Freezing in a two-dimensional Glauber system under continuous cooling

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We study a two-dimensional Ising system under Glauber kinetics with an extrinsic energy barrier, submitted to asymptotically slow continuous cooling. The system will freeze into a nonequilibrium state if an appropriately defined effective time for the cooling schedule does not diverge. Starting in equilibrium beneath the critical temperature T_c, the system freezes into small clusters of flipped spins, with the energy density related to the cooling rate by a power law (for most cooling programs). Cluster-dynamical calculations and Monte Carlo simulations show that, for exponential cooling, the freezing exponent approaches a one-cluster value, which depends upon the energy barrier and the lattice type, via an intermediate regime with a higher effective exponent. Starting in equilibrium above T_c, the frozen state consists of large domains of either phase. Simple interface-dynamical arguments suggest that the frozen correlation function should assume a scaling form, with a (universal) scaling exponent, which is the same as for domain growth after an instantaneous quench. Monte Carlo simulations find evidence for this scaling form at small values of the scaling variable only, suggesting the importance of initial correlations for a very wide regime of cooling rates. In neither case does the temporal evolution of the frozen state follow a Kohlrausch form, suggesting a qualitative distinction from true glassy states.

I. INTRODUCTION

Systems that require an activation energy to relax towards equilibrium can display behaviors somewhat analogous to a glass transition, with a far-from-equilibrium state being frozen in if the system is cooled through temperatures such that the internal rates become slower than the cooling rate.

Microscopic studies of such freezing and of the characteristics of the frozen-in state have recently been made[1–4] on activated one-dimensional kinetic Ising models under continuous cooling. The Ising chain has a phase transition at zero temperature, so the slowing down due to the energy barrier present in the model occurs simultaneously with the critical slowing down as the critical point is approached. The final state does not have long-range order, in contrast to the equilibrium state at zero temperature. However, the processes that lead to relaxation in both the equilibrium and frozen state are not qualitatively different (unless the system is at zero temperature), and so the frozen state is not strictly metastable, i.e., the system is not glassy.

By contrast, true glassy states occur in systems with a phase transition at nonzero temperature. The equilibrium state at low temperature is characterized by long-range order, not present in the glassy state. The divergence of an Arrhenius factor associated with an energy barrier occurs as low temperatures are approached, and so occurs separately from critical slowing down (if present).

It is obviously of importance to study freezing in microscopic models with finite-temperature phase transitions, particularly nonrandom models subjected to continuous cooling. We therefore here investigate a two-dimensional (2D) kinetic Ising model, with uniform nearest-neighbor coupling constants, under cooling to absolute zero. In particular, we allow this system to change state via single-spin-flip kinetics with transition probabilities that satisfy detail balance, but differ from the conventional Glauber flip rates by a temperature-dependent activation factor, which diverges at absolute zero. This prefactor does not affect the equilibrium properties of the model, but can cause this system to freeze when cooled to zero temperature.

The two-dimensional Ising system has the advantage of being one of the few statistical models with nontrivial critical behavior whose static properties are exactly known (in the absence of a magnetic field). Thus, it has been historically a fruitful testbed for theories of critical behavior. It may represent any system of cou-

pled two-state entities, such as binary alloys. Although the dynamics for this system are not exactly solvable, it has also been a popular model for investigating critical dynamics,[5,6] and also far-from-equilibrium behavior such as domain growth and spinodal decomposition.[7] We therefore regard it as a suitable model for gaining a better understanding about freezing. It has been argued that the spin-spin autocorrelation function varies with time as a Kohlrausch stretched exponential beneath the critical temperature,[8] and possibly also in the critical region.[9] It is well known that if the system is quenched from the one-phase to the two-phase region, the system takes an infinite time to approach equilibrium. Thus the two-dimensional Glauber model appears to be a good candidate for displaying glassy behavior under slow cooling.

The two-dimensional Glauber model with an energy barrier has been studied under asymptotically rapid cooling[10] using a decoupling approximation for the higher-order correlation functions that appear in the equation of motion for the spin-spin correlation function. They found that the system did indeed freeze in a nonequilibrium state, but they did not discuss the properties of this state. In contrast, we are interested in the slow cooling regime, where the departure from equilibrium is gradual, and the frozen state should retain some of the characteristics of the freezing temperature. We are also interested in whether this state shows the relaxational features of glasses.

Among other questions addressed in this paper are (i) the situations (i.e., cooling programs) under which freezing can occur, (ii) whether the behavior differs very much for cooling through the critical point, or starting below it, (iii) whether the freezing is into single spins or large domains, (iv) whether freezing exponents are universal and, if not, what they depend upon, (v) whether the frozen structure has any characteristics of a glassy state, e.g., a temporal evolution of Kohlrausch form, (vi) whether initial correlations get forgotten in freezing, and (vii) whether the susceptibility (or other response functions) in the frozen state differs much from the equilibrium value.

The structure of this paper is as follows. We first describe the dynamics of the system under consideration, and the way in which an energy barrier is introduced. Next, we study the system under slow cooling, beginning in equilibrium in the symmetry-broken state. We use arguments based on the dynamics of clusters, and compare them with Monte Carlo simulations. We then study the system under continuous cooling, beginning above the critical temperature. Cluster-dynamical arguments are unsuitable under these conditions, so we use interface-dynamical arguments of the type used to describe domain growth, and compare the predictions of these with simulations. The main conclusions are gathered in the final section.

II. SYSTEM HAMILTONIAN AND DYNAMICS

The system is a two-dimensional Ising model on a square lattice, in the absence of a magnetic field, with the following Hamiltonian:

$$\mathcal{H} = -\sum_{\langle i,j \rangle} J\sigma_i\sigma_j \ , \qquad \sigma_{i,j} = \pm 1 \ , \tag{1}$$

where the sum is over nearest-neighbor pairs of spins at sites labeled by i, j, with nearest-neighbor coupling constant J. The system has a critical point at $J/k_BT_c = (1/2)\ln(1+\sqrt{2}) \approx 0.44$.

We allow the system state to change by single-spin-flip Glauber dynamics, described by a master equation,

$$\frac{dP(\{\sigma\},t)}{dt} = \omega \sum_i (1 - \hat{p}_i)W_i(\{\sigma\})P(\{\sigma\},t) \ , \tag{2}$$

where $P(\{\sigma\},t)$ is the probability of the system being in the state $\{\sigma\} = \{\sigma_1,\sigma_2,\ldots\}$ at time t, and $\hat{p}_i$ is the operator that flips the spin at site i. The rate factor W_i is, as usual, chosen so as to satisfy detailed balance, so that the equilibrium probability distribution is a steady-state solution of (2). This assumes that the system is in contact with a heat bath in equilibrium at some temperature T. The use of this master equation in the case where temperature is a function of time again assumes that the temperature of the heat bath varies on time scales very slow in comparison with its equilibration time.

We have introduced an additional Arrhenius factor into the dynamics

$$\omega(T) = \exp\left(-\frac{\Delta}{k_BT}\right) \tag{3}$$

associated with an $ad\ hoc$ energy barrier Δ. When $\Delta = 0$, the dynamics are the same as those normally used, allowing the state of the system to change at zero temperature by processes that do not involve increasing energy. The presence of the energy barrier Δ does not affect the ergodicity of the dynamics for $T \neq 0$, and equilibrium properties are not affected. The universality class for critical dynamics is not affected either, as ω does not diverge near the critical temperature T_c, in contrast to the one-dimensional case, where $T_c = 0$.

The origin of the energy barrier could be from spatially modulated nearest-neighbor bond strengths. Then, at low temperatures, any antiparallel nearest-neighbor pairs will be connected by the weaker bonds, and the system will map onto a uniform one with an overall energy barrier to all dynamic processes, just as the alternating-bond Glauber chain has been found[2] to be equivalent to the uniform activated model.[1] Close to the critical point, this low-temperature approximation will not, in general, be valid, and some strong bonds will be broken. Nevertheless, the dynamic critical behavior of the exchange-modulated system is the same as for the uniform system.[11]

The energy barrier could arise in many different ways. If the Ising model is representing a magnetic system, then an activation energy may be needed to turn the spin through 180°, by virtue of an anisotropy energy that inhibits the spin's ability to point in any direction other than the "easy" one. If the model represents a lattice gas, there may be a simple activation energy required for

all hopping processes.

