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Glass and polycrystal states in a lattice spin model

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We numerically study a nondisordered lattice spin system with a first order liquid–crystal transition, as a model for supercooled liquids and glasses. Below the melting temperature the system can be kept in the metastable liquid phase, and it displays a dynamic phenomenology analogous to fragile supercooled liquids, with stretched exponential relaxation, power law increase of the relaxation time, and high fragility index. At an effective spinodal temperature T_{sp} the relaxation time exceeds the crystal nucleation time, and the supercooled liquid loses stability. Below T_{sp} liquid properties cannot be extrapolated, in line with Kauzmann's scenario of a lower metastability limit of supercooled liquids as a solution of Kauzmann's paradox. The off-equilibrium dynamics below T_{sp} corresponds to fast nucleation of small, but stable, crystal droplets, followed by extremely slow growth, due to the presence of pinning energy barriers. In the early time region, which is longer the lower the temperature, this crystal-growth phase is indistinguishable from an off-equilibrium glass, both from a structural and a dynamical point of view: crystal growth has not advanced enough to be structurally detectable, and a violation of the fluctuation–dissipation theorem (FDT) typical of structural glasses is observed. On the other hand, for longer times crystallization reaches a threshold beyond which crystal domains are easily identified, and FDT violation becomes compatible with ordinary domain growth. *© 2003 American Institute of Physics.* [DOI: 10.1063/1.1560937]

I. INTRODUCTION

When a liquid is cooled fast enough below its melting point, crystallization is avoided and the system enters the supercooled phase. Relaxation time increases rapidly in this temperature regime, and when it becomes comparable to the largest experimentally accessible time the system falls out of equilibrium, remaining stuck in a disordered phase called *structural glass*.[1]

The configurational disorder of a structural glass is not caused by the presence of intrinsic disorder in the Hamiltonian, since this is just the sum of deterministic interaction elements. This notwithstanding, a lot of attention has been devoted to the phenomenological analogies between structural glasses and mean-field spin-glasses, which are systems directly containing quenched disorder in the Hamiltonian in the form of random couplings among the spins.[2] In particular, models of spin-glasses with p-body interactions and $p \geqslant 3$, seem indeed to have many features in common with structural glasses,[3] with the obvious (but crucial) difference that in mean-field systems there is a purely dynamical transition which is absent in real finite-dimensional glasses. Despite the close phenomenology, however, it is natural to ask why we use models with quenched disorder to understand the behavior of physical systems with deterministic Hamiltonians.

Disorder, one of the characteristics of the glassy state, cannot be expected to arise spontaneously from a deterministic mean-field Hamiltonian, because in this case the mechanically stable configurations are ordered: the local field is the same for all spins, and thus all tend to point in the same direction. Thus if we wish to stick to mean-field and the associated analytical advantages, we must resort to quenched disorder to produce glassy behavior. The argument does not apply to finite range systems, however, and we can ask whether finite dimensional spin systems with no quenched disorder and $p \geqslant 3$ display a glassy phenomenology similar to structural glasses (we of course know that $p=2$, i.e., the Ising model, is not glassy under many respects). This is a relevant question, first because it is important to understand what the key ingredients responsible for glassy dynamics are, and second because lattice spin systems are normally easier to study than off-lattice liquid models.

The answer to this question seems to be affirmative. A number of spin models without quenched disorder now exist that reproduce a phenomenology similar to supercooled liquids and glasses. Generally, one can say that in all these systems the nontrivial dynamic behavior is related to the presence of frustration, due to complex even if nondisordered interaction terms in the Hamiltonian. In the SS model of Ref. 4, this is achieved by mixing nearest- and next-nearest-neighbor interactions, which gives an interesting phenomenology, although not precisely glassy. In the plaquette (PQ) model of Refs. 5, 6, 14, on the other hand, glassiness is achieved by a p-body interaction term with $p=4$, in close analogy with p-spin models of mean-field spin-glasses. In the lattice glass model of Ref. 9 frustration arises from a constraint on the numbers of neighboring particles on the lattice. The PQ model has been heavily studied in recent years, and the results seem to suggest that its phenomenology has at least some points in common with structural

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glasses. In particular, a sufficiently rapid cooling of the PQ model forms an off-equilibrium disordered phase which closely resembles real glasses. Therefore, it would seem that *p*-body interactions in finite dimensional spin models without quenched disorder are sufficient to reproduce a phenomenology similar to supercooled liquids and glasses.

The aim of this paper is to study a model in the same class as those just described, namely the deterministic version of the CTLS model introduced in Ref. 7 (a concise description of some of our results has recently appeared[8]). As discussed below, this model has various advantages with respect to its predecessors and will enable us to check more deeply to what extent lattice spin systems can mimic structural glasses. Moreover, important questions on the low temperature behavior of glasses, such as the stability of the supercooled phase and the role of the crystal, can be addressed, whereas in previous models such an analysis was very limited. Let us now explain why.

Liquids in nature have a crystalline ground state, usually with low degeneracy, and display a first order thermodynamic transition at the melting temperature. In the PQ model in three dimensions a first order transition takes place, but the crystalline ground state has an unusual property for liquids, in that it is strongly degenerate: for linear size L, the PQ model has 2^{3L} different ground states with the same energy. The problem is not the degeneracy in itself (the ground state entropy density is zero), but rather the consequences that this degeneracy has on the possibility to measure the degree of order in the system. More precisely, in the PQ model, given a ground state configuration (for example, the ferromagnetic one), we can obtain another ground state by flipping any plane of spins. Clearly, by iterating this procedure we can produce ground state configurations which look highly disordered. The problem then is how to distinguish a truly disordered, or glassy, configuration, from a configuration made up of many droplets of different ground states. The energy of both configurations will be high, in the first case because it is essentially a liquid, in the second case because of the interfaces among different droplets. In other words, energy is not a sufficiently precise measure of order in the PQ model, and due to the strong ground state degeneracy no configurational means can be devised to quantify order and domain growth.

The system we introduce here does not suffer from this problem: it has a doubly degenerate ground state, such that it is possible to measure the amount of crystalline order and to monitor domain growth. A likely objection is that glassy physics does not have anything to do with the crystal, and that the possibility of measuring the formation and growth of crystal domains is far from essential to study the physics of glasses. We reply to this objection with two observations. First, that simple glass formers usually *do have* a crystalline phase, whose possible connection with the properties of the glass cannot be completely ruled out in principle. In fact, our model explicitly shows such a connection. Second, if on the other hand, spin models with a crystal phase fail somehow to reproduce some basic property of glasses, then we should understand why, and make sure that all spin models are free from this problem. Indeed, the precise nature of what is normally called the glassy phase in systems like PQ[5] and in lattice glass models[9] is the main focus of our work.

Our model shows, in this respect, an interesting phenomenology. As we will show, it has a first order liquid–solid transition at a melting temperature T_m. Crystallization can be avoided by fast cooling, and a supercooled liquid phase, metastable with respect to the crystal, is found. ‘‘Equilibrium’’ measurements can be performed as long as the equilibration time of the supercooled liquid is much shorter than the nucleation time of the crystal. In this phase the behavior of our system is very similar to real supercooled liquids, and in particular to fragile systems. However, a temperature T_{sp} exists, where the crystal nucleation time becomes of the same order as the liquid equilibration time: at this point the supercooled liquid loses stability and it no longer exists below T_{sp}. We call T_{sp} the *effective spinodal* temperature. It is important to stress the following fact: we are able to detect the loss of stability of the liquid only because the equilibration time at T_{sp}, t_{sp}, is shorter than our longest experimental time. We can state this point in a different way. A system falls out of equilibrium when the relaxation time becomes too large for the (real/numerical) experiments, and this is the operational definition of the glass transition temperature T_g. Therefore, the reason why we can observe the loss of stability of the supercooled liquid in our model is that $T_{\mathrm{sp}}>T_g$. The Kauzmann paradox (i.e., the fact that the extrapolated liquid entropy becomes smaller than the crystal entropy at a finite temperature) is avoided by this loss of stability: no equilibrium supercooled liquid exists below T_{sp} and the entropy extrapolation is meaningless. In fact, this is the scenario proposed by Kauzmann himself[10] as solution of the paradox, which is thus exactly reproduced in this system. Below T_{sp} the system enters a completely different phase, where crystal nucleation and crystalline domain growth are the main dynamic processes. However, by quenching to lower temperatures the growth of crystalline order becomes so slow that it is impossible to distinguish this phase from a typical off-equilibrium realistic glass. Moreover, we shall show that dynamical measurements of the fluctuation–dissipation (FD) ratio are compatible with the results obtained in ordinary structural glasses below T_g.

It is our impression that the scenario described above is also shared by the PQ, and possibly other spin models. In particular, that what is normally called the glassy phase for the PQ model is an off-equilibrium regime of very slow crystal growth. However, as already mentioned, without a direct measure of crystalline order it is hard to assess the amount of order in the PQ model, so the question whether there is in fact a glassy phase qualitatively different from the crystal growth phase below T_{sp} is open. This is certainly not the case in the present model, though.

Throughout the paper we will use a notation common to supercooled liquids and glasses. We call T_m the melting temperature. In analogy with mode coupling theory,[11] T_c will be the temperature where a power law fit locates a divergence of the relaxation time, while T_0 will be the temperature where a Vogel–Fulcher–Tamman fit puts the same divergence. The so-called Kauzmann temperature, i.e., the temperature where the extrapolated liquid entropy becomes equal to the crystal entropy, is called T_s. The effective spinodal temperature, i.e., the temperature below which it becomes impossible to observe the metastable liquid is called $T_{\rm sp}$. This temperature is called T_g in Ref. 5, but we reject this choice because, as already mentioned, in the liquid literature the glass transition is defined rather as the point where the equilibration time is longer than the experimental time.

The paper is structured as follows. In Sec. II we introduce our model and describe the properties of the crystalline ground state. In Sec. III we show, by comparing the liquid and crystal free energies, that the model has a first order phase transition at a melting temperature T_m. The dynamics of the supercooled liquid below T_m and the metastability limit $T_{\rm sp}$ are considered in Sec. IV, while aging dynamics and its relation to domain growth are studied in Sec. V. Finally, we draw our conclusions in Sec. VI.

II. THE MODEL

The model is described by the Hamiltonian

$$H=\sum_{i=1}^{N} f_i(1+s_i), \tag{1}$$

where the variables $s_i=\pm 1$ are Ising spins belonging to a two-dimensional square lattice of side L, and the plaquette variable f_i is the product of the four nearest neighbors of spin i:

$$f_i=s_i^W s_i^S s_i^E s_i^N \tag{2}$$

(W is for west, S for south, and so on). The model is studied by Metropolis Monte Carlo simulations with single-spin–flip dynamics for lattices of size $L=100$ and $L=500$.

