}}\right],$$

respectively.

Very recently the kinetics of these herringbone phases has been studied by Mouritsen,[5] who concentrated on determining the growth law governing the average domain size. We have repeated this study and in addition studied the dynamical structure factor of the order parameter and its scaling with one characteristic length scale. The scaling property of the structure factor can give valuable information about the average morphology of the domain growth. Indeed, if scaling holds the domain growth proceeds via self-similar pattern formation. The structure factor is a quantity which also can be measured by spec-

troscopic methods. The study of the structure factor avoids the possible ambiguities involved in determining the domain walls and corresponding interface areas in a lattice model with a continuous single site variable. Any rule which is used to define a domain wall will lead to a wall of finite width, in contrast to the Ising model, for example. That is, the domain wall is "soft" in this herringbone model. In the earlier study of Mouritsen the growth was observed to be very slow. Also Mouritsen interpreted the results of a domain size $\bar{R}(t)$ in terms of two distinct algebraic regions. Namely, an early-time region with $\bar{R}(t)\sim t^{0.4}$ and a late-time region with $\bar{R}(t)\sim t^{0.25}$. These results differ from the Allen-Cahn $t^{1/2}$ prediction[3] and from the log$t$ behavior predicted by Lifshitz[7] and Safran[8] for systems in which the degeneracy p of the ground state of the Hamiltonian satisfies $p\geq d+1$, where d is the dimensionality of the system. In addition, the exponent n which characterizes the behavior is significantly smaller than that found for the q-state Potts model on a triangular lattice[9] (e.g., $n\cong 0.41$ for $q\geq 30$). The late-time exponent for the herringbone model was attributed to the softness of the domain walls caused by the continuous nature of the rotor. The softness of the domain wall was claimed to screen the interaction between different domains and thus to decrease the driving force for the domain growth. In early times, it was claimed that the higher frequency of the coalescence process would decrease the screening and therefore enhance the driving force for growth. We believe, however, that this phenomenon is not what is usually meant by diffusion-driven coalescence, but rather is a "random" curvature-driven effect. As we will discuss below, our results for the average domain size are consistent with those obtained by Mouritsen,[5] but our interpretation for the growth law does not agree with his. Indeed, we find that our results are more consistent with the Allen-Cahn prediction, $\bar{R}\sim t^{1/2}$. In addition, we find that the structure factor satisfies dynamical scaling, with a scaling function very similar to that seen in other order-disorder transitions.

RESULTS AND CONCLUSIONS

We have studied the time evolution of the model in Eq. (1) following an instantaneous quench from a random configuration of rotors ($k_BT/J=\infty$) to a temperature $k_BT/J=0.02$, at which the herringbone phase is the equilibrium state. We have chosen an $M=60\times 60$ triangular lattice with periodic boundary conditions. As in the earlier study, we have used Glauber spin-flip dynamics where the rotor was allowed to change its orientation by any angle up to a maximum value of (a) π or (b) $\pi/5$. Although the latter rule clearly gives rise to a faster evolution of domain sizes, the results for both cases are qualitatively the same, as also noted in Ref. 5. As mentioned above, one can study three equivalent order parameters. Similarly, one can study three equivalent circularly averaged[10] structure factors,

$$S_\alpha(k,t)=\left\langle \left| \sum_{i=1}^{M} \sin(2\phi_i-2\theta_\alpha)\exp[i(\vec{k}+\vec{Q}_\alpha)\cdot\vec{r}] \right|^2 \right\rangle , \quad \alpha=1,2,3 . \quad (3)$$

For simplicity we will often drop the subscript α in what follows.

In order to obtain good statistics we have performed 25 runs and averaged the structure factor data for the component which shows consistent evolution in the time region [0—5000 Monte Carlo steps (MCS)/spin] studied in this paper. We have stopped following the time evolution at 4500 MCS/spin to avoid finite-size effects. Namely, in a few runs after $t\gtrsim 4500$ MCS/spin some of the domains became of the order of the size of the system (i.e., we observed "percolation" phenomena). In Fig. 1 we show a series of snapshots of domain evolution in a typical

