Crystallization of a supercooled liquid and of a glass: Ising model approach

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Using Monte Carlo simulations we study crystallization in the three-dimensional Ising model with four-spin interaction. We monitor the morphology of crystals which grow after placing crystallization seeds in a supercooled liquid. Defects in such crystals constitute an intricate and very stable network that separates various domains by tensionless domain walls. We also show that the crystallization which occurs during the continuous heating of the glassy phase takes place at a heating-rate-dependent temperature.

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I. INTRODUCTION

Although of great experimental and technological importance and the subject of intensive experimental, theoretical, and numerical research, crystallization is still far from completely understood [1]. One of the main difficulties that hinders comparison of numerical results with experiments and phenomenological theories is the fact that most realistic, off-lattice models, which can be studied using molecular dynamics simulations, still constitute an enormous computational challenge. Typically, computationally accessible systems contain only up to 10^4 atoms and can be studied during a time interval that is several orders of magnitude shorter than would be required for comparison with experiment. Recently, however, important developments in this field have taken place and some aspects of the numerical simulations have been successfully compared with experiment and theory [2].

A possible alternative for studing crystallization might be to examine lattice models. Although less realistic, such models are usually much easier to simulate and in some cases analytical approaches can also be used. Since crystallization typically occurs during slow cooling of a supercooled liquid, an appropriate model, depending on the thermodynamic parameters and history, should exhibit crystal, liquid, and glassy characteristics. When the cooling is too fast the liquid does not crystallize but collapses into the glassy phase.

At first sight it seems that a natural candidate for such a model might be a standard nearest neighbor interaction Ising model. Crystal and liquid phases can then be easily related to low- and high-temperature phases of this model. However, the relatively fast dynamics of standard Ising models precludes the existence of a glassy phase. In other words, in such models the liquid usually quickly evolves toward the crystal phase when the temperature is below the transition point and does not get trapped in the glassy phase.

Such behavior is typically observed in studies of most Ising-like models but fortunately there are also some exceptions for which the dynamics *can* be very slow, similar to some glassy systems. Models of this kind might be infinite dimensional (mean field), and thus exactly solvable with respect to some quantities [3], or finite dimensional with certain properties typical of glassy dynamics [4].

A promising finite-dimensional model of glassy systems is a three-dimensional Ising model with the four-spin, plaquette, interaction. Recent work has shown that this relatively simple system exhibits a number of properties characteristic of glasses including strong metastability [5] and slow ordering under cooling [6]. In addition, certain time-dependent correlation functions also behave in a way typical of glassy systems [7]. Since this model is homogeneous (i.e., does not contain quenched disorder) it has a crystal phase and under certain conditions it should crystallize. An extremely strong metastability of the supercooled liquid in this model suppresses (within the computationally accessible system size and simulation time) spontaneous nucleation, however, and crystallization was not observed. However, by keeping a certain fraction of spins fixed, one enhances an ordered structure and under slow cooling the system evolves toward the crystal phase [6].

Since the four-spin model has the properties that are required to model crystallization it would be desirable to examine this process under conditions that more closely resemble experimental realizations. Such an examination is an objective of the present paper. In Sec. II we introduce the model and briefly describe its properties. In Sec. III we examine constant-temperature crystallization. To enhance crystallization we use some crystallization seeds rather than fixing a certain fraction of spins dispersed throughout the system. We then monitor configurations of the system to examine the morphology of the growing crystals. We observe that for small supercooling the growth of crystals is surface-tension dominated while for larger supercooling irregular crystals are formed. We also examine the distribution of defects and their stability.

In Sec. IV we examine crystallization of glass under continuous heating. Without crystallization seeds our model never crystallizes and enters the liquid phase at the equilibrium transition temperature. However, when the crystallization is enhanced we observe crystallization that takes place at a heating-rate-dependent temperature. We also estimate the critical heating rate and show that this is probably larger than the corresponding critical cooling rate. A similar asymmetry between cooling and heating processes was recently observed experimentally [8]. Section V contains our conclusions.