We choose to study the uniform Ising system with this *ad hoc* energy barrier in preference to one with spatially modulated bonds, so that the results may be interpreted in the context of previous work on uniform Ising systems, and also to simplify the simulations.

The master equation (2) may be written in the form

$$\frac{dP}{du} = -LP , \tag{4}$$

where

$$u = \int_0^t \omega \, dt' \tag{5}$$

is an *effective time*, and L is the same pseudo-Liouvillian as for a system without an energy barrier. As in the one-dimensional alternating-bond models,[2,3] it is clear that the introduction of the energy barrier simply changes the interpretation of time, and so, as in those models, is expected to freeze if and only if $u(t)$ does not diverge as $t \to \infty$. The problem of such a system (i.e., in dimensions greater than one) under continuous slow cooling has not been the subject of previous study, even without an energy barrier.

The equations of motion of the moments of (2), i.e., of the order parameter, correlation functions, etc., are not analytically solvable, since the equation of motion of an l-point function depends upon the $(l + 2)$-point function, in contrast to the one-dimensional case. This is because of the extra connectivity of lattices in dimensions greater than one (which is of course also the reason for the statics being much more difficult to solve than for the one-dimensional case). Approximation methods will be introduced where needed but must be used with caution.

Previous studies of the 2D Glauber system have focused upon critical dynamic behavior,[5] and domain growth after a rapid quench from the one-phase region to the two-phase region.[7] Monte Carlo simulation remains the primary tool for obtaining results, and confirming the predictions of approximations, and this is the main approach used here.

III. SLOW COOLING FROM BELOW THE CRITICAL TEMPERATURE

In this section, we treat the case of slow cooling, starting from equilibrium at some temperature beneath the critical point. Although the glass transition occurs when certain systems are cooled through their melting points, there are many cases where a system freezes after cooling without passing through a temperature where it would usually have a phase transition. Examples are low-dimensional spin glasses (with critical point at absolute zero), and the stabilization of crystal faults and defects. It is therefore legitimate to study the behavior of our two-dimensional system under these conditions, to compare with the results obtained in one dimension and also as an interesting problem in its own right. The low-temperature dynamics obtained is not to be confused with critical dynamics. We describe the dynamics of the system in terms of clusters, and then compare the predictions of these arguments with simulations.

A. Cluster dynamics

A typical equilibrium state at a temperature less than T_c consists of a background of the majority phase ("up," for example) with finite domains of the opposite ("down") phase. If these latter domains are big enough, there may be further domains of the majority phase within them, and so on. Under single-spin-flip kinetics, domains of one down spin are thermally nucleated from the majority phase. The tendency for these domains to shrink, on energy grounds, is opposed by the thermally activated processes, which allow domains to grow (or, to put it another way, by entropy). Domains larger than the typical thermal equilibrium size have a tendency to shrink, with their area decreasing at a constant rate with time, this rate being temperature dependent.[12]

In a finite system, these droplet fluctuations cause the magnetization to reverse its sign sporadically, though this is impossible in an infinite system. Such fluctuations lead to an essential singularity and anomalous decay of correlations at the critical point.[13,14] Also, according to Huse and Fisher,[8] these droplets behave as an ensemble of two-level systems, and the very slow relaxation causes the spin-spin autocorrelation function to have a Kohlrausch dependence upon time. The claim of Huse and Fisher that this behavior should be readily obtainable from simulations is doubtful, however, as the behavior occurs at very late times only, where the spin autocorrelation function is very small, and so very high statistics would be necessary to confirm the law over several orders of magnitude of time. Also, since the behavior is sensitive to fluctuations of droplets of large size, significant finite-size effects might be expected.

The approach we take is to describe the system in terms of *clusters* of flipped spins. We define the density n_l of clusters of size l as the number of such clusters divided by the number of spins in the system. In Fig. 17, we illustrate some typical dynamical processes, which may occur for small clusters. By virtue of the dynamics chosen, the only processes that can occur consist of single spin flips. It is clear that the equation of motion of a given cluster density n_l involves not only linear terms in the densities of clusters of size $l \pm 1$, but also nonlinear terms due to two smaller clusters fusing, or one domain splitting into two. The spatial correlation of different clusters is therefore involved. It is also necessary to distinguish between clusters of the same size but different shape.

This cluster picture has been used to describe both critical dynamics and domain growth.[15] In the limit $T \to T_c$, the important clusters are very large, and a continuum approximation is valid, which, together with simplifying assumptions concerning the nonlinear terms, results in a Fokker-Planck equation, reminiscent of classical nucleation theory.[16] The equation is not very successful at describing critical dynamics or domain growth, however. This shows that the random-phase approximation used to treat the nonlinear terms is not accurate, and the geometric cluster density is found to diverge be-

fore criticality is reached. However, we are interested in the opposite regime, where the system departs from equilibrium at low temperature, and so the dominant clusters are, in fact, small. The continuum approximation does then not apply, but we can treat small clusters in a way akin to a low-temperature series expansion for the Ising model statics, which is known to be well behaved.

As the temperature approaches zero, the equilibrium values of the cluster densities vanish. For the square lattice (considered hereafter), the low-temperature expansion is one in terms of the Boltzmann factor $\exp(-4\beta J)$, since the energies of clusters are in units of $4J$. We would therefore expect that truncating the hierarchy of equations of motion for cluster densities at some finite maximum size l would be accurate, if this Boltzmann factor is small, to within a correction of this order. The nonlinear terms will be increasingly more important for larger clusters, but, since we are mostly interested in the densities of small clusters, it is less important to treat large clusters accurately.

If we neglect the nonlinear terms, the equations of motion for the cluster densities may be written in the form

$$\frac{d\mathbf{n}}{du} = \mathbf{M}\mathbf{n} + \mathbf{s} ,$$ (6)

where

$$\mathbf{n} = \begin{pmatrix} n_1 \\ n_2 \\ \vdots \end{pmatrix} , \qquad \mathbf{s} = \begin{pmatrix} \exp(-8\beta J) \\ 0 \\ \vdots \end{pmatrix} ,$$ (7)

and $\mathbf{M}$ is a temperature-dependent matrix containing both constant terms and Arrhenius terms associated with the various spin-flip processes. The inhomogeneous term $\mathbf{s}$ is a source term, which accounts for creation of clusters of size 1, where no cluster was present before.

Under cooling, $\mathbf{M}$ becomes a function of time, and in general the set of equations (6) may not be solved. If the cooling is slow, the commutator $[d/dt, \mathbf{M}]$ is small compared to $\mathbf{M}$, and the equations may be solved approximately in this limit using the standard technique of diagonalization. However, the analytic solution of (6) is laborious even under these conditions, and the result is only reliable in the limit where all $n_l \to 0$, since this equation has not included the nonlinear terms (whose size is of the order of n_3). Therefore, the only reliable solution when clusters of size two or more are important is that obtained by numerical solution of the full, nonlinear set of coupled equations, truncated at some point.

However, if we cool sufficiently slowly, the system will remain in equilibrium until the only clusters present are of size one. It is then possible to truncate the hierarchy of equations at $l = 1$. The equation of motion of the one-cluster density in this limit is

$$\frac{dn_1}{dt} = \exp(-\beta\Delta)[\exp(-8\beta J) - n_1] .$$ (8)

This equation is just that for a two-level system.[17]

We choose to vary temperature so that the Arrhenius factor $\omega \equiv \exp(-\beta\Delta)$ decreases exponentially in time

$$\omega = \omega(0)\exp\left(-\frac{t}{\tau}\right) .$$ (9)

Then the equilibrium value, $n_1^e = \exp(-8\beta J)$, of n_1 also varies exponentially in time, so that the characteristic cooling rate r_c, defined as

$$r_c = \frac{d}{dt}\ln n_1^e ,$$ (10)

is therefore constant in time.