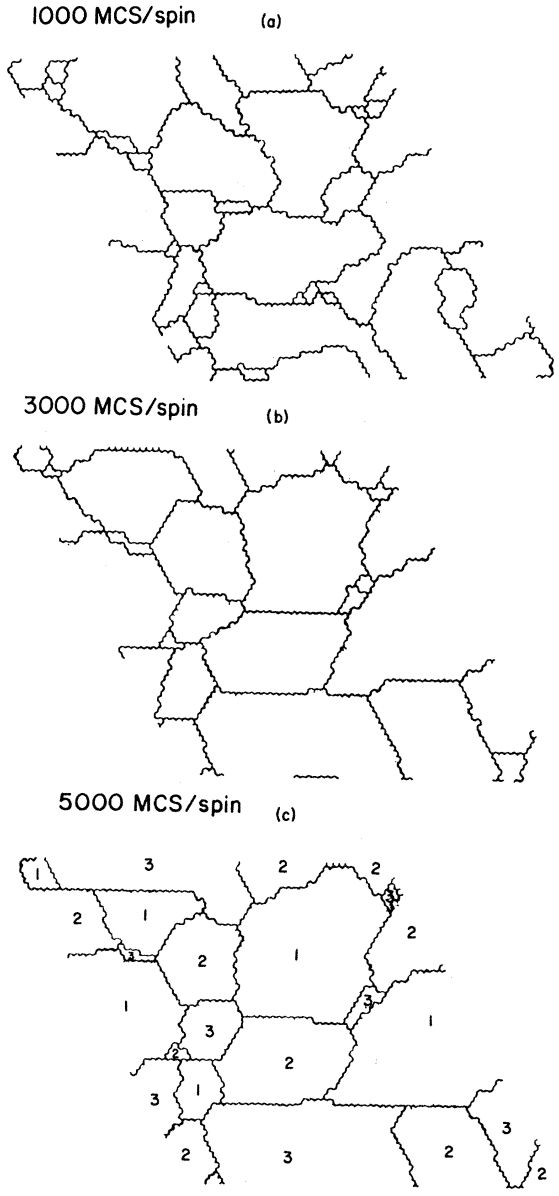

FIG. 1. A typical series of snapshots showing the growth of herringbone domains. Only sharp domain walls, which are the central portion of the soft domain interfaces, are shown. Within the domains the rotors are arranged in three equivalent herringbone structures (with only very small angular deviations). Herringbone domains are indicated by $\alpha=1,2,3$. We do not distinguish between herringbone structures which differ only by a translation.

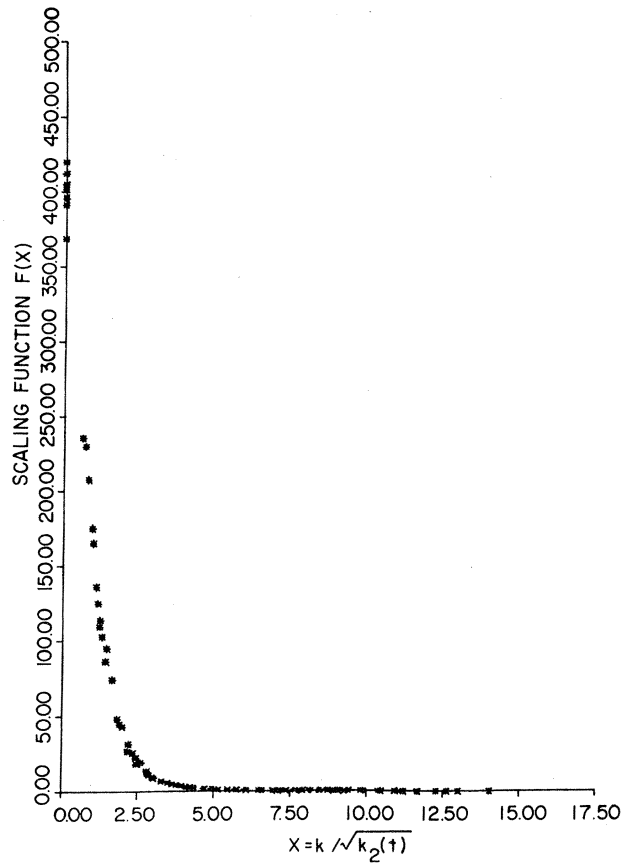

FIG. 2. The scaling function $F(x)$ of the dynamical structure factor. A similar scaling can be done using other choices for the length scale.

quench. The domain interfaces are drawn as sharp lines, rather than as soft domain walls. These sharp interfaces can be visualized as being the center portion of the soft domain interfaces. We have chosen this representation for simplicity. As well, there is no unique definition of a domain wall for the anisotropic rotor model.