II. THE MODEL AND ITS BASIC PROPERTIES

Our model is the three-dimensional (cubic) Ising model with the four-spin (plaquette) interaction, which is described by the Hamiltonian

$$H = -J \sum_{[i,j,k,l]} S_i S_j S_k S_l , \tag{1}$$

where summation is over all elementary plaquettes and $S_i = \pm 1$. In the following we put $J=1$. Recently, model (1) was studied in the context of modeling of conventional glasses [5–7,11]. Morover, this model and its extensions have been used in certain lattice gauge theories [12].

Model (1) has a strongly degenerate ground state. Of course, a ferromagnetic configuration minimizes the Hamiltonian, but one can easily see that any configuration obtained from a ferromagnetic one by flipping an entire plane of spins also belongs to the ground state. Elementary counting shows that the degeneracy of the ground state equals 8^L, where L is the linear system size. Let us note that lamellar structures, for example, made of parallel ferromagnetic layers, also belong to the ground state, and in the next section we discuss the role of such structures in the formation of defects.

Results of various Monte Carlo simulations for this model can be summarized as follows. The model has two equilibrium phases: high- and low-temperature phases referred to as liquid and crystal. A first order transition between them takes place at temperature $T=T_c \sim 3.6$. However, this transition is screened by the very strong metastability of the model upon both cooling and heating. Of particular interest to our study is the metastability of the liquid: in the temperature range $3.4<T<3.6$ the crystal is thermodynamically stable since its free energy is lower than that of the liquid, but nevertheless even very long simulations are not sufficient to transform the liquid into the crystal. Only below $T=T_g \sim 3.4$ does the liquid collapse into the glassy phase. Various characteristics of glassy dynamics have been shown to be present, such as cooling-rate effects [6] and time-dependent correlation functions [7].

An important property of glasses is their slow dynamics. Monte Carlo simulations show that model (1) also has slow low-temperature dynamics [5]. In particular, for $T<T_g$ the excess energy (above the equilibrium value) δE of the random quench decays most likely logarithmically in time, which should be contrasted with the typical nonconservative dynamics decay $\delta E \sim t^{-1/2}$ [14] (t is the time). The slow dynamics of model (1) was conjectured to be due to diverging energy barriers which are generated during the evolution of the quench [5].

It was observed that even upon very slow continuous cooling the liquid always collapses into the glass (and not the crystal) [6]. To transform the liquid into the crystal one has to enhance crystallization. One possibility already used [6] is to fix a certain fraction of spins as, e.g., ''up.'' The fixed spins are randomly distributed throughout the system. Such a procedure strongly favors the ferromagnetic ground state, and it was observed that upon slow cooling the liquid indeed crystallizes. However, such a procedure differs considerably from typical experimental setups used in crystal growth. In particular, the resulting crystal phase is basically homogeneous and does not contain any large scale defects. The objective of the next two sections is to examine the model under conditions that are more representative of real crystal growth experiments.

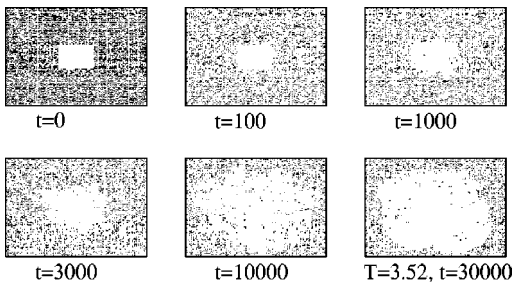

FIG. 1. A planar section showing the distribution of ''unsatisfied'' plaquettes. Simulations were done at temperature $T=3.4$ and for system size $L=140$ with a crystal seed of size $L'=35$. Only for the bottom right plot was the temperature $T=3.52$. Periodic boundary conditions in all directions are used.

III. CONSTANT-TEMPERATURE GROWTH

First we examine the constant-temperature crystallization of a supercooled liquid (i.e., $T_g<T<T_c$). As an initial configuration we take a random configuration of spins and to enhance crystallization we add a centrally placed crystal seed of a cubic cluster of ''up'' spins. This configuration then evolves according to the standard Metropolis algorithm [13]. When the size of the seed is sufficiently large the surrounding liquid will gradually crystallize.