Using the effective time $u \equiv \int \omega dt$ the solution to (8) under these conditions is

$$n_1(u) = \omega^\gamma(0)\exp(-u) + \int_0^u \exp(-x)\left(\omega(u) + \frac{x}{\tau}\right)^\gamma dx ,$$ (11)

since $n_1(0) = \omega^\gamma(0)$, where

$$\gamma = \frac{8J}{\Delta} .$$ (12)

For $u \gg 1$, there is no memory of the temperature at which the cooling began, since the first term on the right-hand side of (11) becomes negligible, and the rest may be written in the dynamic scaling form

$$n_1(u) = \tau^{-\gamma} f(\omega(u)\tau)$$ (13)

where

$$f(x) = \begin{cases} \text{constant} & \text{as } x \to 0 \\ x^\gamma & \text{as } x \to \infty. \end{cases}$$ (14)

The system therefore departs from equilibrium at the point, where $\omega\tau \sim 1$, and the frozen one-cluster density varies with cooling time as

$$n_1 \propto \tau^{-\gamma} .$$ (15)

Note that the factor 8 in (12) is lattice specific, so the exponent γ is nonuniversal with respect to lattice type.

For other cooling schedules (i.e., ones where ω does not vary exponentially in time), both the scaling form and scaling variable would be different, since the cooling rate would then be a function of time. The frozen cluster density would also vary with a different power of the cooling time parameter τ. Such generalizations of (15), and the equation itself, can be obtained by the following crude procedure (analogous to that given in Ref. 3 for the freezing in the alternating-bond Glauber chain): we expect the system to freeze at about the time t_F when the cooling rate $r_c = 8J\frac{d\beta}{dt}$ [Eq. (10)] is equal to the equilibration rate $\omega = \exp(-\beta\Delta)$ in (8). For a given cooling program (β a known function of $\frac{t}{\tau}$) this determines $t_F(\tau)$, which inserted into $n_1^e = \exp[-8\beta(t_F(\tau)J)]$ provides the dependence of the frozen one-cluster dependence on τ.

If the freezing takes place at a higher temperature (by virtue of more rapid cooling), densities of larger clusters become more significant. Being unable to solve exactly the full hierarchy of coupled equations, we turn to numerical integration.

We integrated Eqs. (6) for the square lattice, truncated to order $\exp(-16\beta J)$, for several values of τ and Δ. Details of the specific equations used are to be found in
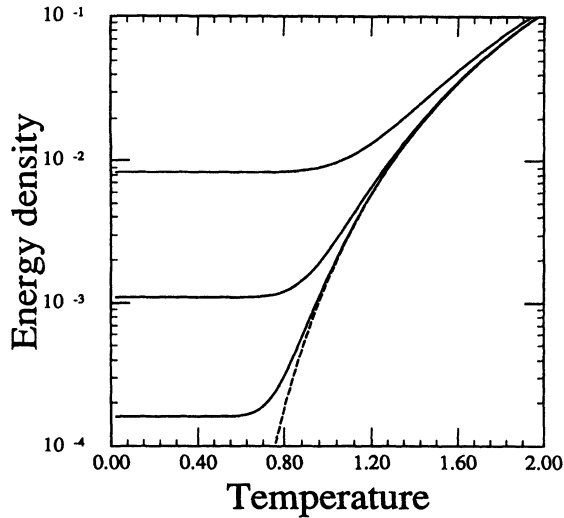
FIG. 1. Energy density during cooling as a function of temperature for slow quenches starting at $T = 2J$, from a numerical integration of Eqs. (A1)-(A7), for $\Delta = 10J$. Solid curves, top to bottom: $\tau = 3 \times 10^3$, 3×10^4, and 3×10^5. Dashed curve: equilibrium value.

FIG. 3. Energy density during cooling as a function of temperature for slow quenches starting at $T = 2J$, from a numerical integration of Eqs. (A1)-(A7), for $\Delta = 40J$. Solid curves, top to bottom: $\tau = 10^{11}$, 10^{12}, and 10^{13}. Dashed curve: equilibrium value.

the Appendix. Figure 1 shows the energy density during cooling for three values of τ at $\Delta = 10J$. For the smaller values of τ, the system departs from equilibrium early in the cooling but freezes only gradually, the final value of the energy density being much smaller than that at the point where the system departs from equilibrium. For larger values of τ, the freezing is also very gradual (as a function of temperature), but the system stays close to equilibrium for the first part of the cooling schedule; the data for these values of τ therefore should not contain a memory of the initial equilibrium state.

Figure 2 shows the frozen values of the energy density, magnetization, and one- and two-cluster densities, as a function of cooling time τ, on a log-log scale, for

$\Delta = 10J$. The curves for the first three quantities all approach the theoretical limit of a straight line of gradient -0.8 (dashed lines) as τ diverges, in accordance with (15). However, there is a wide regime of intermediate values where the curves have a gradient higher than this value, due to the contributions from larger clusters. The asymptotic gradient of the data for n_2 is $1.2 = \frac{12J}{\Delta}$, showing that the two-cluster density behaves as an *independent* ensemble of two-level systems of energy $12J$.

Figure 3 is a plot of the energy density as a function of temperature for slow cooling with $\Delta = 40J$. Here, the system freezes very abruptly, in contrast to the case
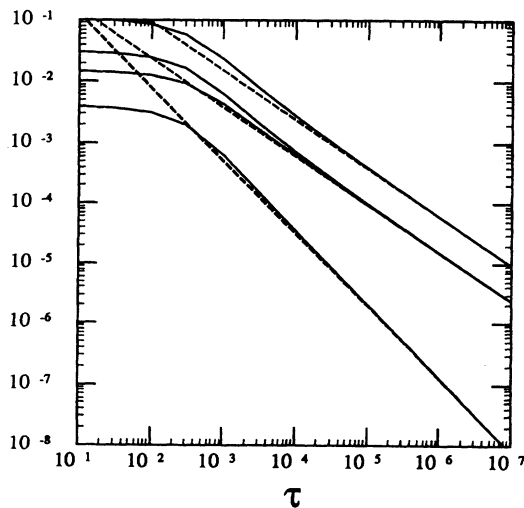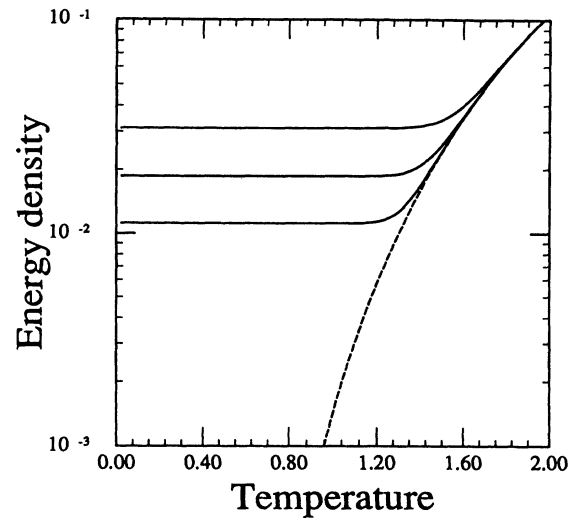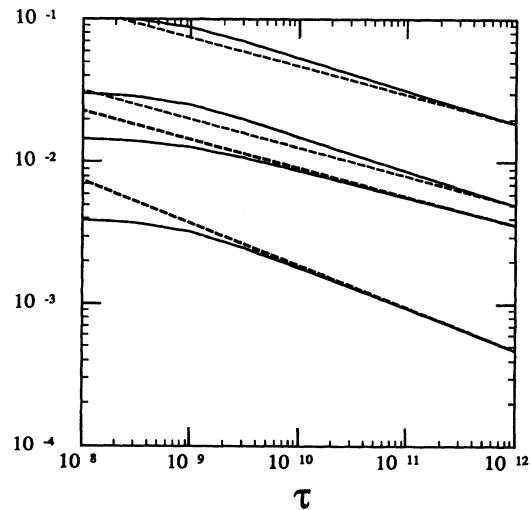

FIG. 2. Solid curves, from top to bottom: frozen values of the energy density, magnetization, and one- and two-cluster densities, respectively, as a function of τ, obtained from numerical integration of Eqs. (A1)-(A7), with $\Delta = 10J$. Dashed curves: asymptotic fits to the exponents described in the text.

FIG. 4. Solid curves, from top to bottom: frozen values of the energy density, magnetization, and one- and two-cluster densities, respectively, as a function of τ, obtained from numerical integration of Eqs. (A1)-(A7), with $\Delta = 40J$. Dashed curves: asymptotic fits to the exponents described in the text.