We have also calculated the magnitudes of the mth ($m=1,2$) moments of the average structure factor[12] defined as

$$k_m(t)=\frac{\sum |k|^m S(k,t)}{\sum S(k,t)}, \quad m=1,2 \tag{4}$$

to analyze the scaling of the structure factor and the growth law of the average domain size. We have carried out the scaling with the second moment, i.e.,

$$F(x)=k_2(t)S(k,t), \quad x=k/[k_2(t)]^{1/2} \tag{5}$$

or alternatively with the first moment,

$$\tilde{F}(\tilde{x})=k_1^2(t)S(k,t), \quad \tilde{x}=k/k_1(t)\ . \tag{6}$$

In Fig. 2 we show the scaling function for Eq. (5). As can be seen, scaling holds so that the growth is governed by a single time-dependent length scale. We have also performed the scaling using the first moment Eq. (6), and the results exhibit slightly greater scatter, but are otherwise very similar to those shown in Fig. 2. A third possible form of scaling would involve using the average domain size $\bar{R}(t)$ as a characteristic time-dependent length. Although we have calculated the average domain area $[\sim\bar{R}^2(t)]$, we have not tested this form of scaling. Nevertheless, we expect that scaling with $\bar{R}(t)$ would yield similar results to those shown in Fig. 2, since the behavior

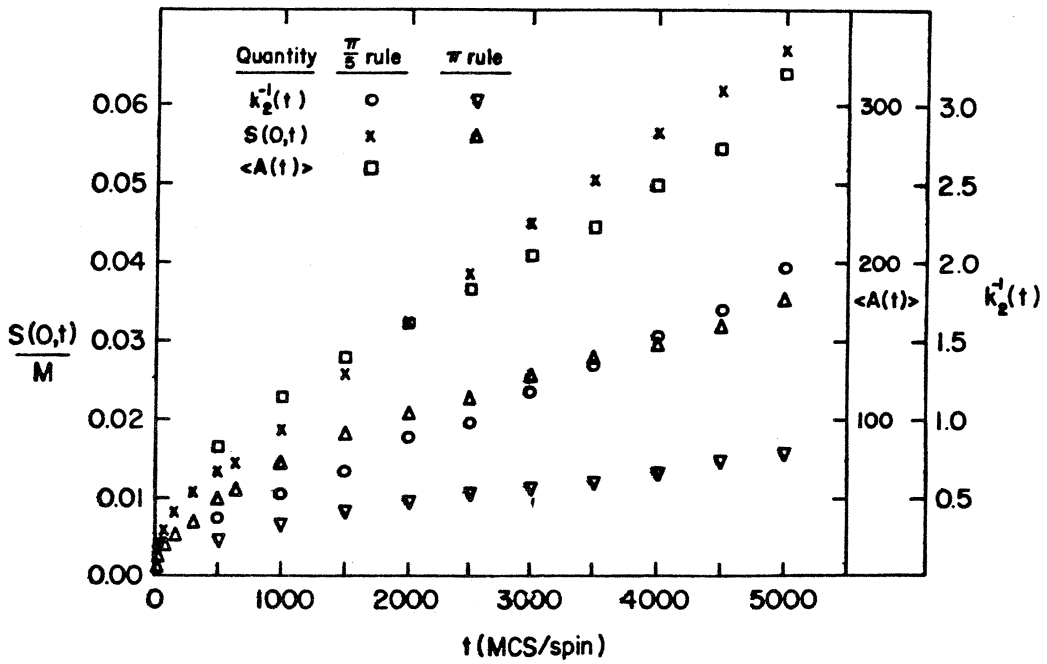

FIG. 3. The growth rate of the average domain area $\langle A(t)\rangle$, $k_2^{-1}(t)$, and $S(0,t)$. The results are shown for two different rules, as discussed in the text. (Note the difference in scales in this figure.)

of $\bar{R}^2(t)$ is quite similar to $k_2^{-1}(t)$, as will be discussed below. Finally, we note that the scaling function is extremely similar to that found in studies of the antiferromagnet[11] and clock models.[12]

In order to study the growth rate of average domain size, we have used three different definitions of a length scale. The first is the inverse second moment $k_2^{-1}(t)$ [Eq. (4)], which to a good first approximation is related to the average domain area. The second length scale has been proposed by Sadiq and Binder,[13] namely from the sum rule