A disordered version of this model was first introduced in Ref. 7, as a way to model two-level systems in a lattice, interacting with their nearest neighbors, whence its name CTLS (coupled two level systems). In fact, one can take the spin s_i to be the variable describing the state of a two-level system sitting at site i. Then state $s_i=-1$ has always zero energy, while the other state can be at 1 or -1 depending on the factor f_i. Thus when one of the neighbors switches, the relative height of the two states at i is reversed. In Ref. 7, however, quenched random coupling constants were considered. Here we shall see that the multibody nature of the interaction is sufficient to give a nontrivial dynamic and static behavior.

Frustration in the CTLS comes from the fact that it is not possible to satisfy simultaneously the four-spin and the five-spin interaction. After careful inspection of the Hamiltonian it is found that the ground state of the CTLS is obtained by covering the lattice with the following nonoverlapping elements:

$$s_i=-1, \quad s_i^W=s_i^S=s_i^E=s_i^N=+1. \tag{3}$$

As Fig. 1 shows, the covering can be done in two ways, giving rise to two different ground states which we call dextrocrystal and levocrystal. These two crystals are connected by the symmetry $x\to -x$, $y\to y$, or $x\to x$, $y\to -y$, while they are both invariant under $x\to -x$, $y\to -y$. Therefore, the CTLS has a crystalline ground state, with energy density $E_{\rm GS}=-1.6$. In Fig. 1 it can be seen that the crystal can be obtained by periodic repetition of a 5×5 unit cell. Apart from the two distinct dextro and levo forms, additional crystals can be formed by translating the unit cell up to five lattice spacings in each direction. There are then different ways to cover the lattice, which are not locally compatible with each other. Upon a quench, the system will greedily optimize the energy locally in an uncoordinated way, creating many different competing domains with boundaries that turn out to be pinned, thus giving rise to slow dynamics.

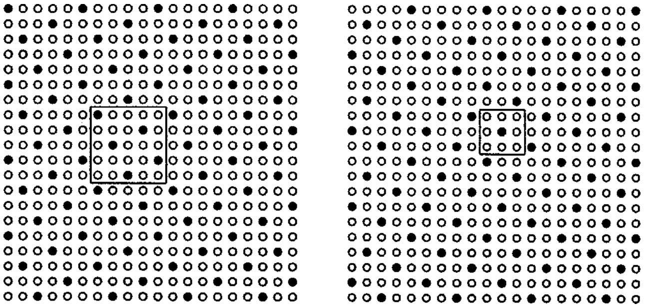

FIG. 1. Dextrocrystal (left) and levocrystal (right): empty circles correspond to positive spins, full circles to negative spins. In the left figure the square marks the five-element unit cell. In the right figure the small square shows the elementary unit used in the definition of the crystal mass (see Sec. III).

III. THERMODYNAMICS

In the present section we will show that the CTLS has a first order phase transition at a melting temperature T_m. We start with the numerical observation of hysteretical behavior typical of first order transitions: we find that, in a range of temperatures, the system stays for very long times [10^6 Monte Carlo steps (MCS) or more for $L=100$] in the phase (liquid or solid) in which it was prepared. In Fig. 2 we plot the equilibrium internal energy as a function of the temperature for the crystal and the liquid phases.

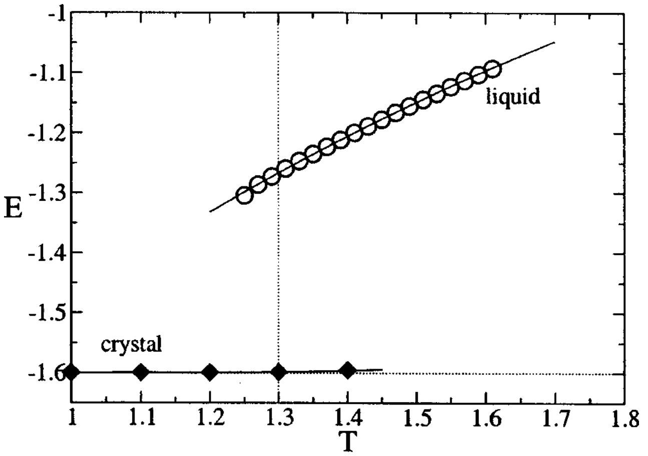

FIG. 2. Liquid and crystal energy per spin as a function of temperature. The continuous lines correspond to the two fits reported in the text. The horizontal dotted line marks the energy of the crystal at zero temperature $E_{\rm GS}=-1.6$. The vertical dotted line marks $T_m=1.30$. $L=100$.

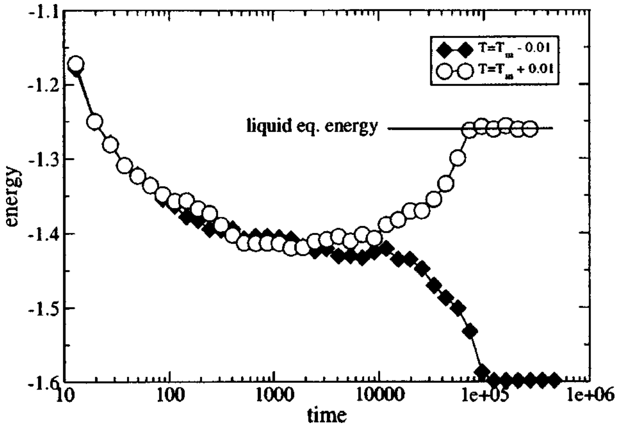

FIG. 3. Energy per spin as a function of time below and above T_m. $L=100$.

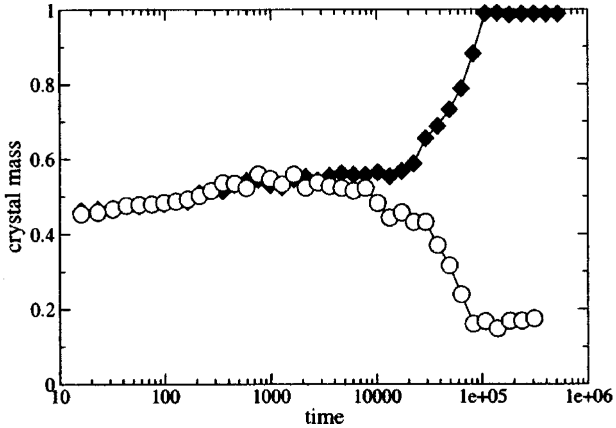

FIG. 4. Crystal mass m as a function of time below and above T_m. Same temperatures and symbols as in Fig. 3.

To find T_m we need to compute the free energy in the two phases by integration of the internal energy. To this aim, we fit the liquid energy (LQ) as

$$E_{\mathrm{LQ}}(T)=-a\tanh(b/T),\quad a=1.84,\quad b=1.10, \tag{4}$$

while for the crystal (CR) we find

$$E_{\mathrm{CR}}(T)=E_{\mathrm{GS}}+cT^n,\quad c=5.5\times10^{-5},\quad n=13. \tag{5}$$

By using the thermodynamic formula,

$$\beta F(\beta)=\beta_0 F(\beta_0)+\int_{\beta_0}^{\beta} d\beta'\, E(\beta'),\quad \beta=1/T, \tag{6}$$

we obtain the free energy of the liquid and crystal phases:

$$F_{\mathrm{LQ}}(T)=-T\log 2-\frac{a}{b}T\log\cosh(b/T), \tag{7}$$

$$F_{\mathrm{CR}}(T)=E_{\mathrm{GS}}-\frac{c}{n-1}T^n, \tag{8}$$

where we have taken $\beta_0=0$ for the liquid, and $\beta_0=\infty$ for the crystal. The melting temperature is fixed by requiring $F_{\mathrm{LQ}}(T_m)=F_{\mathrm{CR}}(T_m)$, which gives

$$T_m=1.30. \tag{9}$$

We have checked that our energy data are independent of system size for $100\leqslant L\leqslant 500$.

In order to check that a first order liquid-crystal transition actually takes place at T_m we proceed as in Ref. 5: we consider an initial condition where half of the system is in the crystal phase and half in a random phase, and we run this configuration at $T_m+0.01$ and at $T_m-0.01$. If our determination of T_m is correct, after a transient time the system should relax either to the liquid or crystalline phase, since the stable phase will expand and take over the whole system after a sufficiently long time. The time evolution of the energy is shown in Fig. 3, confirming our previous determination of T_m.

Even though the energy of a configuration may be considered as an index of the degree of crystallization of the system, it is certainly not a very sensitive one. Given that we know the crystal in this system, and thanks to its low degeneracy, we introduce some methods to directly quantify the amount of crystalline order in our samples. This can be done either by measuring the typical crystal droplet size ξ, or by measuring the total crystal mass m. To measure ξ we observe that both crystals have a periodic structure with a unit cell of size 5. Thus, the Fourier transform of the spatial correlation function,

$$G(r)=\frac{\langle s(0)s(r)\rangle-\langle s\rangle^2}{1-\langle s\rangle^2}, \tag{10}$$

has a peak at $k_0=2\pi/5$. The width λ of this peak is proportional to the inverse of the typical crystalline domain size. We want to extract from λ a measure of how large is the typical crystal domain, a question which is better answered by comparing it to the system size. So we actually define ξ as a density, i.e., $\xi=1/(\lambda L)\in[0:1]$. It is important to note that this definition of ξ has a limited power of resolution: in a random configuration we find on average that $\xi_0=0.05$, which can therefore be considered as the effective zero for ξ. But a complementary measure of crystal order is needed: in a configuration entirely made up of tiny mismatched crystallites ξ would be very small, even though the total amount of crystal is large. The crystalline mass m can be measured by counting the fraction of crystallized spins. To this aim, we have to define an elementary unit, which is large enough to have a small probability to be formed randomly, but small enough to be sensitive to small amounts of crystal. We choose the nine-spin unit shown in Fig. 1(right): in the pure crystal each minus spin is surrounded by eight pluses, and in the unit cell we have five of these elements (which clearly overlap). To count all the spins in the cell we must multiply the number of these units by 5. Thus, we define the crystal mass density $m\in[0:1]$ as the number of these elementary units times 5 normalized by L^2. As for ξ, we have a random average value of the mass, $m_0=0.01$, which is the effective zero of m. Had we chosen the 5×5 unit cell, the accuracy would be higher, but the sensitivity would decrease as well. In order to test the definition of ξ and m, we measure their time evolution in the experiment described above for the determination of T_m. The results are shown in Fig. 4. Note that in the liquid phase at $T=T_m+0.01$ we have $m\sim0.15\gg m_0$ (whereas ξ is compatible with zero), meaning that also in the liquid above T_m there is a certain amount of short range order. Both these quantities are thus excellent configurational indicators of the amount of crystalline order in the system.