$\Delta = 10J$, with the system initially remaining close to equilibrium even for smaller values of τ. The frozen state therefore shows little memory of the initial state. Figure 4 shows the energy, magnetization, and one- and two-cluster densities in the frozen state as a function of τ on a log-log scale. Again, there is a wide regime (more pronounced in this case due to the freezing taking place at higher temperature) where the gradient is steeper than the theoretical one-cluster value, due to contributions from larger clusters.

B. Simulation

The above type of cooling is amenable to Monte Carlo simulation. Since the important configurations at low temperatures consist of small clusters, finite-size effects are unimportant. For this reason, only one lattice size was studied (128×128), and periodic boundary conditions were used.

The lattice was separated into two interlocking sublattices so that interacting nearest-neighbor spins reside on different sublattices. Then one sublattice was chosen at random, and all of the spins in the sublattice were tested in parallel using the vector processor on the Stardent 3000 machine. One such sweep corresponds to one half Monte Carlo step per spin.

The probability per attempt for a spin flip changing energy by δ is

$$p(\delta) = \begin{cases} a & \text{for } \delta < 0 \\ \frac{a}{2} & \text{for } \delta = 0 \\ a \exp(-\beta\delta) & \text{for } \delta > 0, \end{cases} \tag{16}$$

which resembles the Glauber choice for flip rates as $\beta \to \infty$. Even for $\beta \sim 1$, the small differences between the above choice and Glauber's choice are insignificant. The parameter a was chosen to be ~ 0.1 initially, and during the cooling it was reduced (since it is proportional to the Arrhenius parameter ω). This ensures that the Markov chain produced by the dynamics has the same properties as that produced by true Glauber dynamics (i.e., it ensures that the effects of using discrete time are insignificant). In particular, it reduces the problem of correlated domain-wall motion that can affect the results of such a vectorized algorithm.

Equilibrium configurations were created by allowing the system to relax for a large number of sweeps ($\sim 10^5$) at a temperature of $0.88T_c$, starting with all spins up. A typical configuration is shown in Fig. 5. Even though this temperature is quite close to the critical temperature, the configuration consists of domains of small size. Thermal equilibrium was ensured by monitoring the temporal evolution of the magnetization and the energy density during the relaxation. Since preparation of 10 such configurations took some 20 h of CPU time, the same set of initial configurations was used for each cooling program, rather than generating a new set of configurations each time. This would, in principle, lead to correlations between the data for different cooling conditions, but the averaging involved is still adequate for our purposes.
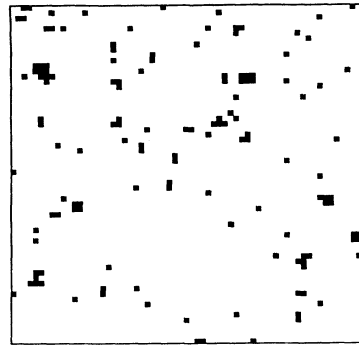

FIG. 5. Typical spin configuration at $T = 0.88T_c$ ($= 2$), showing the predominance of small clusters. A single black square represents a down spin. Shown is an area of 64×64 spins from the full lattice of 128×128 spins used.

A quench was simulated by reducing the temperature in steps so that at each step the Boltzmann factor $\exp(-2\beta J)$ changed by a constant factor ϵ (≈ 0.95–0.98), the parameter a in (16) changed by $\epsilon^{\frac{4}{7}}$, and n_{sw} sweeps were carried out. The characteristic cooling time is then

$$\tau = \frac{\gamma n_{sw}}{8 \ln \epsilon}, \tag{17}$$

which took values in the range 20–50 000.

The results for each cooling schedule were averaged over the 10 independent initial conditions, each with a different seed for the random number generator. Error bars were estimated from the statistical variation over the independent runs.

The structure was characterized by the energy density (taking the ground state as zero energy), which is proportional to the number of broken bonds, or, equivalently, the total length of domain walls. The energy density is zero in equilibrium at zero temperature, and so freezing is characterized by a nonzero-energy density at the end of the cooling program. Other possible "order parameters" exist: the magnetization per site is well defined for this system, since the cooling begins in the symmetry-broken state. The full spatial dependence of the spin-spin correlation function, which is very important in studies of domain growth, is not a very interesting quantity to study in this case, since the long-distance behavior is dominated by the nonzero magnetization.

Simulations were run of cooling with various values of the cooling time τ, for a range of values of the barrier Δ. The results are summarized below.

1. For $\Delta < 8J$

For a small value of the energy barrier, the system needed to be cooled sufficiently rapidly for the freezing to be significant (i.e., for the error bars on the frozen energy density to be smaller than the density itself). But then the system departed from equilibrium early in the cooling process, so the final state contained a high density of relatively large (i.e., more than one spin) domains, and a strong memory of the initial temperature condition.

The reason for the system's readiness to depart from

equilibrium early in the cooling but to return close to equilibrium later on is that the effective time required for a domain to disappear is proportional to its area.[12] Since larger domains predominate at higher temperatures, this means that the effective time for equilibration actually decreases as zero temperature is approached. From (5), using (9) and (12), a typical Boltzmann factor at effective time u during the cooling is given by

$$\exp(-8\beta J) \propto \left(1 - \frac{u}{\omega(0)\tau}\right)^{\gamma} . \tag{18}$$

For $\gamma > 1$, which is the case here, the system spends more effective time at lower temperatures than higher temperatures. Thus, if the system spends enough time at higher temperatures for the characteristic domain size to be close to equilibrium, the system spends a very long effective time at lower temperatures, and so the structure is capable of relaxing near to equilibrium.

Since the final structure is so clearly dependent upon the initial state, no attempt was made to fit the data to the power law obtained in Eq. (15), which was derived under the assumption that the system departs slowly from equilibrium, and that only clusters of size one contribute. Much higher run statistics would be necessary to obtain accurate values for the frozen energy density when the system departs slowly from equilibrium.

2. For $\Delta > 8J$

When the exponent $\gamma < 1$, it is clear from Eq. (18) that the system spends more time at higher temperature than at low temperature. The system would then be expected to be capable of having more significant (measurable) freezing than for smaller values of the energy barrier, even for cooling that is sufficiently slow that the system only departs slowly from equilibrium. This is indeed what was
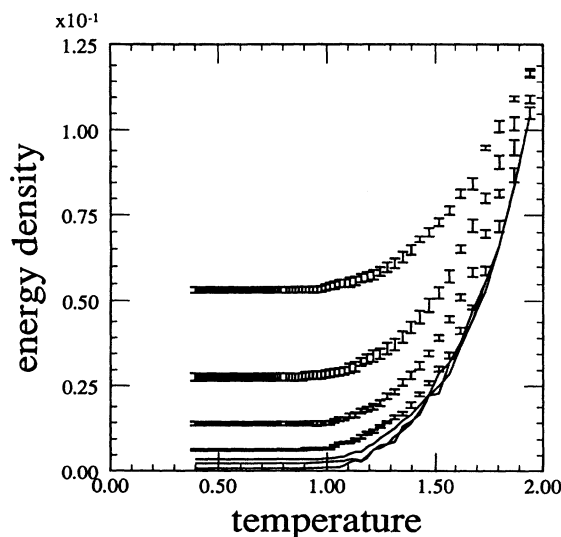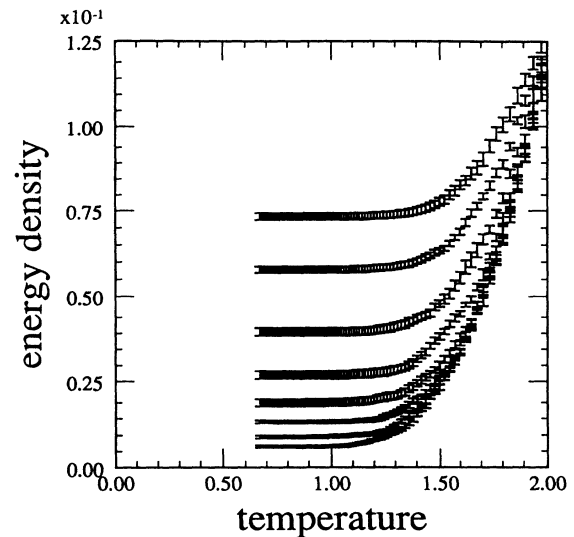

FIG. 7. Energy density during cooling as a function of temperature for a number of cooling schedules starting at $T = 2J$, with $\Delta = 20J$, from Monte Carlo simulations.

observed: slow cooling gave rise to freezing at very low temperatures, where the contributions were mostly from very small clusters, with small error bars.