Due to the strong degeneracy of the ground state many varieties of domains are formed during the evolution of the model and visualization of the process constitutes a nontrivial problem. To overcome this difficulty we decided to monitor plaquettes that are ''unsatisfied,'' i.e., for which $S_i S_j S_k S_l = -1$. In this a way we monitor plaquettes contributing to the excess energy $\delta E = E - E_0$, where E_0 is the energy of the ground state.

A typical evolution of our system is shown in Fig. 1. For $t=0$ unsatisfied plaquettes are found only in the surrounding liquid. After a short time ($t=100$) the central seed is basically unchanged but the density of unsatisfied plaquettes is diminished. This is because, due to the relatively fast dynamics of the liquid, the random configuration of the external spins has relaxed to a typical liquid configuration, which apparently contains a smaller concentration of unsatisfied plaquettes than a genuinely random configuration. Further growth leads to a relatively irregular crystal, which is related to the large supercooling, $T=3.4$. For smaller supercooling ($T=3.52$) the resulting crystal (also shown in Fig. 1) is more regular and with sharper boundaries.

In Fig. 1 one can see that the crystal contains a certain fraction of unsatisfied plaquettes. An important question is concerns is the structure of these excitations: are they point like excitations, which are basically thermal fluctuations, or are they large size excitations caused by the complicated

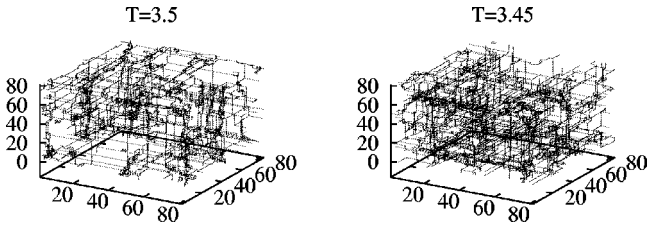

FIG. 2. A distribution of ''unsatisfied'' plaquettes. Simulations were done for a constant temperature and for system size $L=100$ with crystal seed of size $L'=25$. (Only a portion of the system is shown.) Simulation time was larger than the time needed for the crystal to fill the whole lattice.

dynamics of the model? To answer this we looked at the three-dimensional structure of the growing crystal (let us note that Fig. 1 shows only two-dimensional cross sections). Our results, shown in Fig. 2, strongly suggest that the latter possibility holds. Indeed, especially for $T=3.5$, one can see that the unsatisfied plaquettes are not randomly scattered but constitute an intricate network.

At this point we recall that in model (1) tensionless structures can be formed [6,11]. For example, when a cubic cluster of linear size L' of ''down'' spins is surrounded by ''up'' spins then the excess energy of such a configuration scales linearly with L' and not as L'^2 as for the ordinary two-spin Ising model. Such scaling is due to the fact that the unsatisfied plaquettes in this case are only those that are located at the edges of the cubic cluster and not those on its surface as in the standard Ising model. The linear nature of the excitations in Fig. 2 confirms that the resulting crystal is composed of various domains separated by tensionless domain walls.

It is well known that metastability, which is an important property of our model, appears also in other models. For example, let us consider the ferromagnetic two-spin Ising model below its critical temperature in a phase with positive magnetization. Applying a negative magnetic field, the majority phase becomes metastable [9]. When the magnetic field is weak this metastability might be quite strong, and by placing a crystallization seed (i.e., the negatively magnetized cluster of spins) we can observe a gradual but slow growth of the thermodynamically stable phase. Using a similar approach a number of interesting results concerning crystal growth have already been obtained [10] with the ferromagnetic two-spin Ising model. Why then, it is natural to ask, do we study a similar phenomenon in a more complicated four-spin Ising model? In our opinion, there are certain reasons to believe that crystallization as observed in a four-spin model (1) is more realistic. First, like real crystals, our crystals are imperfect. These defects appear because crystallization, which takes place on different faces, leads to formation of different domains. This effect is caused by the strong degeneracy of the ground state in the model (1). In particular, since lamellar structures are also ground state configurations, we find that on one side of the $(+)$ seed we might have an accumulation of $(+)$ spins while the other side of the seed might accumulate $(-)$ spins. Such growth inevitably produces defects, which must appear on the junctions of these different domains. This effect is clearly absent in the two-spin Ising model: due to a doubly degenerate ground state a growing crystal is basically homogeneous.