We finish this section by noting that if we extrapolate $E_{\mathrm{LQ}}(T)$ and $F_{\mathrm{LQ}}(T)$ to low temperatures, we can find the temperature T_s where the entropy of the supercooled liquid becomes equal to the entropy of the crystal. We find

$$T_s = 0.91. \tag{11}$$

T_s is the temperature where the Kauzmann paradox occurs:[10] below T_s the supercooled liquid entropy would become smaller than that of the crystal. This temperature is usually called Kauzmann temperature in the literature, a denomination we find somewhat unsatisfactory given that Kauzmann himself did not believe the extrapolation was really meaningful.

IV. DYNAMICS

The aim of this section is to study the dynamical behavior of the CTLS in the supercooled liquid phase (i.e., for $T < T_m$) and in particular to analyze how the relaxation time increases when decreasing the temperature. There is a marked difference in the behavior of the system if our observational time window is longer or shorter than a given time $t_{\mathrm{sp}} \sim 10^4$ MCS. For $t < t_{\mathrm{sp}}$ the supercooled liquid is stable at all temperatures where equilibration may be achieved: we can either study the equilibrium supercooled liquid or the off-equilibrium glass, formed by a sufficiently fast cooling. On the other hand, if we are able to observe the dynamics on time scales $t > t_{\mathrm{sp}}$ we discover that the supercooled liquid loses stability at low enough temperatures, and the system enters a completely different regime. Therefore, it is useful to divide our dynamical investigation into two parts: first we shall assume that our maximum experimental time t_{exp} is shorter than t_{sp} and we will measure the equilibrium properties of the supercooled liquid. Second, we will consider times larger than t_{sp}, to analyze the loss of stability of the supercooled liquid.

A. Moderate times dynamics: $t < t_{\mathrm{sp}}$

In this section we will assume that the longest experimental time available to us is $t_{\mathrm{exp}} \leqslant t_{\mathrm{sp}} \sim 10^4$ MCS. To probe the dynamics of the CTLS we measure the equilibrium relaxation time τ as a function of the temperature T. This can be obtained from the decay rate of the (normalized) equilibrium spin–spin correlation function, defined as

$$C(t,t_w) = \frac{\langle s(t_w)s(t_w+t)\rangle - \langle s\rangle^2}{1-\langle s\rangle^2}, \tag{12}$$

where $\langle\cdots\rangle$ indicate averages over spins and initial configurations. We quench the system from infinite temperature down to the target temperature T and wait for it to equilibrate. At equilibrium the dependence on t_w disappears and $C = C(t)$. This is our first equilibration test. The correlation function can be adequately fit with a stretched exponential, which is the expected equilibrium behavior for $C(t)$ in supercooled liquids,

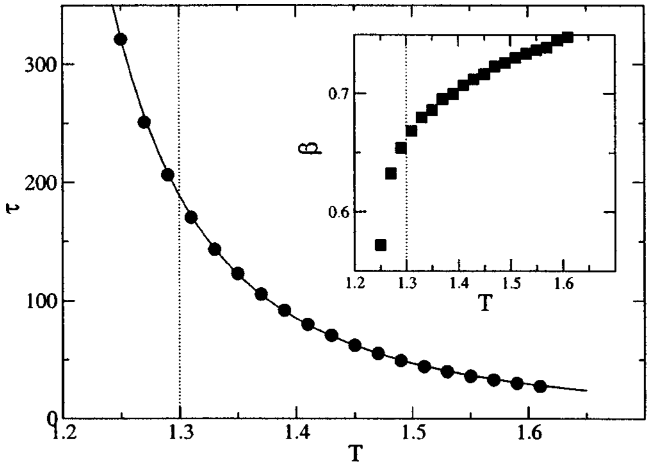

FIG. 5. Relaxation time as a function of temperature. The full line is the power law fit Eq. (14). Inset, Kohlrausch β exponent of the stretched exponential fit vs temperature. $L = 500$.

$$C(t) = \exp[-(t/\tau)^{\beta}]. \tag{13}$$

From this fit we extract the relaxation time τ. To be sure that the system has equilibrated we check that at each temperature the equilibration time that we have waited for is much larger than τ. More precisely, since $C(t)$ decays to zero in approximately 20τ we require $t_{\mathrm{eq}} \geqslant 20\tau$.

The relaxation time as a function of the temperature is plotted in Fig. 5. We note that there is no dynamic signature of the melting transition T_m. Below T_m the supercooled liquid is metastable with respect to the crystal, and there is a sharp increase of the relaxation time. In the inset of Fig. 5 we can see that the Kohlrausch β exponent of the stretched exponential fit decreases with the temperature, as it happens for realistic models of liquids (see, for example, the data of Ref. 12).

In the temperature regime of Fig. 5 the relaxation time can be fitted very well by a power law,

$$\tau = \frac{A}{(T-T_c)^{\gamma}}, \quad \text{with} \quad T_c = 1.06, \quad \gamma = 2.29. \tag{14}$$

This fact suggests that the CTLS is a fragile system.[13] To support this conclusion, we compare the CTLS with an Arrhenius/strong system, like the PQ model in $d = 2$.[14] To give a quantitative measure of fragility we need to fit the relaxation time with a Vogel–Fulchner–Tamman form,

$$\tau = \tau_0 \exp\left(\frac{\Delta}{T-T_0}\right). \tag{15}$$

The fit works pretty well for the CTLS and gives $T_0 = 0.76$ for $T \in [1.2{:}1.7]$, and $T_0 = 0.90$ for $T \in [1.2{:}1.4]$. The quantity $K_{\mathrm{VFT}} = T_0/\Delta$ is a measure of the degree of fragility of the system.[13] For the two models, we find

$$2d\mathrm{PQ}: \quad K_{\mathrm{VFT}} = 0.017, \tag{16}$$

$$\mathrm{CTLS}: \quad K_{\mathrm{VFT}} = 0.095, \tag{17}$$

consistent with a high fragility of the CTLS. Incidentally, we note that an Arrhenius fit of the $2d$–PQ correlation time gives a barrier size $\Delta = 5.8$. This can be reconciled with the result $\Delta = 3$ of Ref. 14 noting that the spin coupling constant is taken as 1/2 in that work.

For $T < 1.25$ we are no longer able to equilibrate the system within our experimental time $t_{\rm exp} = 10^4$, therefore this is our glass transition temperature within this time regime. If, however we give up the requirement to be at equilibrium, we can explore the low temperature region. For quenches below $T = 1.25$ the system should be considered, according to usual definitions, as an out of equilibrium glass. In fact, out-of-equilibrium glasses can be formed when cooling the liquid at low temperatures at a rate fast enough to prevent equilibration. In Fig. 8 we show the results of cooling experiments with a linear cooling schedule $T = T_{\rm in} - rt$ with cooling rate $r = dT/dt$ and $T_{\rm in} = 1.67$. We plot the system energy as a function of T for different cooling rates. In the same graph we report the equilibrium supercooled energy $E_{\rm LQ}(T)$, which of course must be extrapolated below the last equilibrium temperature. Considering for now only the three fastest rates, we find as expected that at high temperatures even for relatively fast coolings the system stays in equilibrium, whereas $E(T)$ departs from the equilibrium curve at lower temperatures. The slower the cooling, the lower the temperature where the energy freezes in the glassy phase: this is the glass transition $T_g(r)$ corresponding to that particular cooling rate. Since we have set a maximum experimental time $t_{\rm exp}$, to bring the system through the interesting temperature region of width $T \in [0.8{:}1.3]$, within a time $t_{\rm exp}$ we can afford at most cooling rates of the order of 5×10^{-5}. Slower rates will be considered in the next section.

The energy of the configurations reached at $T = 0$ upon cooling, as a function of the cooling rate, is a quantity which is considered as an important indicator of glassy behavior. What we find for $r \in [5 \times 10^{-4}, 0.01]$ is a slow dependence of $E - E_{\rm GS}$ on r, compatible with a power law with low exponent or with logarithmic behavior (see Fig. 13 and Sec. V for a wider discussion of this point), which is very similar to what was observed in real glasses.

Summarizing the results of this section, for times smaller than $t_{\rm sp} \sim 10^4$ MCS we observe in the CTLS a phenomenology typical of fragile structural glasses: in the supercooled liquid the correlation function displays stretched exponential relaxation. The relaxation time τ grows very sharply and is well fitted by a power law, and the stretching exponent β decreases with decreasing temperature. The fragility index is much larger than a typical Arrhenius/strong spin system. Finally, on rapid cooling, the system goes out of equilibrium remaining stuck in the glassy phase, at a glass transition temperature which is lower the smaller the cooling rate.

B. Long times dynamics: $t > t_{\rm sp}$ and the metastability limit $T_{\rm sp}$

We analyze now the behavior of the system for times longer than $t_{\rm sp} = 10^4$. In Fig. 6 we plot the energy as a function of time for three different temperatures below T_m, with random initial condition.

At the higher temperature, $T = 1.26$, the system relaxes in the supercooled liquid and remains in this phase up to our actual experimental time, $t_{\rm exp} = 2 \times 10^6$. On the other hand, for $T = 1.23$, after initial equilibration in the supercooled liquid phase, the system makes the transition to the crystal. Note that at $T = 1.23$ the supercooled liquid survives up to 10^5 MCS when the transition to the crystal starts, and crystallization is completed in 10^6 MCS. At $T = 1.18$, on the other hand, we see that the supercooled liquid lasts roughly 10^4 MCS, while the approach to the crystal takes more than 10^6 MCS. In other words, the lower the temperature, the faster is the departure from the liquid, but the slower is the completion of the crystal. If we further decrease the temperature, the plateau corresponding to the supercooled liquid disappears, and the energy decreases steadily toward the crystal ground state. The dynamics becomes ever slower in this temperature regime, and the system remains out of equilibrium up to very long times (see Sec. V). These results can be interpreted in terms of nucleation theory.[15] Even in the supercooled liquid phase the system nucleates droplets of crystal with finite probability. Most of these droplets are too small to be stable and soon disappear, however a critical size exists such that whenever a droplet of that size is created it will not shrink back, but rather expand and bring the system into the stable crystal phase. This phenomenon, critical nucleation, is characteristic of metastability and determines the average lifetime of the metastable phase. The time needed by the system to nucleate critical droplets, i.e., the nucleation time $\tau_{\rm nuc}$, depends on temperature and may be very long. It is often not accessible experimentally, so that the loss of stability of the metastable phase cannot be observed. Once critical nucleation takes place, critical crystal droplets start to grow until all the system has a crystalline structure. However, the growth of the crystal may become very slow if kinetic constraints are present. What we observe in the CTLS is that the lower the temperature, the faster is crystal nucleation, but the slower is crystal growth.