The energy density is plotted as a function of temperature in Figs. 6 and 7, for $\Delta = 10$ and $\Delta = 20$, respectively, for a variety of values of τ. The frozen energy density and magnetization are plotted as a function of τ on log-log scales in Figs. 8 and 9. These curves support the conclusion that the scaling of cluster densities is a power law, but, while there is some evidence in the energy density of Fig. 8 of an approach to the theoretically predicted line of gradient $(-\gamma)$ for large values of τ, the results in Fig. 9 appear to have an effective exponent higher than the predicted value. This is qualitatively in agreement with the results of the numerical integration

FIG. 6. Energy density during cooling as a function of temperature for a number of cooling schedules starting at $T = 2J$, with $\Delta = 10J$, from Monte Carlo simulations. The error bars have been omitted for the lower curves for clarity.
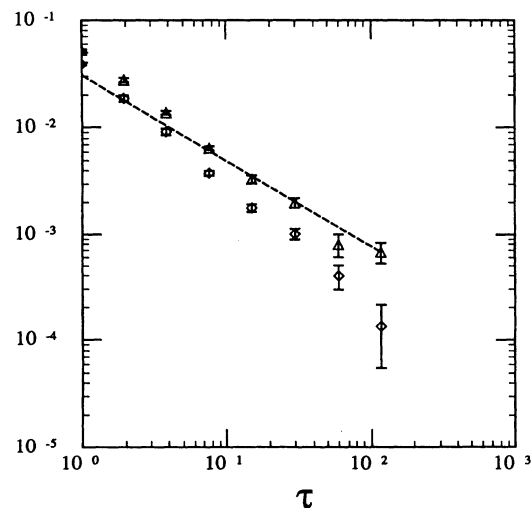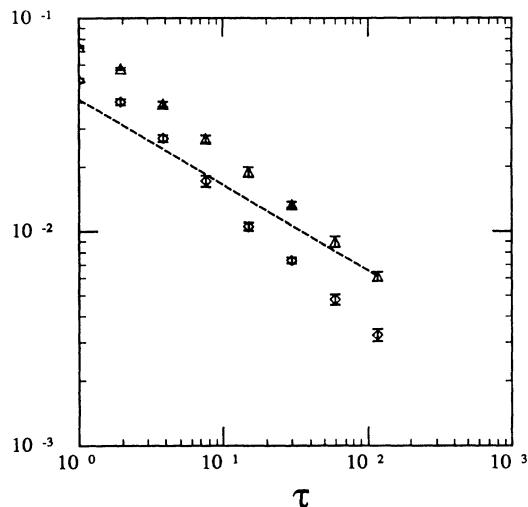

FIG. 8. Log-log plot of frozen values of the energy density (triangles) and magnetization (diamonds) for the cooling schedules shown in Fig. 6, as a function of τ. The dashed curve has gradient 0.8, equal to the theoretical one-cluster value.

FIG. 9. Log-log plot of frozen values of the energy density (triangles) and magnetization (diamonds) for the cooling schedules shown in Fig. 7, as a function of τ. The dashed curve has gradient 0.4, equal to the theoretical one-cluster value.

of the cluster equations of motion in the last section, i.e., the asymptotic region for larger values of Δ was found to occur at much larger values of τ. For intermediate values of τ, the gradient is steeper, again implying important contributions from clusters of size greater than 1. The effect appears more pronounced than for the numerical solution of Eqs. (6), presumably because of the truncation used in the Appendix. For small values of τ, the system departs from equilibrium early on in the cooling schedule, so the curves tail off, showing dependence upon the initial state. Figure 10 shows a typical configuration for the slowest cooling schedule with $\Delta = 20J$, showing the predominance of single-spin clusters.

The simulations appear to confirm at least qualitatively the predictions of the cluster dynamics arguments, in the limit of very slow cooling. The limit in which the power law (15) is valid is only just accessible by simulation. To reach further into the large τ regime requires not
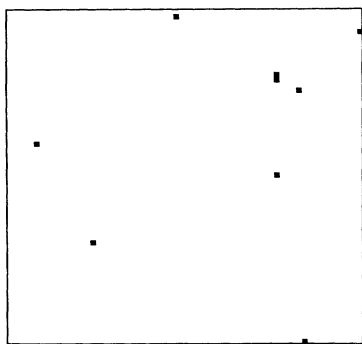

FIG. 10. Typical frozen state for the slowest cooling schedule in Fig. 7, showing the predominance of single spin clusters. A single black square represents a down spin. Shown is an area of 64×64 spins from the full lattice of 128×128 spins used.

only a longer time for each run, but also more independent runs need to be averaged over in order to achieve a comparable relative error. Since the number of runs needed is proportional to the square of the error required, it is clear that the CPU time required for such investigations diverges dramatically. Running 10 independent quenches at the slowest cooling used above required more than 50 h of CPU time on the Stardent 3000 machine (roughly $\frac{1}{3}$ as powerful as a Cray XMP supercomputer).

IV. SLOW COOLING FROM ABOVE THE CRITICAL TEMPERATURE

We now turn our attention to the case of cooling beginning above the critical temperature. This is the case that is of most interest to us as a model for the glass transition. We first discuss the problem from the point of view of interface dynamical arguments and then compare these with simulations.

A. Interface dynamical arguments

The case of an instantaneous quench to the two-phase region has been extensively studied; the system approaches the symmetry-broken state by separation of the two phases. Even though the order parameter is not conserved, the system still requires an infinite time to relax to equilibrium because, while the system is capable of breaking symmetry locally, in order to reach the final state one particular phase has to be established over an infinite length scale.

During the phase separation, the correlation function displays dynamic scaling, even though the system is far from equilibrium.[7] In the asymptotically long-time regime, the structure function $g(k,t)$ is found to be of the form[18]

$$g(k,t) = L^d f(kL) ,\tag{19}$$

where the functional form of f is independent of time, and the characteristic domain size L scales with time as

$$L \propto t^\alpha , \qquad \alpha = \tfrac{1}{2} .\tag{20}$$

The value of the exponent α has been confirmed by Monte Carlo simulation,[19] and is explained by Allen and Cahn[20] in terms of the motion of the phase boundary in a continuum fluid model. The force upon the phase boundary is determined by its curvature. In the language of the lattice Ising system, this is because a highly "curved" domain wall is less smooth, implying that there are more possible sites where a spin may flip without requiring extra energy. The number of possible processes per unit time per unit length is therefore greater for a wall of higher curvature. According to Allen and Cahn, the force upon the interface is inversely proportional to the radius of curvature. The equation of motion for the average domain size is then

$$\frac{dL}{dt} \approx \frac{A(T)}{L} ,\tag{21}$$

where $A(T)$ is a temperatu e-dependent prefactor, which

departs from the prediction of Allen and Cahn close to the critical temperature in the two-dimensional Glauber system.[12] Integrating (21) at constant temperature reproduces (20).

Although the system takes an infinite time to relax to equilibrium, the state that ensues has nontrivial temporal dependence and so would not be describable as being frozen. However, our model possesses an energy barrier, so we expect it to freeze if it is cooled towards absolute zero in a way [e.g., (9)] that does not cause the effective time u to diverge.

If the two-dimensional Glauber system with an energy barrier is cooled from equilibrium at some temperature still above the critical point, it will fall out of equilibrium when it is at some temperature above the critical point, by virtue of critical slowing down. When the temperature of the heat bath is lower than the critical temperature, the system will attempt to break symmetry locally, and the domains in the system will begin to coarsen. However, the temperature-dependent prefactor A in Eq. (21) is now a function of time. Also, there is now an additional Arrhenius factor ω due to the energy barrier, which decreases rapidly as temperature is reduced. Although the average domain size does not therefore scale simply with the square root of time, in the long-time and long-length limits Eq. (21) is still instantaneously valid. The final domain size is obtainable from (21) (generalized with the Arrhenius factor ω accompanying A),

$$L^2(\infty) = \int_0^\infty \omega A \, dt \ . \tag{22}$$

The long-time behavior of the integrand on the right-hand side of (22) is dominated by the Arrhenius factor ω, so the final structure is indeed again found to be frozen if $u(\infty)$ is finite.