$$S(0,t)=M\sum_{\alpha}\langle\psi_{\alpha}^2(t)\rangle\ . \tag{7}$$

For the equivalent domains it is natural to define a length scale by

$$L(t)=[M^{-1}S(0,t)]^{1/2}/\psi(T)\ , \tag{8}$$

where $\psi(T)$ denotes the equilibrium value of the order parameter. Thus at low temperatures [where $\psi(T)\simeq 1$], $S(0,t)/M$ corresponds to a measure of the average domain area. The third quantity we have used is the average domain area $\langle A(t)\rangle$ as calculated from the number of domains appearing on the lattice at any given time. In contrast to averaging over 25 runs as we have done for $k_2^{-1}(t)$ and $S(0,t)$, we have obtained data for $\langle A(t)\rangle$ by averaging over only 10 runs, due to the difficulties involved in this procedure. The determination of $\langle A(t)\rangle$ may give rise to some error because the definition of the domain interface is not unique, as explained above. We have chosen to use "sharp" walls, as shown in Fig. 1, to determine the domains. In Fig. 3 we have shown our data for all these choices of length scale. The growth in all cases seems to be very slow as already noted by Mouritsen.[5] After an initial period less than 1000 MCS the behavior is linear until the point at which "percolation" becomes imminent ($\sim$5000 MCS). Our analysis and conclusions are based on performing a least-squares analysis for three different types of power-law behavior: (a) $y=At+B$, where B takes into account the initial transient region, (b) $y=At^{2n}$, which does not allow any kind of initial transient, and (c) $y=At^{2n}+B$, which takes into account a transient period. One would usually expect a transient region during which the domains are being formed. After this transient time the domains then grow or shrink in size. In the herringbone phase the determination of domains is not unique. Therefore, the determination of the time when the domains have formed is difficult, if not impossible. Apart from neglecting the transient effect the fit given by (b) weights too heavily the early-time region. This is clearly demonstrated in Fig. 4, where the least-squares fit (b) for the quantity $S(0,t)/M$ gives an effective exponent $2n=0.567$. The fit (a) assumes the validity of the Allen-Cahn growth law. Judging from the usual tests of the goodness of the fit (the χ^2 test and the correlation factor), this fit is very good for our data for all choices of length scale [$k_2^{-1}(t)$, $S(0,t)/M$, and $\langle A(t)\rangle$] in the time region 1000–4500 MCS/spin. The fit (c) also supports the Allen-Cahn picture. In order to avoid making a three-parameter fit, we have discarded

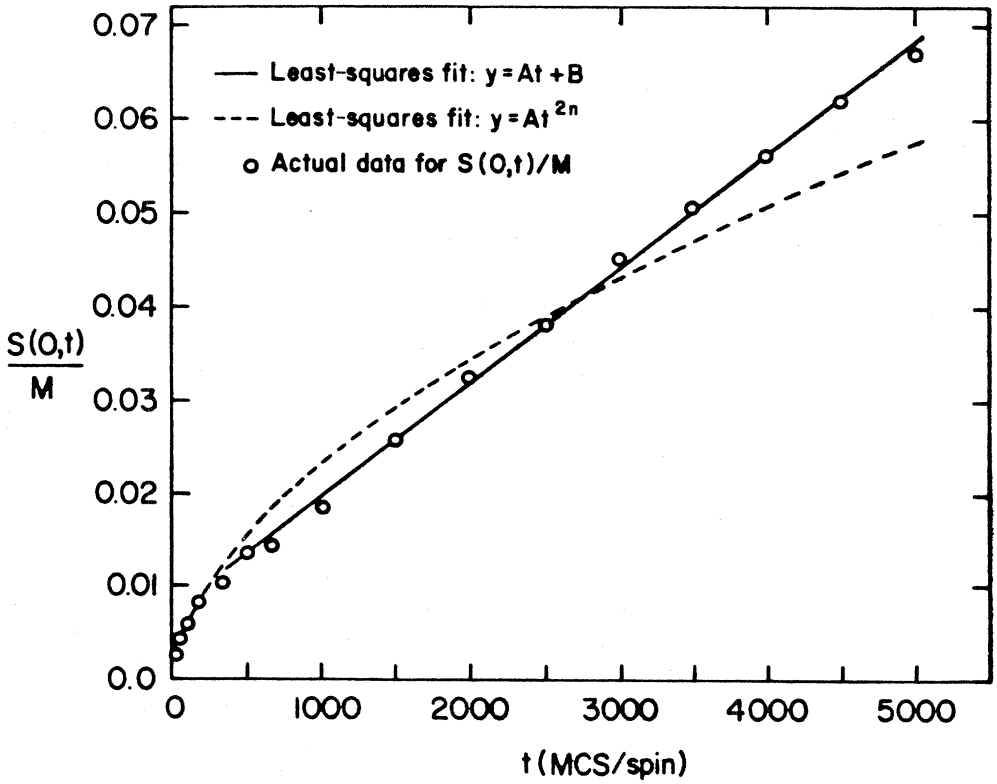

FIG. 4. Two different least-squares analyses of the Monte Carlo results for $S(0,t)/M$: (a) $y=At+B$; (b) $y=At^{2n}$ (the Allen-Cahn reduction). (a) Assuming that the early-time behavior is a "transient regime" clearly fits the data points much better than (b).