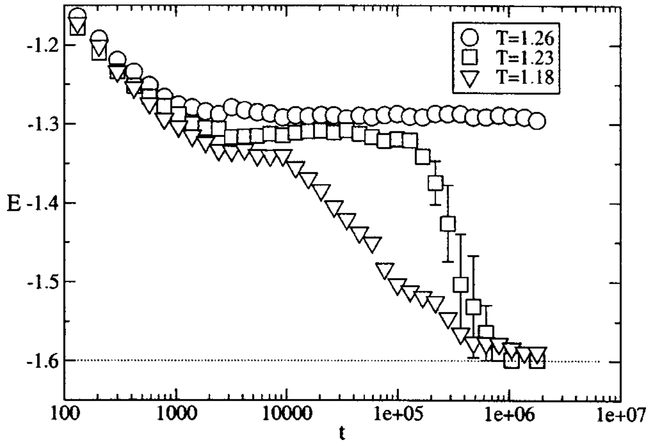

FIG. 6. Energy per spin close to the spinodal as a function of time. The dotted line marks the energy of the crystal. $L = 100$. Error bars are only shown if larger than symbols size.

We can formalize the loss of stability of the liquid by estimating the nucleation time $\tau_{\rm nuc}$. In two dimensions, the free energy difference due to formation of a crystal droplet of size ξ in the liquid phase is given by[15]

$$\Delta(\xi) = A\sigma\xi - B\delta f \xi^2, \tag{18}$$

where A and B are geometric factors depending on the shape of the droplet, $\sigma(T)$ is the surface tension, and $\delta f(T) = F_{\mathrm{LQ}}(T) - F_{\mathrm{CR}}(T)$ is the bulk free energy difference between supercooled liquid and crystal below T_m. The function $\Delta(\xi)$ has a maximum at a value of the droplet size $\xi^\star$, with an associated value $\Delta^\star$ of the excess free energy:

$$\xi^\star(T) = \frac{A}{2B}\,\frac{\sigma(T)}{\delta f(T)}, \quad \Delta^\star(T) = \frac{A^2}{4B}\,\frac{\sigma(T)^2}{\delta f(T)}. \tag{19}$$

For $\xi < \xi^\star$ the system still needs energy to enlarge the droplet which therefore naturally shrinks its size to zero; for $\xi > \xi^\star$ on the other hand, it becomes favorable for the droplet to grow. Therefore, $\xi^\star$ is the critical droplet size and $\Delta^\star$ is the free energy barrier to crystal nucleation. The Arrhenius estimate for the time τ_{nuc} of crystal nucleation is then

$$\tau_{\mathrm{nuc}}(T) = \tau_0 \exp\left(\frac{A^2}{4B}\,\frac{\sigma(T)^2}{T\,\delta f(T)} \right). \tag{20}$$

A necessary condition for the existence of the supercooled liquid phase at temperature T is that the nucleation time $\tau_{\mathrm{nuc}}(T)$ is much longer than the time to make an equilibrium measurement, i.e., the equilibration time $\tau_{\mathrm{eq}}(T)$. In other words, only if $\tau_{\mathrm{nuc}}(T) > \tau_{\mathrm{eq}}(T)$ can we speak of a metastable supercooled liquid. We want now to test this relation in the CTLS. To find τ_{nuc} we need the surface tension σ, which we estimate at a reference temperature T_{ref} and assume that depends weakly on T close to T_{ref}. To do this we invert formula (20),

$$\sigma^2 = 4BT_{\mathrm{ref}}\,\delta f(T_{\mathrm{ref}}) \log[\tau_{\mathrm{nuc}}(T_{\mathrm{ref}})/\tau_0]/A^2, \tag{21}$$

and after setting $\alpha = T_{\mathrm{ref}}\,\delta f(T_{\mathrm{ref}})/T\,\delta f(T)$, we can write

$$\tau_{\mathrm{nuc}}(T) \approx \tau_0 \exp\left\{ \alpha \log\left[\frac{\tau_{\mathrm{nuc}}(T_{\mathrm{ref}})}{\tau_0} \right] \right\} \tag{22}$$

$$= \tau_{\mathrm{nuc}}(T_{\mathrm{ref}})^{\alpha}\, \tau_0^{1-\alpha} \tag{23}$$

$$\approx \tau_{\mathrm{nuc}}(T_{\mathrm{ref}})^{\alpha}, \tag{24}$$

where the last approximation is valid when T is near T_{ref}, since then $\alpha \approx 1$. To have a result as accurate as possible close to the loss of stability of the liquid, we take $T_{\mathrm{ref}} = 1.234$, where $\tau_{\mathrm{nuc}} = 5 \times 10^4$.

Regarding the estimate of $\tau_{\mathrm{eq}}(T)$, we have already noticed that the correlation function $C(t)$ drops to zero after roughly 20 relaxation times, and this we take as a reasonable estimate of the equilibration time. The relaxation time is given by the power law fit, Eq. (14).

In Fig. 7 we plot τ_{nuc} and τ_{eq} versus T from the above estimates. We see that the nucleation time drops below the equilibration time at a temperature $T_{\mathrm{sp}} = 1.22$, which therefore marks the metastability limit of the supercooled liquid phase. Below T_{sp} the liquid can only be observed on time scales shorter than the equilibration time, meaning that what we are actually observing is an out-of-equilibrium glass. Therefore, the equation

$$\tau_{\mathrm{nuc}}(T_{\mathrm{sp}}) = \tau_{\mathrm{eq}}(T_{\mathrm{sp}}) \tag{25}$$

can be considered as a definition of the effective spinodal temperature T_{sp} for the metastable liquid phase. Note that the two curves cross at a time $t_{\mathrm{sp}} \sim 10^4$ MCS: this is the reason why if our maximum experimental time is smaller than t_{sp} we do not detect this metastability limit. As we have already said, the glass transition temperature T_g is fixed by the experimental time $t_{\exp}$ via the relation $\tau_{\mathrm{eq}}(T_g) = t_{\exp}$. Therefore, if $T_{\mathrm{sp}} < T_g$ the metastability limit cannot be observed, whereas we detect it if $T_g < T_{\mathrm{sp}}$.

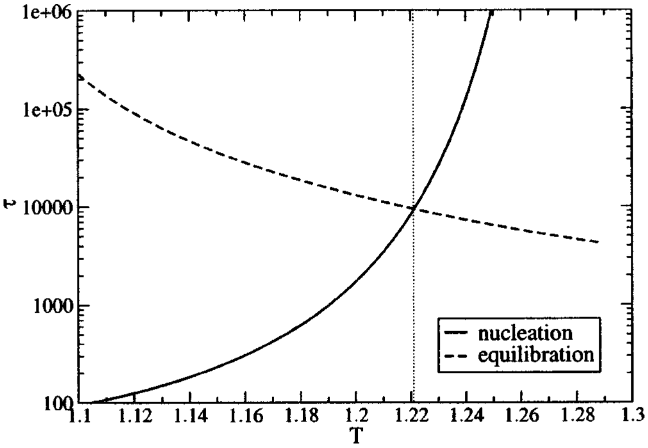

FIG. 7. Nucleation and equilibration times vs temperature.

The presence of a lower metastability limit T_{sp} is clearly visible also in cooling experiments. If our experimental time exceeds $t_{\mathrm{sp}} = 10^4$ MCS, we can afford smaller cooling rates than $r_{\mathrm{sp}} \sim \Delta T/t_{\mathrm{sp}}$ to explore the relevant region $T \in [0.8{:}1.3]$. The results are reported in Fig. 8. For $r > r_{\mathrm{sp}} \sim 5 \times 10^{-5}$ the energy departs from the equilibrium line remaining *above* it, while for $r < r_{\mathrm{sp}}$ it drops *below* it. We can understand qualitatively this behavior in terms of equilibration and nucleation processes. For $r > r_{\mathrm{sp}}$, given the fast cooling rate, the system has not the time to equilibrate at low temperatures where the equilibration time becomes very large and its energy therefore remains higher than the equilibrium one. On the contrary, for $r < r_{\mathrm{sp}}$ the cooling is so

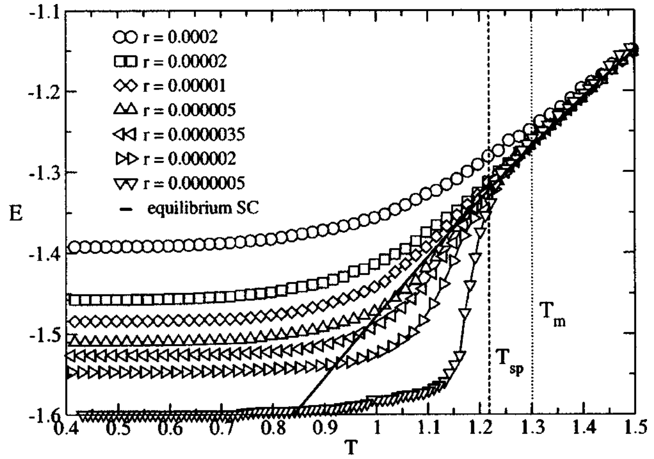

FIG. 8. Cooling experiments above and below the spinodal cooling rate r_{sp}. The cooling protocol is linear, $T(t) = T_{\mathrm{in}} - rt$, from $T_{\mathrm{in}} = 1.67$ down to $T = 0$. $L = 100$.

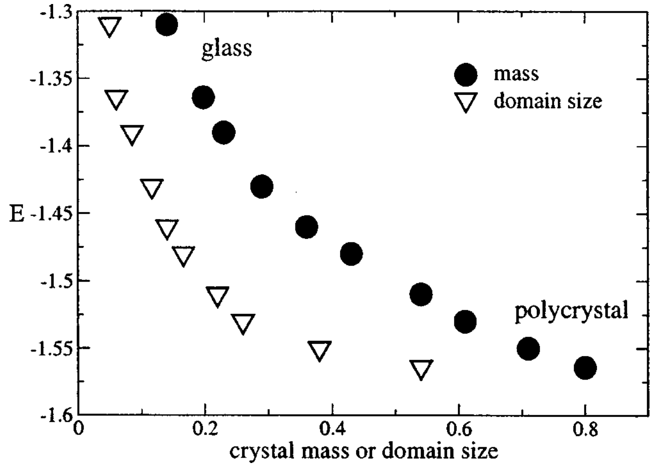

FIG. 9. Energy of the configurations reached at $T=0$ during cooling experiments as a function of the mass and the domain size. $r \in [10^{-6}, 10^{-3}]$, $L=100$.

slow that at low enough temperatures the system has the time to nucleate critical crystal droplets and its energy is driven toward the ground state one, thus becoming smaller than the supercooled liquid energy. In both cases, however, the system eventually remains stuck in an off the equilibrium phase.