If we choose a particular class of cooling program, where ω depends upon time as

$$\omega = h_1\left(\frac{t}{\tau}\right) \ , \tag{23}$$

and such that $u(\infty)$ is finite, then the temperature, and hence A, is also a function of the ratio (t/τ) only. Then Eq. (22) may be written in the form

$$L^2(\infty) = \int_0^\infty h_2\left(\frac{t}{\tau}\right) dt \tag{24}$$

$$= \tau \int_0^\infty h_2(x) \, dx \ , \tag{25}$$

where $h_2(x)$ is some function of x, whose behavior is unimportant except for the fact that the integral in (25) is convergent. We therefore predict that for any cooling program of the form (23) giving rise to freezing [$u(\infty)$ finite], the frozen domain size scales with cooling time as

$$L \propto \tau^{\frac{1}{2}} \ , \tag{26}$$

in the limit of large τ. This exponent is independent both of the class of cooling, and also of the energy barrier, in contrast to the results obtained for freezing in the absence of a phase transition.

It is plausible also that the full correlation function assumes a scaling form such as (19), since any domain of length L grows deterministically according to the generalization of Eq. (21).

The final state is clearly metastable, in the strict sense of Binder and Müller-Krumbhaar,[21] since its evolution in time is slower than characteristic equilibration time scales. For the frozen state to evolve, the cooling needs to be stopped at some very low temperature, just as in the one-dimensional case studied elsewhere.[27] When this happens, the evolution simply follows domain coarsening, with exponent $\frac{1}{2}$, just as in an instantaneous quench to low temperatures, and no Kohlrausch form is observed.

The result may also be extended to other systems. There are many other cases in which the correlation function assumes a form such as (19) after an instantaneous quench from a one-phase to a two-phase region. For example, the conserved-order-parameter kinetic Ising ("Kawasaki") system displays scaling with exponent[22] 1/3, some dynamic polymer systems are seen to scale with exponent[23] 1/2, though this is complicated by the importance of more than one length scale, and amorphous membranes have been observed to grow with exponent[24] 3/4. The behavior observed in the Kawasaki system has been explained by Huse,[25] after Lifshitz and Slyozov,[26] by deriving an approximate equation of motion for the characteristic domain size of the form

$$\frac{dL}{dt} = \frac{B(T)}{L^2} + (\text{corrections}) \ . \tag{27}$$

It is consistent to postulate that, in all cases where domain growth scaling governed by exponent α is observed, an approximate equation of motion for the domain size of the form

$$\frac{dL}{dt} = \frac{C(T)}{L^{\frac{1}{\alpha}-1}} \tag{28}$$

is valid. We then predict that, if such a system possesses an energy barrier that inhibits dynamics at low temperatures, and a slow cooling schedule of the form (23) is chosen, with a nondiverging effective time, the frozen domain size varies with τ as

$$L \propto \tau^\alpha \ . \tag{29}$$

B. Simulation

Continuous quenches starting from equilibrium at $T = 3J$ were simulated in a lattice 512×512 spins, using periodic boundary conditions. An equilibrium state was prepared at $T = 3$ by letting the system evolve for 100 Monte Carlo steps (MCS) per spin, which was found to be sufficiently long for the correlation function to reach its equilibrium value at this temperature. Then, as the system evolved, the temperature (and hence the spin-flip probabilities) was altered according to a cooling program of form (9), in such a way that each Monte Carlo lattice sweep corresponded to one unit of effective time, until the temperature changes per sweep became larger than

a threshold value δT (taken to be $\delta T = 0.03$). From this point onwards, the spin-flip probabilities were normalized in such a way that the increment in effective time corresponded to a change in temperature of δT. One hundred independent runs (with independent initial conditions) were carried out for each value of Δ and τ considered. Since the important structures in which we are interested are large domains, the use of the sublattice simulation routine does not introduce significant undesirable correlations in the motion of domain walls, in contrast to the case of small clusters considered in Sec. III B.

The energy density as a function of the temperature during the cooling is shown in Figs. 11 and 12 for four values of τ at $\Delta = 10$ and $\Delta = 20$, respectively. As before, the freezing occurs more abruptly for larger values of the energy barrier.

The circularly averaged correlation function $C_{CA}(x)$ in the frozen state was obtained from the two-spin correlation function $C(\mathbf{r}) \equiv N^{-1} \sum_{\mathbf{x}} \langle \sigma(\mathbf{x})\sigma(\mathbf{x}+\mathbf{r}) \rangle$ by splitting C_{CA} into bins at position x_i, the value of C_{CA} in the ith bin being the average of C over all $\mathbf{r}$ values satisfying $i - 0.5 < |\mathbf{r}| < i + 0.5$ and the value of x_i being the average of all $|\mathbf{r}|$ values in the ith bin. This frozen correlation function is plotted as a function of $\tau^{\frac{1}{2}}$ in Figs. 13 and 14 for the various quenches simulated at the two values of Δ, respectively. While there is some evidence of scaling for lower values of $x/\tau^{\frac{1}{2}}$ (the deviations at lower values of τ being assignable to discrete lattice effects in the definition of the circular average), at higher values of $(x/\tau^{\frac{1}{2}})$ the correlation function may not be described by any single scaling variable.

Since the correlation function does not assume a scaling form for the values τ used in the simulations, there is no unique way of defining the frozen domain size. In Figs. 15 and 16 we plot $l_{CA} \equiv \sum_i C_{CA}(x_i)$ and e^{-1} (where $e = [1 - S(1)]$ is the energy density) as a function of $\ln \tau$,
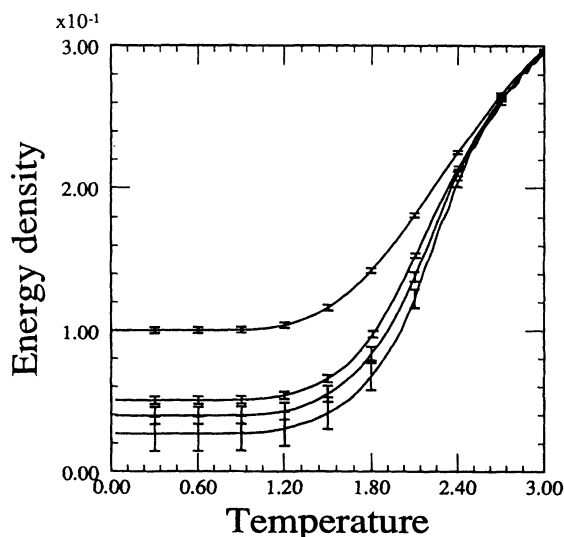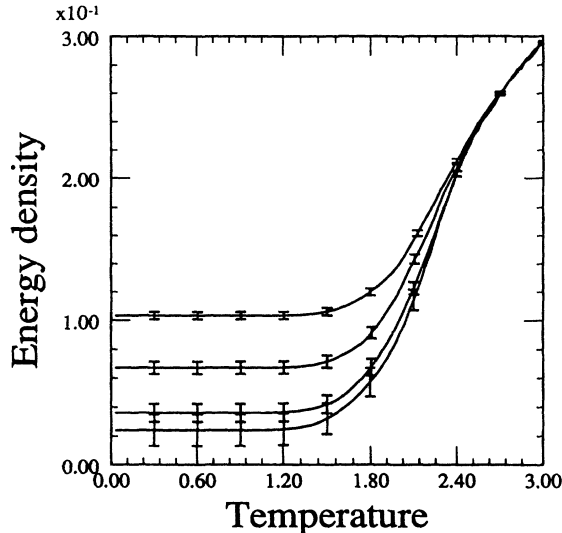

FIG. 12. Energy density during cooling as a function of temperature during simulations of slow cooling programs beginning at $T = 3J$, with $\Delta = 20$. Top to bottom: $\tau = 10^5$, 3×10^5, 10^6, and 3×10^6.