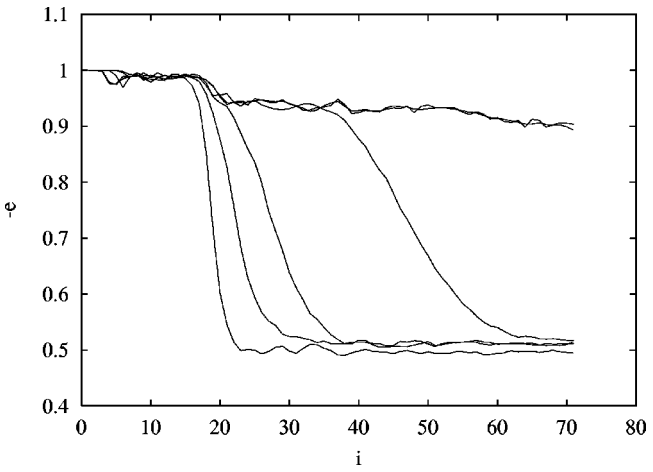

FIG. 3. The inverse energy/plaquette $-e$ as a function of distance of the shell from the center *i*. Initial configuration as in Fig. 1. Simulations were made for $T=3.4$. As the time proceeds one can see a crystallization front moving from left ($t=100$) to right ($t=50\,000$). Note that the two late-stage curves for $t=20\,000$ and $t=50\,000$ are almost indistinguishable, which indicates that the resulting pattern of defects is almost constant in time.

It is also important to note that this network of defects is very stable. We monitored the distribution of energy in cubic shells centered at the center of the crystal seed and the results, averaged over the number of spins in a given shell, for several times t are shown in Fig. 3. One can see the propagation of the crystallization front from the center outward. Once it reaches size of the system ($t\sim 20\,000$) the profile of $-e$ stabilizes at values smaller than unity, which confirms formation of a stable network of unsatisfied plaquettes. Let us note that the late stage profile of $-e$ is also a decreasing function of the distance i from the origin, which indicates that the density of defects in the resulting crystal increases with i.

The stability of this network of defects is most likely due to energy barriers that appear in this model. We have previously conjectured that these are also responsible for the slow kinetics of the model below the glassy transition [5,6].

IV. HEATING OF GLASS

Depending on the speed of the process, the cooling of liquid is an important technique used to produce crystals or glasses. A parallel technique is based on the heating of glass. Recently, this technique has been applied to certain metallic glasses, which are rather bad glass formers [8]. As in the cooling process, there is a critical heating rate that separates the slow and fast heating regimes. Only slow heating of glass leads to crystallization while fast heating transforms a glass directly into a liquid.

We performed a series of simulations to check whether model (1) exhibits similar behavior. To prepare an initial glassy configuration we quenched a random configuration of spins at $T=0$ and let the system relax until the system reached the local minimum-energy configuration. Such a

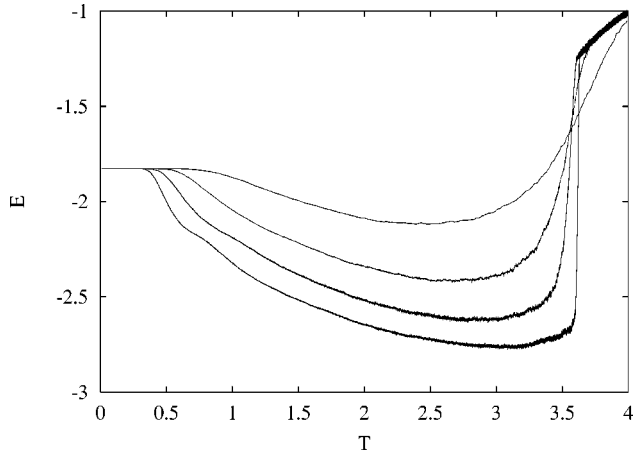

FIG. 4. The energy of the model as a function of temperature during continuous heating ($L=60$) with the heating rate (from top to bottom) 0.01, 0.001, 0.0001, and 0.000 01. Initial configuration is obtained by quenching a random sample at $T=0$ and relaxing the system until the system reaches a stationary state (i.e., a local energy minimum).