This experiment poses an interesting question about the actual nature of the out-of-equilibrium glassy phase. For fast cooling rates the system remains stuck at a high energy level, into a clearly disordered, or glassy-like, phase. On the other hand, for the slowest cooling rates the system approaches the ordered crystal phase, even though it remains stuck in an out-of-equilibrium polycrystalline configuration (this can be clearly seen inspecting configuration snapshots visually). The decrease in energy, and the associated increase in crystalline order that we observe as we slow down the cooling is a continuous process, making it very difficult to distinguish what is a glass and what is a highly disordered polycrystal.

This *structural continuity* from glass to polycrystal can be appreciated quantitatively in Fig. 9, where we plot the energy of the asymptotic configurations the system reaches at $T=0$, as a function of the corresponding crystalline domain size ξ and crystal mass m, for various cooling rates r. All the points on this plot correspond to configurations obtained with a well-defined cooling experiment. Moreover, all these configurations are (local) minima of the energy. As we can see, the data interpolate without gaps between crystalline (or polycrystalline) configurations with low E and high ξ or m, to glassy configurations with high E and low ξ or m. In this sense we may say that in the present system there is no qualitative difference between the off-equilibrium disordered, i.e., glassy, regime, and the crystal growth regime. On the other hand, thanks to the presence of the pseudospinodal transition, there is a clear distinction between *equilibrium* liquid and crystal phases.

C. Metastability limit and relaxation time divergence: T_{sp} versus T_c

It has been shown in Ref. 6 that in the PQ model the temperature T_c where a power law fit of the relaxation time locates a divergence, is very close to the metastability limit T_{sp}. The interpretation of this fact given in Ref. 6 is very clear: in mean-field the PQ model has a sharp spinodal temperature at the point where the liquid metastable state disappears, and this transition is accompanied by a divergence of the correlation times. Therefore, it is argued that in the finite-dimensional version of the PQ model the temperature T_c is actually a remnant of the mean-field spinodal. The same view has been advanced for off-lattice models: in Ref. 16 the behavior of a supercooled two-component Lennard-Jones system in $d=2$ has been interpreted as due to the influence of a pseudospinodal, while in Ref. 17 arguments are given to explain why in $d=3$ spinodal effects may be much harder to detect.

The situation is very similar in the CTLS, even though our definition of T_{sp} makes it indispensable to distinguish between the two temperatures. The temperature T_c where the relaxation time would diverge is not actually a true critical temperature: when the temperature is decreased the equilibration time increases and finally becomes as large as the nucleation time at T_{sp}, when $\tau_{\mathrm{eq}}=\tau_{\mathrm{nuc}}$ is still finite. Therefore we have by definition $T_{\mathrm{sp}}>T_c$. This is simply due to the finite-dimensional nature of the CTLS. In mean-field systems a metastable state has infinite lifetime and is separated from the stable phase by an infinite free energy barrier: the spinodal temperature, which marks the disappearance of the metastable state, corresponds to the temperature where the barrier goes to zero, and is naturally associated with a divergent time scale. In a finite-dimensional system like the CTLS, on the contrary, the metastable phase (the liquid) is separated from the stable one (the crystal) by a finite free energy barrier—see Eq. (19)—and has always a finite lifetime. An effective spinodal temperature can only be defined by comparing the different and finite time-scales present in the system, as done in the preceding section. However, the physical interpretation of Ref. 6 may remain valid, i.e., the increase of the relaxation time close to T_{sp} may be an effect of approaching incoming instability of the supercooled liquid.

We stress again that had our maximum experimental time been shorter than $t_{\mathrm{sp}}=10^4$ MCS, we would not have detected the metastability limit at T_{sp}, while we still would fit the equilibrium relaxation time as a power law with critical temperature T_c. In that case, it would have been harder to realize the connection between divergence of the relaxation time and loss of stability.

D. Kauzmann's resolution of the Kauzmann paradox

In 1948, Kauzmann outlined in a famous paper[10] the paradox now named after him. In the supercooled phase the viscosity of the system increases with decreasing temperature, until at the glass transition T_g relaxation time becomes too long and equilibration cannot be achieved within experimentally accessible times. However, Kauzmann noted that if the entropy of a supercooled liquid is extrapolated below T_g, it becomes equal to the crystal entropy at a temperature $T_s>0$, and even smaller than zero if extrapolated further. This *entropy crisis* is never actually observed, because the glass transition intervenes before. However, Kauzmann found it paradoxical that it was just a kinetic phenomenon (the glass transition) that saved the liquid from thermodynamic nonsense.

In the context of the Adams–Gibbs–DiMarzio theory,[18] the entropy crisis has however an interpretation: the entropy difference between crystal and liquid is related to the configurational entropy Σ, that is the entropic contribution due to the presence of an exponentially high number of different glassy minima. The vanishing of Σ at T_s signals a thermodynamic transition to a new phase, characterized by a subexponential number of glassy states, separated by infinite free-energy barriers. This picture is exact for some mean-field spin-glass systems,[19] and it may be the correct resolution of the Kauzmann paradox even for real structural glasses. According to Adam–Gibbs–DiMarzio, the entropy crisis is accompanied by a divergence of the relaxation time at T_s given by $\tau \sim \exp(A/T\Sigma)$. Expanding linearly the configurational entropy close to T_s a Vogel–Fulchner–Tamman behavior is obtained [see Eq. (15)] with $T_0 = T_s$. T_0 and T_s have been observed to be quite close in various systems,[1] a fact that has been advocated as an indirect argument in favor of this interpretation.

Despite recent analytic and numerical work supporting the entropy crisis scenario,[20,21] there is another way to avoid the Kauzmann paradox, which, interestingly enough, was proposed by Kauzmann himself.[10] He rejected the idea of a thermodynamic glassy phase, and instead hypothesized the existence of a metastability limit of the supercooled liquid phase, below which crystal nucleation becomes faster than liquid equilibration. More specifically, he defined an effective spinodal temperature $T_{\rm sp} > T_s$ below which "*the free energy barrier to crystal nucleation becomes reduced to the same height as the barrier to simpler motions*." Below $T_{\rm sp}$ the supercooled liquid is operationally meaningless and thus the paradox is avoided.

We have shown in this paper that the CTLS is a system with a supercooled phase and a fragile-glass phenomenology that precisely reproduces the scenario hypothesized by Kauzmann. If we look at the behavior of the extrapolated excess entropy $S_{\rm LQ} - S_{\rm CR}$ we find that in this model T_s and T_0 are actually very similar (see Secs. III and IV A). However, despite this fact, no entropy crisis does actually take place. The metastable liquid ceases to exist below $T_{\rm sp} = 1.22$ and thus the paradox is avoided.

As we have already stressed, the metastability limit may prove impossible to observe experimentally if the equilibration time at $T_{\rm sp}$ is much larger than the experimental time, that is if $T_{\rm sp} \ll T_g$. One is then tempted to suggest that the Kauzmann's resolution of the Kauzmann paradox that we have explicitly analyzed in the CTLS model possibly applies to many other systems, but is actually out of experimental recognition. However, we must be careful in judging how general this behavior can be.

The nucleation time $\tau_{\rm nuc}$ of the CTLS has a minimum at a temperature $T = 0.98$, below which it starts increasing again. This is simply due to the balance between the free energy barrier $\Delta^\star(T)$ and T in the Arrhenius factor, and it is certainly a very model-dependent property. In the CTLS all this is of little relevance, because $\tau_{\rm nuc}$ and $\tau_{\rm eq}$ cross at a much higher temperature, as shown in Fig. 7 and also in Fig. 10 (left). Yet, in general the interplay between $\sigma(T)$, $\delta f(T)$, and T may be such that a minimum of $\tau_{\rm nuc}(T)$ actually occurs *and* that at this minimum $\tau_{\rm nuc} \gg \tau_{\rm eq}$. However, even in this case it may still happen that the curves cross below the minimum of $\tau_{\rm nuc}$, as shown in Fig. 10 (center). In this case the Kauzmann paradox would still be resolved by the metastability limit, exactly as in CTLS. Note that this particular scenario may actually prove to be quite deceiving: at temperatures smaller than the minimum of the nucleation curve one can think that the "dangerous" zone for crystal nucleation has been safely crossed and that crystallization is therefore ruled out at lower temperatures. However, very careful extrapolations of both $\tau_{\rm nuc}$ and $\tau_{\rm eq}$ would be needed to recognize that a metastability limit actually exists at $T_{\rm sp} \ll T_g$.

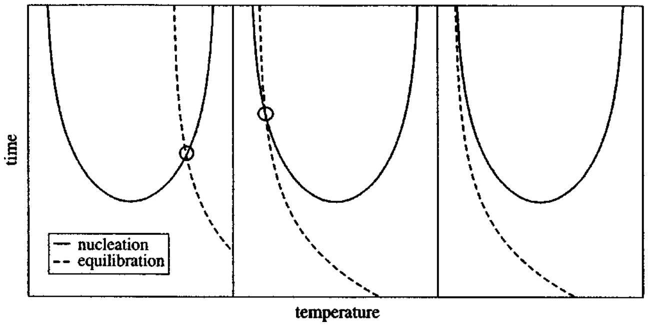

FIG. 10. Pictorial view of three different scenarios: Left, $\tau_{\rm nuc}$ and $\tau_{\rm eq}$ cross at a spinodal temperature $T_{\rm sp}$, which is larger than the temperature where $\tau_{\rm nuc}$ has a minimum, as in the CTLS. Center, $\tau_{\rm nuc}$ and $\tau_{\rm eq}$ cross at a spinodal temperature $T_{\rm sp}$, which is smaller than the temperature where $\tau_{\rm nuc}$ has a minimum. Right, $\tau_{\rm nuc}$ and $\tau_{\rm eq}$ both diverge at the same temperature $T_s = T_{\rm sp}$. The circles indicate the spinodal temperature $T_{\rm sp}$.

But is it possible that $\tau_{\rm nuc} \gg \tau_{\rm eq}$ at *all* temperatures? The answer is yes for strong liquids, where $T_s = 0$, and thus $\tau_{\rm eq}$ stays finite for $T > 0$; but this case is of little interest for us since then the Kauzmann paradox does not arise. However in fragile liquids, where $\tau_{\rm eq}$ is supposed to diverge at T_s, the condition for the existence of the liquid, $\tau_{\rm nuc} \gg \tau_{\rm eq}$, requires that $\tau_{\rm nuc}$ diverges at a temperature $T_{\rm nuc} \geq T_s$. In our opinion it is possible that $T_{\rm nuc} = T_s$, since at low temperatures the contribution of τ_0 in Eq. (20) could be important due to kinetic constraints.[22] In nucleation theory, this prefactor is taken as proportional to the viscosity, in which case $\tau_{\rm nuc}$ would diverge when the viscosity does, that is at T_s. But it is hard to imagine how $\tau_{\rm nuc}$ could diverge *strictly above* the thermodynamic transition temperature T_s. Therefore, it seems to us that the best one can have is $T_{\rm sp} = T_s$, as in Fig. 10(right).