which would both be proportional to the domain size L if S were a function of x/L only. For $\Delta = 10J$, the gradients in Fig. 15 lead to values $\alpha_{CA} = 0.482 \pm 0.001$ and $\alpha_e = 0.531 \pm 0.04$ for the effective growth exponents defined by $l_{CA} \sim \tau^{\alpha_{CA}}$ and $e \sim \tau^{-\alpha_e}$. From Fig. 16, the values of these exponents for $\Delta = 20J$ are $\alpha_{CA} = 0.444 \pm 0.001$ and $\alpha_e = 0.418 \pm 0.05$. Also plotted in the same figures is the square of the magnetization, $< m^2 >$, which should be proportional to the domain length squared if (19) holds; the large fluctuations of this quantity derive from important contributions from corre-
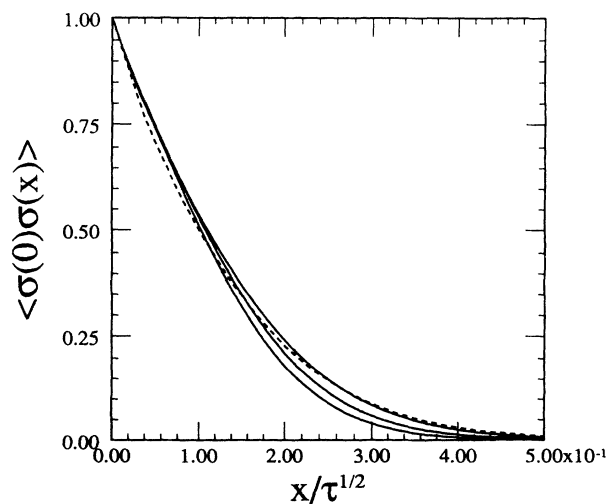

FIG. 13. Frozen correlation function after the quenches illustrated in Fig. 11, plotted as a function of $x/t^{\frac{1}{2}}$. Dotted curve: $\tau = 10^3$. Solid curves (top to bottom): $\tau = 3 \times 10^3$, 10^4, and 3×10^4. Statistical errors for each point are of the order of the width of the lines in the figure, but the error bars have been omitted for clarity.
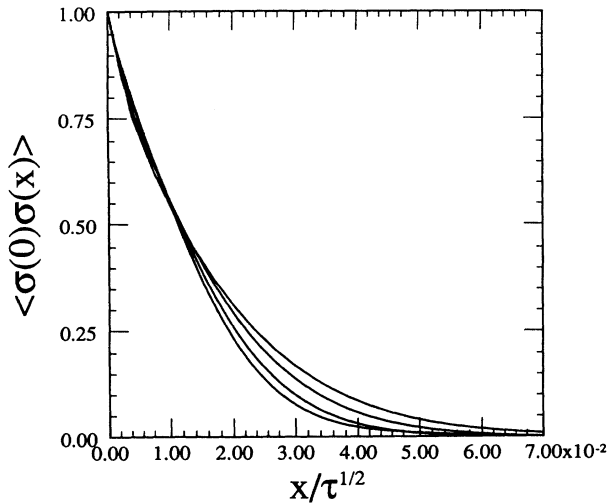

FIG. 11. Energy density during cooling as a function of temperature during simulations of slow cooling programs beginning at $T = 3J$, with $\Delta = 10$. Top to bottom: $\tau = 10^3$, 3×10^3, 10^4, and 3×10^4.

FIG. 14.   Frozen correlation function after the quenches illustrated in Fig. 12, plotted as a function of $x/t^{\frac{1}{2}}$, for (top to bottom) $\tau = 10^5$, 3×10^5, 10^6, and 3×10^6, respectively. Statistical errors for each point are of the order of the width of the lines in the figure, but error bars have been omitted for clarity.

lations at long range, which have been suppressed in the definition of C_{CA}. Least-squares fits yield $< m^2 > \sim \tau_\tau^\alpha$, where α_τ takes the values 0.76 ± 0.02 and 0.98 ± 0.12 for $\Delta = 10J$ and $\Delta = 20J$, respectively.

C. Discussion

Apart from the possibility of finite-size effects, which might affect some of the data at the largest value of τ, the lack of a scaling collapse at large distances might be due to two reasons.

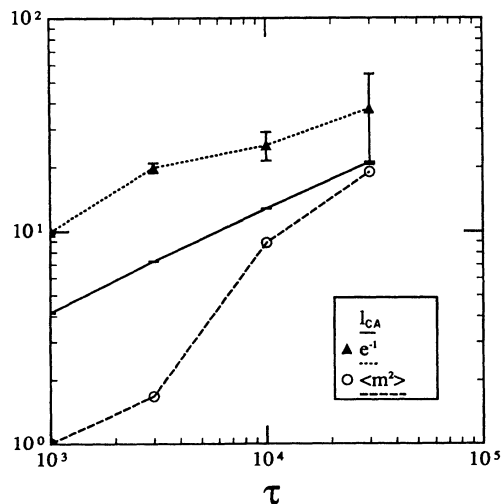(i) The value of τ in the simulations is not large enough

FIG. 15.   Log-log plot of the three measurements of domain size as a function of τ, for the cooling programs illustrated in Fig. 11. The curve for $< m^2 >$ has been shifted vertically.
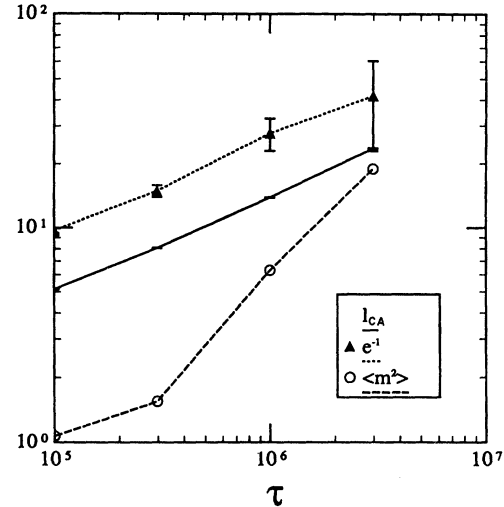

FIG. 16.   Log-log plot of the three measurements of domain size as a function of τ, for the cooling programs illustrated in Fig. 12. The curve for $< m^2 >$ has been shifted vertically.

for the domain coarsening to be described by the Allen and Cahn theory.

(ii) The state when the system leaves equilibrium may contain strong spatial correlations.

As the system is cooled from above the critical point, it departs from equilibrium when the relaxation time is comparable to the cooling time. Just as in the one-dimensional case,[1-3,27] the correlations on long-length scales will fall out of equilibrium before correlations on short-length scales. If τ is increased, the system will have more time below T_c for these correlations to decay, but the system will also depart from equilibrium at a later stage, and therefore its correlations will be of longer range. These correlations will take longer to become unimportant, and it is not at all obvious that merely increasing τ will eventually make it possible for the system to be described by the Allen and Cahn theory (21).

It has been shown[28] that long-range (algebraically decaying) correlations can affect the universality class for the spin-spin autocorrelation function and can also change the form of the scaling function for the one-time spin-spin correlation function. For a system that departs from equilibrium near the critical point, the correlation length will be very long, and so there will be a very wide spatial range within which the dominant decay of correlations will be algebraic. We therefore expect that there will be a regime of intermediate values of τ where the frozen structure shows evidence of effectively algebraic initial correlations. For still smaller values of τ, the value of the correlation length at the point where the system departs from equilibrium may be important.

The correlations at range r will fall out of equilibrium near a point satisfying $r \sim \tau^{\frac{1}{z}}$, where z is the dynamic critical exponent. Thus, the correlation function takes substantially its equilibrium value until a temperature is reached where $\xi \sim \tau^{-\frac{1}{z}}$ (where ξ is the correlation length). These correlations will subsequently take a time

$$t \sim \xi^{\alpha} \propto \tau^{\frac{\alpha}{z}} \qquad (30)$$

to become unimportant. We might expect the value of α to be of the order of 2, since the decay of correlations is controlled by domain wall diffusion. Since[29] $z \approx 2.08$ the significance of the initial correlations is very sensitive to the precise value of α.

The result (26) made no assumption about the functional form of h_1 in Eq. (23). We might therefore expect that it would be possible to choose a given form for h_1 such that, for some large value of $\tau = \tau_1$, the system spends long enough below T_c for the initial correlations to be unimportant. The law (26) would then be expected to hold in the vicinity of τ_1, but it is still not clear whether the law would be valid for $\tau \rightarrow \infty$. In particular, we could choose a very small value for Δ. In the limit $\Delta \rightarrow 0$, the system spends almost all of its effective time near $T = 0$, and so for a very wide range of values of τ the cooling program would be equivalent to an instantaneous quench from $T = 3$ to zero. However, the regime that interests us in this paper is that where the system remains close to equilibrium at the beginning of the cooling program, which would only be achievable for very large values of τ; under these conditions, the system will spend such a long time beneath the critical temperature that any simulation data for these values of Δ, τ would suffer greatly from finite-size effects.