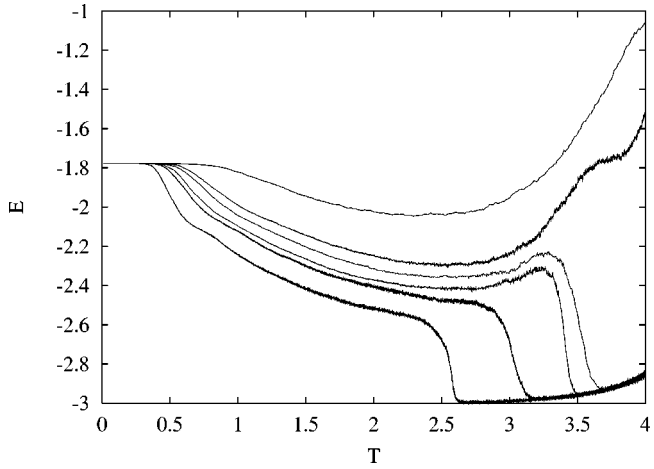

FIG. 5. The energy of the model as a function of temperature during continuous heating ($L=60$) with 5% of spins being fixed (all up) and with the heating rate (from top to bottom) 0.01, 0.001, 0.0005, 0.0002, 0.0001, and 0.000 01. Initial configuration is the same as in Fig. 4. For $r \leqslant 0.0005$ the system crystallizes and its energy in the high-temperature part is the same as during heating of one of the ground state configurations.

configuration was subsequently heated with the temperature changing linearly in time:

$$T(t)=rt, \tag{2}$$

where r is the heating rate. (The unit of time is defined as the time needed on average for a single, update of each spin.)

The results of our simulations are shown in Fig. 4. One can see that within computationally accessible heating rates crystallization of the glass was not observed. These data suggest that for infinitely slow heating the temperature of melting of the glass approaches the equilibrium transition temperature at $T=3.6$.

To enhance crystallization we used the simplest approach of fixing a certain fraction of spins as ''up.'' As shown in Fig. 5 this dramatically changes the behavior and for slow heating the glass crystallizes. The observed temperature of crystallization depends sensitively on the heating rate r.

In our simulations we fixed 5% of spins, which is the same amount as during the cooling [6]. Earlier simulations indicated that for such a fraction of fixed spins the critical cooling rate r_c satisfies the inequality $0.0002<r_c<0.0005$. Results in Fig. 5 suggest that for the critical heating rate r_h we have the bound $0.0005<r_h<0.001$. These estimates suggest that $r_c<r_h$. Let us note that a similar asymmetry of these two processes is also observed experimentally [8].

V. CONCLUSIONS

In the present paper we have shown that the four-spin Ising model can be used to model crystallization. We observed crystal growth from the supercooled liquid at constant temperature and found that crystals of different morphology were obtained depending on how supercooled the liquid was. We also examined the structure of defects in the resulting crystals and showed that they form a very stable network which provides a tensionless separation of different domains of the crystal. We also examined the evolution of the glassy phase of our model under continuous heating.

Crystallization is, of course, a very complex phenomenon which involves diffusion, adsorption at the growth, surface, crystal growth and sometimes also additional processes [15]. Each of these processes is complicated and to develop some understanding one has to introduce some simplifying assumptions. As a result certain aspects of crystallization can be studied using phenomenological models like the Swift-Hohenberg model [16] or the Kolmogorov-Avrami model [17]. In principle, however, all aspects of the crystallization process are determined by the underlying microscopic dynamics of the model. Evolution of our model is driven by the Metropolis dynamics which is a standard dynamics for Ising-type models. In this respect our method is similar to the molecular dynamics simulations and although our model is less realistic than off-lattice models it is computationally much less demanding. We consider the results presented here as rather preliminary but they clearly indicate that more detailed studies of the four-spin Ising model are warranted, which will hopefully clarify other aspects of crystallization.

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