Let us stress once again the fact that crystal nucleation is a different process from crystal growth: saying that nucleation is fast, is not the same as saying that the critical crystal droplets will grow quickly, since the speed of growth will strongly depend on kinetic considerations. From an experimental point of view, it is clear that having a very long nucleation time (longer than the experimental time) and fast growth, is not much different from having a fast nucleation of very small, undetectable, crystal droplets, which however grow exceedingly slowly. In order to avoid crystallization

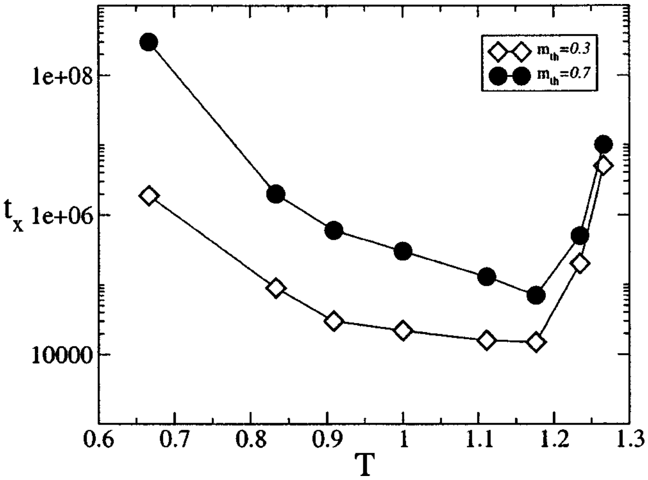

FIG. 11. TTT curves for two different values of the threshold value m_{th}. $L=100$.

and form the glass we have either to avoid nucleation, or to ensure that crystal growth is kinetically blocked. To clarify this point, we can ask how long is the time t_x the system takes to develop a substantial amount of crystalline order, large enough to prove that crystallization has started. We can answer this question by following the time evolution of the crystal mass $m(t)$ at various temperatures, and defining t_x from the relation $m(t_x) \geqslant m_{th}$, where m_{th} is an arbitrary threshold. The function $t_x(T)$ is normally called in the context of supercooled liquids time–temperature–transformation (TTT) curve, and it is the only experimentally available means to check how likely crystal formation is at a given temperature. Note that the value of $t_x(T)$ will strongly depend on m_{th}, and it cannot therefore be *quantitatively* compared to τ_{eq}.

In Fig. 11 we plot the TTT curves of the CTLS for two different values of m_{th}. As in realistic supercooled liquids, the TTT curves have a minimum at a temperature T_x: here crystallization has the fastest rate, in the sense that at T_x we have to wait the minimum possible time to reach a level m_{th} of crystallization. The origin of this minimum is obvious in CTLS: for high temperatures t_x is large because *crystal nucleation* is very slow, i.e., because τ_{nuc} is very large, whereas for small temperatures t_x is large because *crystal growth* is very slow, which is essentially due to the high viscosity of the system (i.e., to the same reason why, if the liquid still existed, τ_{eq} would be very large). Thus, in CTLS the two branches of the TTT curve correspond to two different phenomena, that is nucleation and growth. Not surprisingly we find $T_x \sim T_{sp}$. On the other hand, in a system where the scenario depicted in Fig. 10 (center) holds, also the left branch of the TTT curve for $T<T_x$ would be due to slow nucleation,[23,24] until $T_{sp}<T_x$ is reached. In this case the minimum of the TTT curve would be an effect of the minimum of $\tau_{nuc}(T)$ described above. Below T_{sp}, however, the TTT curve would again increase due to slow crystal growth.

It may be argued that there is little experimental difference between the case where crystallization at low T is blocked because of arrested nucleation or arrested growth. However, from a theoretical point of view these two situations are quite different: in the first case the equilibrium liquid phase exists, at least on certain time scales, whereas in the second case it does not, the only liquid phase is the out-of-equilibrium glass and the Kauzmann paradox is avoided. We can characterize these two scenarios as *equilibrium arrested nucleation* vs *off-equilibrium arrested growth*.

V. OFF-EQUILIBRIUM BEHAVIOR: DOMAIN GROWTH AND AGING

In this section we study the dynamical behavior of the CTLS after a quench to $T<T_{sp}$. We shall first focus on one-time quantities, and in particular on the behavior of energy, crystal domain size, and crystal mass. Then we will analyze two-time quantities to understand whether our system exhibits aging, and of what kind. The key result of this section is that there are two time regions for off-equilibrium dynamics. In the earlier time regime there is the formation of a large number of critical crystal droplets all over the system. As we have seen, this mixture of crystallites cannot be structurally distinguished from a glass or liquid configuration, as long as the crystallites are very small. Their growth is controlled by activation, and thus this regime will last longer the lower the temperature. In this phase, which we call *bubbling*, off-equilibrium dynamics is similar to what was found in structural glasses. The later time regime kicks in when the energy barriers to crystal growth have been crossed, so that crystal domains are large enough to be structurally recognizable. This phase we call *coarsening*, and off-equilibrium dynamics in this regime is consistent with models where simple coarsening occurs, as the Ising model. The minimum time we have to wait to see the coarsening regime in our system (and thus realize that crystal domains are actually growing) is as long as the time needed to directly see the loss of stability of the liquid, that is t_{sp}. In other words, the dynamical checks for the growth of the crystal are as inefficient as the structural ones we considered in the former section.

A. One time quantities

The rate of decay of the energy gives a useful characterization of the off-equilibrium dynamics. In Fig. 12 we report the behavior of the excess energy $\delta E = E - E_{GS}$ as a function of time, together with power law fits of the form $\delta E = A t^{-\nu}$. For all temperatures $T<T_{sp}$ we find an initial time regime where $\nu<0.2$, which is compatible with that found in some model systems of structural glasses (see, e.g., Refs. 25 and 26). This is followed by a second late time regime where the energy decreases faster, with $\nu \sim 0.5$. However, the data show that the crossover to this second regime takes place at a time which increases on lowering the temperature. At $T=0.67$ we are unable to enter this late time region within our maximum experimental time, and we only observe the slow regime.

The existence of these two different regimes can be related to the presence of *activated coarsening*, as is commonly found in frustrated lattice spin models.[4,5] Below the spinodal temperature the system rapidly nucleates small stable crystal domains, which tend to grow. However, due to the high viscosity, local spin rearrangements are difficult, and moving a domain boundary may be rather costly. Thus, contrary to the case of standard coarsening in the Ising model,

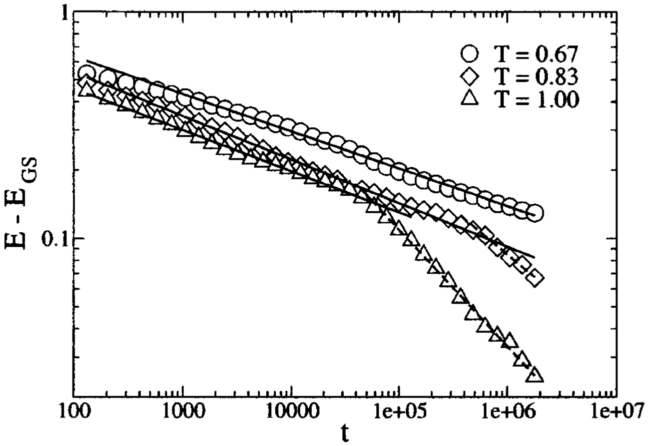

FIG. 12. Excess energy as a function of time after a quench at $T<T_{\mathrm{sp}}$. Full lines, power law fit of the early (slow) time region: $\nu=0.17$ for $T=0.67$; $\nu=0.19$ for $T=0.83$; $\nu=0.18$ for $T=1.00$. Dashed lines, power law fit of the late (fast) time region: $\nu=0.40$ for $T=0.83$; $\nu=0.51$ for $T=1.00$. $L=100$.

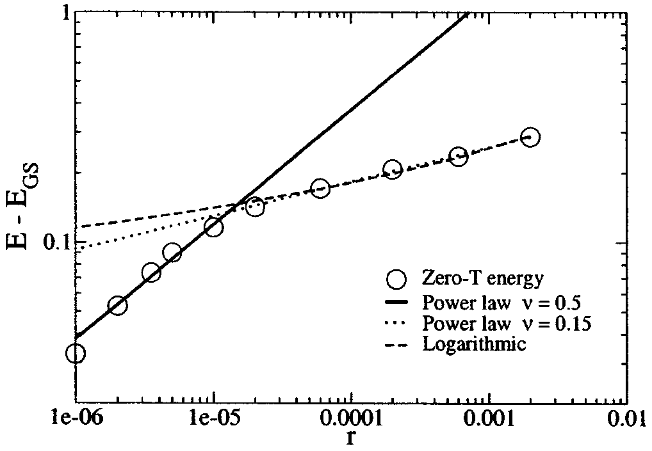

FIG. 13. Energy of the configurations reached at $T=0$ during cooling experiments (see Fig. 8) as a function of the cooling rate, together with power law and logarithmic fits. $L=100$.

when frustration is present domain boundaries are pinned, and domain growth requires overcoming some energy barriers. The system therefore needs activation to grow crystal domains, and this may lead to a nonstandard decay of the energy as a function of time.

More precisely, according to Ref. 27 we must distinguish two classes of activated coarsening, depending on whether or not the maximum barrier Δ to domain growth depends on the linear domain size $L\xi(t)$, and therefore on t itself. In the first class of systems Δ does not depend on $\xi(t)$. In this case the system evolves slowly within a time scale $t_\Delta \sim \exp(\beta\Delta)$, while for $\log t > \log t_\Delta$ barriers are no longer a problem, and a standard power law behavior is recovered, i.e., $E-E_{\mathrm{GS}} \sim t^{-1/2}$ (we are only considering systems with nonconserved order parameter). On the contrary, if the barrier to domain growth is proportional to $\xi(t)$, then it is larger the longer the time. In this second class of activated coarsening one expects a logarithmic asymptotic dependence of the energy on time.

The data regarding the energy in Fig. 12 show that, after an early slow regime, the standard $t^{-1/2}$ decay of the energy is recovered. This fact suggests that our model belongs to the first class of activated coarsening, and that the early time regime is due to activated domain growth with a constant energy barrier.[28] The same can be inferred from the behavior of $\xi(t)$, which has two regimes: a first in which ξ fluctuates around its effective zero, and a second where it increases with an exponent close to 1/2.