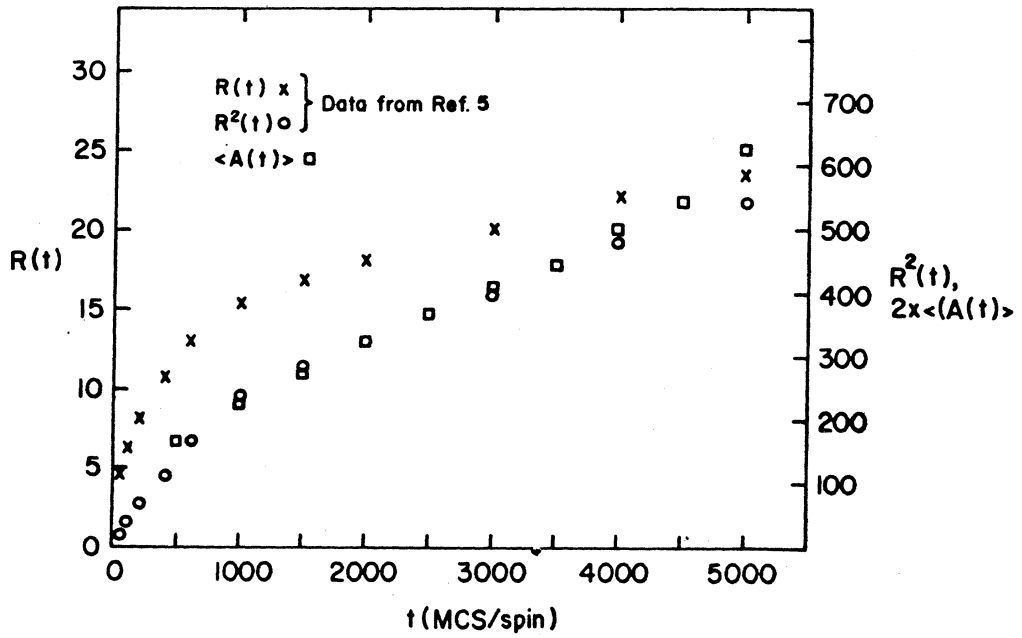

FIG. 5. A comparison of our results with those obtained in Ref. 5. Apart from the last data point at 5000 MCS/spin (for which our data is affected by finite-size effects), the agreement between the two studies is excellent.

data points in the transient region by moving the origin to different data points. Thus, the fit given by (c) is rewritten in the form

$$y' = y - B = At'^{2n} = A(t - t_0)^{2n} .$$

In the time region from 640–4500 MCS/spin we obtain an exponent $2n = 1.0 \pm 0.05$. Therefore, we conclude that Allen-Cahn curvature-driven growth is likely to describe the growth of domains when the system is quenched from a disordered equilibrium state to the herringbone phase region. This conclusion is consistent with all three quantities chosen to determine the growth rate. Two of these quantities, $k_2^{-1}(t)$ and $S(0,t)/M$, can actually be measured by spectroscopic methods in a herringbone structure. These quantities have the additional advantage of avoiding the difficulty involved in defining a domain wall. However, since the behavior of $\langle A(t) \rangle$ is quite similar to $k_2^{-1}(t)$ and $S(0,t)/M$, the definition of the domain interface and its "softness" does not seem to play a role in the growth law exponent. The softness does seem to affect the nonuniversal features of the growth rate, making the evolution of domains very slow. We should also mention that the exponents obtained here are at best describing dominant time behaviors. One could expect the growth laws also to have correction terms somewhat similar to the corrections to scaling near the critical point (due to irrelevant eigenvalues). In the light of this possibility one could be obtaining "effective" exponents by analyzing the data in terms of a simple power-law behavior.

Finally, we compare our results for the average domain size with those obtained by Mouritsen[5] for the same quantity. As is seen from Fig. 5, our results are almost identical with Mouritsen's in the region 500–4500 MCS/spin. (In the log-log plot our data points are virtually indistinguishable from those obtained by Mouritsen). Therefore we believe that his results are correct but that his interpretation of the growth law is incorrect. This is a system which clearly warrants theoretical study to determine which interpretation of the data is correct. In our opinion, however, the most consistent interpretation of the available data is that the domain growth satisfies an Allen-Cahn $t^{1/2}$ law.

ACKNOWLEDGMENTS

We are grateful to Dr. Martin Grant for many useful discussions and suggestions during this work. This work was supported by a grant from the National Science Foundation DMR-80 13700.

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