V. CONCLUSION

We have studied a two-dimensional Glauber system with an energy barrier under continuous cooling approaching absolute zero. The condition for freezing to occur is that the effective time associated with the Arrhenius factor does not diverge as time $t \rightarrow \infty$. The behavior depends critically upon whether the initial temperature is above or below the critical point.

For cooling that begins in the symmetry-broken state below the critical point, the system freezes into small clusters of spins antiparallel to the direction of magnetization. In the case of asymptotically slow cooling, in the region where the system departs from equilibrium it behaves as an ensemble of two-level systems consisting of single spins. The freezing exponent governing the dependence of the frozen energy density upon cooling rate is found to be nonuniversal with respect to lattice type (hexagonal, square, etc.) and depends upon the ratio of the nearest-neighbor coupling strength to the ad hoc energy barrier. It would be useful to solve the equations of motion for the cluster densities numerically, to see if the relationship between frozen structure and cooling time observed in the simulations may be reproduced for the regions where larger clusters are important.

The relaxation time for such frozen structures is of the same order of magnitude as the equilibration time for the system, although the fact that there may be more large clusters present means that it will be larger (relaxation time for a given cluster is proportional to its area). The response to a magnetic field will be dominated by the presence of single-spin clusters, and so the response function will be simply exponential. The frozen structure

does not, therefore, have many of the characteristics of a glassy state. As in the frozen Glauber chain,[27] this can be seen as due to the fact that the processes that occur in the frozen state are not qualitatively different from those that occur near equilibrium.

If the system is initially in equilibrium at a temperature above the critical point, then under cooling the system falls out of equilibrium in the vicinity of the critical temperature, and thereafter the structure evolves by standard domain coarsening. We have argued that, in the limit of slow cooling, the correlation function follows a scaling law, with the relation between frozen domain size and cooling time governed by the same exponent that controls domain coarsening at constant temperature. However, in our simulations the scaling form appeared to be valid for small values of the scaling variable only. The regime of validity for the scaling form was wider for smaller values of the energy barrier, which is consistent with the fact that an instantaneous quench corresponds to the limiting case $\Delta \rightarrow 0$. For larger values of Δ, the initial correlations remain significant at large distances, so the Allen-Cahn regime is not approached. We have argued that there should be regimes in which the scaling law is valid, though not necessarily as $\tau \rightarrow \infty$, but simulations of such situations do not appear to be currently feasible, requiring very large systems to avoid finite-size effects. If the exponent is correct, it is universal, being independent of the discrete structure of the lattice, energy barrier, etc.

Although the temporal evolution of such a frozen state is not of a Kohlrausch form, the relaxation time is infinite, and the processes that occur could be described as qualitatively different from the equilibrium state (although there is locally broken symmetry). The dependence of the structure upon the cooling rate enters entirely through the allowed evolution after the system is out of equilibrium, in contrast to the case of real glasses. The response of such a structure to a magnetic field will be broadly dependent upon the domain wall density (just as in the frozen Glauber chain[27]), and so the susceptibility will be much larger in this frozen state than near equilibrium.

To investigate the analogy with glasses more carefully, cooling programs that do not allow significant relaxation below the critical temperature (and therefore are always well away from the Allen-Cahn regime) should be investigated; the relaxational properties of such states will be more complex than the domain scaling postulated in this paper.

The Kohlrausch form of Huse and Fisher is only valid in the long-time regime, near equilibrium, and so we do not see any sign of it here. However, the freezing observed does have some of the properties of glassy states, with a lifetime much longer than equilibration times, and the frozen state is qualitatively distinct from equilibrium.

We have suggested that the exponent governing freezing after cooling through the critical temperature is, in general, of the same universality class as domain coarsening, and this needs to be investigated for the case of other systems, such as the three-dimensional Glauber system, an Ising model under Kawasaki dynamics, dynamical

polymer systems, etc. The last case is particularly interesting, since polymeric liquids such as polyvinylacetate are classic glass-forming substances.

ACKNOWLEDGMENTS

APPENDIX: EQUATIONS OF MOTION OF CLUSTER DENSITIES FOR THE SQUARE LATTICE

Since we are interested in the case where a system is cooled continuously, starting in equilibrium at a temperature beneath the critical temperature, the contribution to macroscopic quantities (e.g., energy, magnetization) from a cluster of energy E is always less than $\exp(-E/kT_F)$, where T_F is the temperature where this cluster falls out of equilibrium. The lowest-order term comes from single spins (henceforth "1-clusters"), with energy $E = 8J$. We can derive the equations of motion up to order $\exp(-16J)$ without needing to include correlations between the clusters, since the only configuration of this order that involves the interaction between two clusters is the case where two 1-clusters are nearest- or next-nearest neighbors. We treat such configurations exactly to this order by defining them as as separate cluster types.

Figure 17 illustrates the possible clusters and processes that occur to order $16J$. From the figure, the equations of motion of the cluster densities are

$$\frac{dn_1}{dt} = [x^2(1 - 21n_1) - 4xn_1 - n_1]$$
$$+ 2n_{101} + 2n_{11} + 2n_2 , \tag{A1}$$

$$\frac{dn_2}{dt} = 4xn_1 - 6xn_2 + 2n_{21} + 2n_3 - 2n_2 , \tag{A2}$$

$$\frac{dn_{11}}{dt} = n_{21} - 2n_{11} + 4x^2 n_1 - 2n_{11} , \tag{A3}$$

$$\frac{dn_{101}}{dt} = n_3 - 3n_{101} + 4x^2 n_1 , \tag{A4}$$

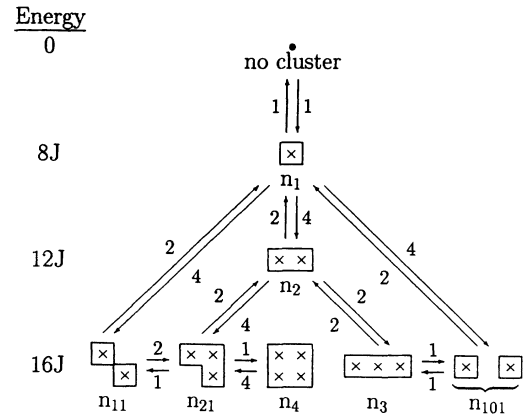$$\frac{dn_3}{dt} = 2n_2 x + n_{101} - 3n_3 , \tag{A5}$$

FIG. 17. Possible processes and definitions of the cluster densities up to order $\exp(-16\beta J)$ for the Glauber Ising model on a square lattice. The crosses ($\times$) represent down spins against a background of up spins. The numbers adjacent to the arrows are the combinatoric factors appropriate to the illustrated processes.

$$\frac{dn_4}{dt} = n_{21} - 4n_4 , \tag{A6}$$

$$\frac{dn_{21}}{dt} = -4n_{21} + 4xn_2 + 4n_4 + 2n_{11} , \tag{A7}$$

where $x \equiv \exp(-4\beta J)$ and the cluster densities are defined in Fig. 17. Trivially, these equations satisfy

$$\frac{d}{dt}(n_1 + n_2 + n_{11} + n_{101} + n_{21} + n_3 + n_4) = x^2(1 - 13n_1) - n_1 \tag{A8}$$

since the only processes that do not conserve the total number of clusters are the birth and death of 1-clusters. The term $-n_1$ on the right-hand side represents the fact that only the death of 1-clusters leads to a reduction in the total number of clusters. The factor (-13) in the term in $(n_1 x^2)$ arises from the fact that, for each 1-cluster, there are 13 sites (i.e., the site, plus its nearest- and next-nearest neighbors) where no new 1-cluster may be nucleated (such processes being taken into account by the inclusion of terms in n_2, n_{101}, n_{11}).

The terms that have not been included are all of order $\exp(-20\beta J)$ or lower, and include interractions between 1-clusters and 2-clusters, etc.

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