The behavior of the system when we perform a cooling experiment is consistent with the interpretation above. The configurations reached at $T=0$ for low cooling rates exhibit the typical pattern of a coarsening system and are stable, indicating that coarsening is indeed activated. Besides, if we plot the excess energy δE as a function of the cooling rate r, once again we find two regimes (Fig. 13): for fast coolings (short time) we have a slow energy decay, which can be fitted either with a logarithm, or with a power law $\delta E \sim r^{\nu}$, with $\nu \sim 0.15$. On the other hand, for slow coolings (long time) we find $\nu \sim 1/2$, as in standard coarsening for the Ising model. This behavior of $\delta E(r)$ is what we expect for activated coarsening of the first class and can be qualitatively explained in the following way. As we have seen, below T_{sp} the system exhibits a nontrivial dynamical behavior where the energy evolution is determined by the formation and growth of pinned crystal domains. In a cooling experiment it is then crucial how much time the system spends below the spinodal temperature before remaining trapped in the asymptotic state. If we call T_f the temperature where the system reaches the asymptotic $T=0$ energy value,[29] then at a given cooling rate r the time elapsed from T_{sp} to T_f is given by $t(r)=(T_f-T_{\mathrm{sp}})/r$. During this time the energy of the system evolves approximately as described previously in this section, i.e., $\delta E=At^{-\nu}$. Therefore we have $E(r)-E_{\mathrm{GS}} \sim t(r)^{-\nu} \sim r^{\nu}$ and the two regimes observed in Fig. 13 are nothing else than a manifestation of the two regimes already discussed for Fig. 12. The exponent ν corresponds to the first regime value if $t<t_{\mathrm{sp}}$, that is if $r>r_{\mathrm{sp}}$, while for $r<r_{\mathrm{sp}}$ the standard value $\nu=1/2$ is recovered.

B. The bubbling and coarsening regimes

The two regimes we have presented above can be explicitly related to different patterns of domain dynamics. In order to do this we compare the different time dependence of the domain size ξ and crystal mass m.[30] Up to now we used both quantities as equivalent markers of crystal order, but in fact in the growth phase their role is quite different.

After a quench to $T \ll T_{\mathrm{sp}}$ we expect that fast nucleation will lead to an increase in m due to the formation of many crystallites, but that the typical domain size ξ will remain very small, actually smaller than our resolution. This picture is confirmed by Fig. 14, where we plot ξ and m as a function of time for two different temperatures below T_{sp}. In both cases we see that the initial increase of m is faster than that of ξ. For $T=1.0$, which is quite close to $T_{\mathrm{sp}}=1.22$, we can see a rise of ξ only for times longer than 10^5 MCS, while for $T=0.67$ there is practically no increase of ξ up to $t=10^6$ MCS, while a clearly detectable increase of m can be seen.

To further support this picture we plot in Fig. 15 the mass m as a function of domain size ξ for many different

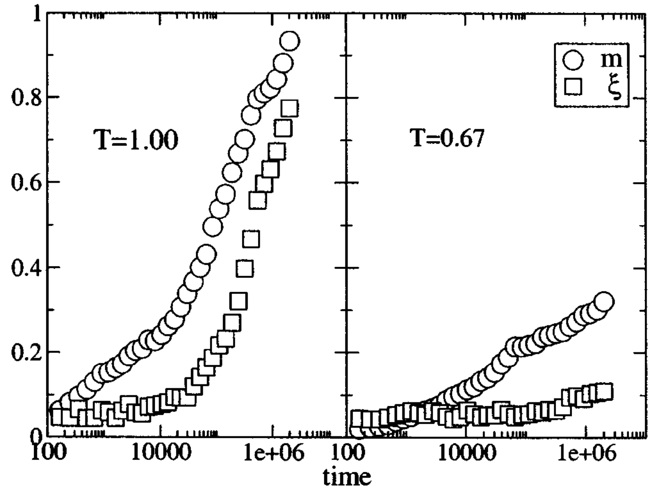

FIG. 14. Mass and domain size as a function of time for two different temperatures. $L=100$.

temperatures below T_{sp}, and for different times. All these data collapse on a master curve, which shows that for short times (small ξ and m) the crystal mass grows much faster than the domain size, whereas for long times m tends to saturate, and ξ start increasing rapidly.

We can therefore define two time regimes for crystal domain growth. For shorter times, in what we may call a *bubbling* regime, many small crystallites form at the expenses of a liquid background, their linear size growing very little with time, whereas the total crystal mass grows quite sharply.[31] In this phase domains are so small that they are not even well defined, in the sense that their linear size $L\xi$ is of the same order as the width a of the interfaces (or domain walls) among them. The excess energy is dominated by the regions not yet crystallized, and the interfacial and domain contributions are of the same order. For longer times, the largest part of the system is crystallized, so the mass m saturates, and the small domains start growing one at the expense of each other.

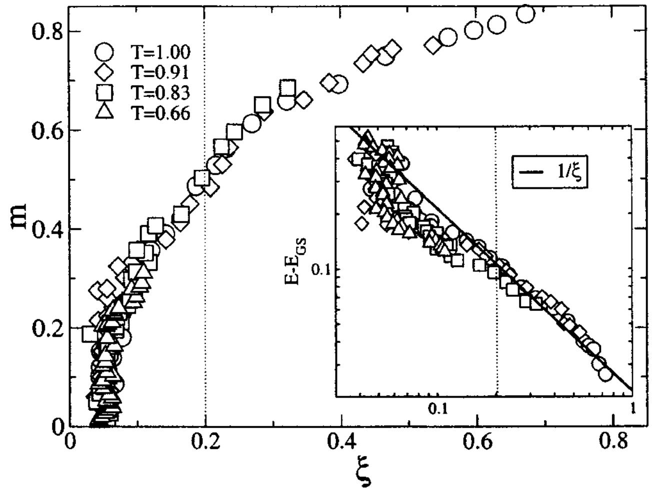

FIG. 15. Crystal mass as a function of the domain size parametrically in t, after a quench at various temperatures. Inset, excess energy as a function of the domain size. Full line, $1/\xi$ fit. All runs are 2×10^6 MCS long, $L=100$.

Therefore a proper *coarsening* regime starts with a clearly increasing ξ, and $L\xi \gg a$. Now domains are well defined and the excess energy is concentrated in the interfaces. These are now much thinner than the domain size and can be considered as lower dimensional manifolds. This must give,

$$E(t)-E_{\mathrm{GS}}\sim\frac{\xi(t)^{d-1}}{\xi(t)^{d}}=\frac{1}{\xi(t)}, \tag{26}$$

as in standard coarsening.[27,32] In Fig. 15 we plot the excess energy $E(t)-E_{\mathrm{GS}}$ versus ξ for a number of temperatures and times. Consistently with our conclusions, for shorter times there is a drop in energy with basically no increase in ξ. On the other hand, for $\xi>0.2$ the $1/\xi$ law fits reasonably well the data, suggesting that this is the late-time coarsening regime.

C. Two time quantities

We now focus on the behavior of two-time quantities, for quenches below T_m. In equilibrium dynamics, correlation functions $C(t,t_w)=\langle A(t_w)A(t)\rangle$ and their associated response functions $R(t,t_w)=\delta\langle A(t)\rangle/\delta h(t_w)$ (A is a generic variable and h is the field conjugate to it), depend only on the difference $t-t_w$. This is not the case when the system is out of equilibrium. The aging regime is that in which one-time quantities (such as energy or density) are stationary or change very little, but two-time quantities depend explicitly on both times t_w, t.[33]

An important quantity which allows to distinguish among different kinds of aging behavior[33] is the fluctuation–dissipation (FD) ratio,

$$X=T\frac{R(t,t_w)}{\partial C(t,t_w)/\partial t_w}. \tag{27}$$

In equilibrium, the fluctuation–dissipation theorem (FDT) states that $X=1$, while out of equilibrium the FDT is violated and X depends on t, t_w in a nontrivial way. It has been conjectured[34] that during aging X depends on time only through the correlation function, conjecture that has proved valid in all systems studied to date. If one considers the susceptibility, or integrated response,

$$\chi(t,t_w)=\int_{t_w}^{t}R(t,s)ds, \tag{28}$$

which is much easier to compute numerically, then assuming $X=X[C(t,t_w)]$ one finds from (27),

$$\chi(t,t_w)=\beta\int_{C(t,t_w)}^{C(t,t)}X(C)dC. \tag{29}$$

Therefore one can plot χ vs C at fixed t_w, and extract X from the slope of the curve. In equilibrium $X=1$ and the curve is a straight line $\chi(t-t_w)=\beta[C(0)-C(t-t_w)]$, with slope $-1/k_BT$. For a system out of equilibrium one finds in general two regimes: a short time quasiequilibrium regime, corresponding to equilibration of fast degrees of freedom, where the curve follows the equilibrium straight line and FDT holds; and the aging regime at larger times where $\chi(t,t_w)$ departs from the equilibrium line. In particular, for structural glass models studied so far via numerical simulations[25,35] it

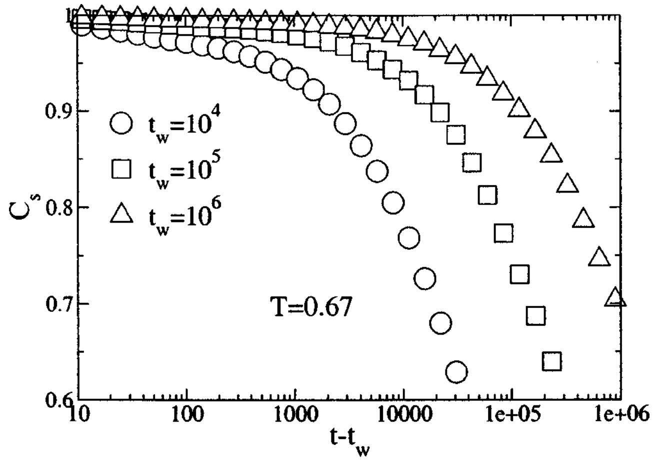

FIG. 16. Correlation function as a function of $t-t_w$, at different values of the waiting time t_w. $T=0.67$, $L=500$.

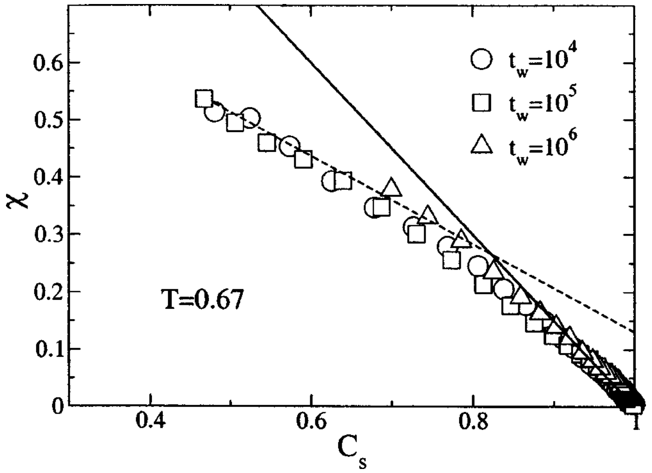

FIG. 17. Parametric plot of $\chi(t,t_w)$ vs $C_s(t,t_w)$, at various values of the waiting time t_w for $T=0.67$, well below the spinodal temperature. $L=500$. The full line represents the equilibrium relation $\chi=\beta(1-C_s)$.

has been found that after leaving the equilibrium line, the curve follows another straight line, with smaller (in absolute value) slope.

To study the FD relations in CTLS we follow (as has been done before in other spin systems)[36] the evolution of the staggered magnetization ($\eta_i=\pm 1$ are quenched, independent random variables),

$$m_s(t)=\frac{1}{N}\sum_i \eta_i s_i(t), \tag{30}$$

when adding a term $-hNm_s$ to the Hamiltonian. If the field h is applied at time t_w, the η-averaged susceptibility $\chi(t,t_w)=\overline{m_s(t)}/h$ is related to the spin–spin correlation function:[37]

$$C_s(t,t_w)=\overline{\langle Nm_s(t)m_s(t_w)\rangle}=\frac{1}{N}\sum_{ij}\overline{\eta_i\eta_j}\langle s_i(t_w)s_j(t)\rangle$$
$$=\frac{1}{N}\sum_i \langle s_i(t_w)s_i(t)\rangle. \tag{31}$$

We have used fields $h=0.1k_BT$ and $h=0.15k_BT$, and checked that they are within the linear regime. The results presented here correspond to the highest field.

We look for aging behavior in the regions $T_{\text{sp}}<T<T_m$ and $T<T_{\text{sp}}$. We first quench the system to $T=1.25$ (above the spinodal). A plot of χ vs C_s for different waiting times (not shown) gives a straight line with slope $-1/k_BT$, independent of t_w, i.e., the FDT is obeyed. No aging is observed, and the behavior is compatible with a system in equilibrium: this is the *metastable liquid*. On the other hand, a quench to $T=0.67\ll T_{\text{sp}}$ shows aging very clearly (Fig. 16). The FD ratio (Fig. 17) also shows very clearly that the system is out of equilibrium. In fact, we know that the liquid is unstable at this temperature, and that the crystal phase is growing. In a system undergoing coarsening, like the Ising model quenched below T_c, the susceptibility rapidly saturates at the value corresponding to the low-temperature phase, because the contribution of the interfaces is negligible. The correlation function, however, continues to drop because of the movement of the domain walls. Thus the FD curve is flat for small values of the correlation function.[36,38,39] We would expect this same behavior whenever the dynamics is given by growing domains with bulk equilibrium properties, separated by sharp interfaces. However, the FD curve does not become flat in the CTLS at $T=0.67$, even for our longer waiting times. Instead, the system shows FDT violations similar to those commonly exhibited by structural glass models[25,35] and certain mean field spin-glasses (solved by a one step replica broken solution, one-step RSB).[34] There are two regimes: a quasiequilibrium one with slope $-\beta$ and an off-equilibrium one with slope $-\beta_{\text{eff}}=-X\beta$. Note that the FD curves hardly depend on t_w, at least for the times the simulations can reach.

Taken at face value, this result would lead to interpret this as an out-of-equilibrium glassy phase (i.e., a liquid with weakly broken ergodicity). However, in the light of the discussion of the preceding section we known that for $T<T_{\text{sp}}$ the crystal growth dynamics proceeds through two qualitatively different time regimes. Due to the extremely slow activated dynamics the bubbling regime can last for long, and indeed at very low temperatures it is the only one accessible in our simulation times. In this case, we do not expect to see in the response– correlation relation the FDT violations typical of coarsening systems, since the coarsening regime has not yet been attained. This is exactly what happens for $T=0.67$: we can check that the crystal mass for the longest time explored in Fig. 17 is $m\sim 0.3$ [Fig. 14(right)], well below the value $m\sim 0.5$ that characterizes the crossover to the coarsening regime. The 1-RSB-like FDT violation observed at $T=0.67$ thus occurs in the bubbling regime, while if we could wait longer times we would observe a crossover to typical coarsening behavior.

Since the duration of the bubbling regime is shorter for higher temperatures, we expect to explicitly observe an FDT crossover to the coarsening regime at higher temperatures. From the former sections we know that at $T=1.00$ the crossover from the bubbling to the coarsening regime takes place at about 10^4-10^5 MCS. In Fig. 18 we plot the FD curves for $T=1.00$, and the data confirm our expectations. For short

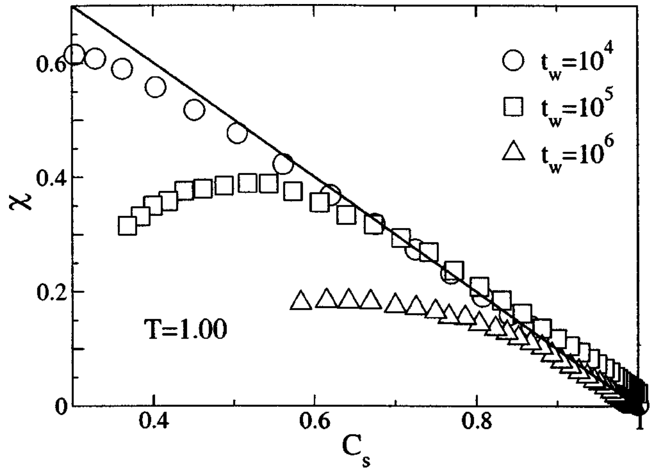

FIG. 18. Parametric plot of $\chi(t,t_w)$ vs $C_s(t,t_w)$, at various values of the waiting time t_w for $T=1.00$, below the spinodal temperature. $L=500$. The full line represents the equilibrium relation $\chi=\beta(1-C_s)$.

waiting times, the curves initially follow what seems to be the path of a 1-RSB-like violation. This is the bubbling phase, pretending to be a glass. The curves depend strongly on waiting time, and for higher t_w evolve toward the normal domain-growth curve (two straight lines, with slope $-\beta$ at short times and 0 at long times), which is nearly reached for $t_w=10^6$ MCS.

VI. CONCLUSIONS

We have presented a lattice model, the deterministic CTLS, which exhibits a phenomenology typical of glass forming systems: it has a melting transition and a low temperature crystalline ground state, but it exists as a supercooled liquid for a wide range of temperatures; in the metastable supercooled phase the relaxation time increases in a way resemblant of typical fragile glasses and upon fast cooling crystallization can be easily avoided to bring the system in disordered glassy-like states.

The feature that makes this model particularly interesting is that it displays a metastability limit which can be explicitly observed within the time scales available for numerical simulations. What we have shown is that the typical phenomenology of fragile glass forming systems is entirely compatible with the existence of a metastability limit of the supercooled phase, even if it is plausible that, contrarily to the CTLS, for many models this limit cannot be observed. A crucial point in this regard concerns the length of experimental times under which measurements are performed. By definition the supercooled liquid loses stability at T_{sp}, when crystal nucleation becomes faster than liquid equilibration. If the equilibration time at T_{sp} is much larger than the experimental time, however, the metastability limit cannot be observed. Since the glass temperature T_g is the lowest temperature at which the system is equilibrated within the experimental time, this situation takes place when $T_{\mathrm{sp}}<T_g$.

If the system has a metastability limit, below the pseudospinodal T_{sp} the dynamical behavior basically consists of very slow crystal growth. This suggests some criteria to detect whether a system has such a metastability limit or not, even when T_{sp} is experimentally inaccessible. For example, one would *a priori* think that there is a qualitative difference between a disordered glassy configuration, obtained by quenching a liquid, and a crystalline configuration, however rich in defects this is, and however slow crystal growth may be. Also, since off-equilibrium dynamics of simple domain growth has very peculiar characteristics one would hope to detect crystal growth by analyzing the dynamical behavior of the system, and in particular the pattern of FDT violations. What we have shown in the CTLS is that actually neither of these criteria is sharp enough, and if our experimental time were not long enough to *explicitly* observe the loss of stability of the liquid at T_{sp}, it would be impossible to make statements about it, either by structural or dynamical means. On the other hand, on shorter time scales the system exhibits an off-equilibrium behavior which is typical of structural fragile glasses. Indeed, we have seen that there is a long time regime where FDT violations are 1-RSB like, as in most fragile glass models studied so far, while the proper coarsening regime is attained only at much larger times. Also, there is structural continuity between the low-temperature configurations reached via fast coolings and those approached with slower cooling rates, which means that the degree of order in the system increases gradually: what appears as a disordered glassy like configuration is just the beginning of a continuous process that eventually, on much longer time scales, leads to the crystal. The reason for this behavior is that below T_{sp} crystal nucleation is fast, but crystal growth becomes very slow, with many crystal droplets trying to expand in a liquid background. In such a situation distinguishing between a truly disordered glass and a mixture of tiny mismatched crystallites becomes very hard, and FDT violations are nontrivial.

An important consequence of the metastability limit scenario in the CTLS is that the Kauzmann paradox is avoided: below T_{sp} the liquid does not exist in any reasonable sense, thus extrapolation of the excess entropy is meaningless. This was the resolution of the paradox proposed by Kauzmann himself in his paper. While we cannot claim that this is the case for real glasses (and we have discussed qualitative alternative scenarios in terms of crystal nucleation and growth), this system shows that Kauzmann's way out of the Kauzmann paradox should be considered seriously. In the study of glassy systems the crystal phase is often neglected, assuming that if crystallization is avoided at T_m, then the crystal does not play any role in the low temperature physics. What this model shows is that the stability of the supercooled liquid should not be taken for granted.

Finally, even if stability were to be proved not to be a concern in real systems, this remains a cautionary note when formulating nondisordered glass models, especially on the lattice, which is so attractive. One can also wonder if these considerations might be applicable to disordered systems, or systems with complex (highly degenerate) low-temperature phases, were the supercooled liquid could be unstable with respect to a crystal in disguise.

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[29] T_f can be estimated as the temperature where thermal activation becomes extremely rare even for simple rearrangements, i.e., $\delta/T_f \gg 1$ where δ is the *smallest* barrier to kinetic motion.

[30] We recall that both these quantities are define as densities. The actual linear length of a domain is $L\xi$, and the total crystal mass is $L^2 m$.

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