Cooling-rate effects in a model of (ideal?) glass

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Abstract

Using Monte Carlo simulations we study cooling-rate effects in a three-dimensional Ising model with four-spin interactions. During coarsening, this model develops growing energy barriers which at low temperature lead to very slow dynamics. We show that the characteristic zero-temperature length increases very slowly with the inverse cooling rate, similarly to the behaviour of ordinary glasses. For computationally accessible cooling rates the model undergoes an ideal glassy transition, i.e. the glassy transition for very small cooling rate coincides a thermodynamic singularity. We also study cooling of this model with a certain fraction of spins fixed. Due to such heterogeneous crystallization seeds the final state strongly depends on the cooling rate. Only for sufficiently fast cooling rate does the system end up in a glassy state while slow cooling inevitably leads to a crystal phase.

\S 1. Introduction

Although intensively studied for several decades [1], glasses are still not fully understood due to their very complicated structure. However, gradual progress can be clearly observed. Recently, very interesting theoretical results were obtained concerning for example, aging in some models with glassy dynamics [3]. From the theoretical point of view, one of the problems is the lack of sufficiently simple models of glasses. Although recently important progress has been made, the most realistic off-lattice models still constitute an enormous computational challenge [3]. A possible alternative might be lattice models. Even when existence of the lattice structure is questionable, such simplified models sometimes do provide a satisfactory description of a macroscopic system. A prime example is that the critical point of certain binary alloys is in the universality class of the three-dimensional ferromagnetic Ising model [4]. However, an Ising model with only ferromagnetic interactions is not a good candidate for a model of glasses, since its relatively fast dynamics cannot trap the system in the disordered (glassy) phase and the system quickly reaches the low-temperature (crystal) phase. The simplest way to slow down the dynamics is to introduce randomness into the Hamiltonian of the model [4]. However, glasses under certain experimental conditions might be transformed into translationally invariant crystals, and it is unlikely that random Hamiltonians lead to translationally invariant solutions. This suggest one should look for translationally invariant Hamiltonians with a glassy phase resulting exclusively from the dynamics of the model and not from built-in randomness.

In random systems slow dynamics is mainly due to energy barriers [4]. Is it possible to generate energy barriers in non-random models? A positive answer to this question was given
some years ago by Shore et al. [7, 8]. who showed that in the three-dimensional Ising model with nearest- and frustrating next-nearest-neighbour interactions (SS model) there exist energy barriers, which diverge with the size of correlated regions. These barriers are due to the fact that the energy of an excitation in this model depends not only on the area of its boundary (like in the ordinary Ising model) but also on the total length of edges of this boundary. At sufficiently low temperature, due to these barriers, the dynamics of the model is able to trap the system in the disordered phase, which we can tentatively identify as a glassy phase. The trapping mechanism is effective only for temperatures below the corner-rounding transition $T_{cr}$. For $T > T_{cr}$ the trapping mechanism is not effective, fast (ordinary) dynamics is restored, and the system quickly evolves toward the low-temperature phase. However, Shore et al. argued that their model is not yet a satisfactory model of glasses because these barriers vanish at the corner-rounding transition, which in turn implies unrealistically fast increase of zero-temperature characteristic length $l_0$ with the inverse cooling rate $r^{-1}$. It would thus be interesting to look for some other non-random models which generate energy barriers and which, hopefully, would be free of this deficiency.

Recently, it has been shown that the three-dimensional Ising model with plaquette interactions also generates diverging energy barriers which slow down the low-temperature dynamics [9, 10]. The energy barriers in this model appear due to the same mechanism as in the SS model. However, in a number of respects the behaviour of this model is quite different from the SS model. Firstly, there exists a temperature $T_g$ (later identified as a glassy transition temperature) which separate two regimes: For $T > T_g$ the random quench, after short transient, reaches the liquid phase in which it is seems to be stable, at least during computationally accessible time scale. For $T < T_g$ the random quench evolve toward the low-temperature phase, but due to the above mentioned energy barriers, it gets trapped in the glassy phase. However, the crystal sample undergoes a transition into the liquid phase at the temperature which is considerably higher than the glassy transition $T_g$. It means that in a certain temperature range, due to very strong metastability, the system remains either in a crystal or liquid phase, depending on the initial configuration. In addition, numerical calculations suggest [10] that in this model energy barriers exist even for temperatures $T > T_g$, and thus this model might be free of the cooling-rate anomaly of the SS model.

The objective of the present paper is to examine the behaviour of this model under cooling. We show that the characteristic zero-temperature length indeed increases much more slowly with the inverse cooling rate than in the SS model and it is probable that this increase is logarithmic $l_0 \sim -\ln r$, as is expected for ordinary glasses.

However, for extremely slow cooling rates such an increase of $l_0$ in our model is unlikely to hold. We observed [10], that although very strong, metastability in this model is only a quantitative effect and for a sufficiently large system size a droplet nucleation mechanism should be effective. It means that for temperature below the critical temperature (which is determined from the crossing point of the free energies of the liquid and crystal phases) the model prepared in the liquid state should collapse onto the crystal (or glassy) phase within a finite time. However, the estimated size of critical droplets is rather large which suggests [10] that this finite time is also large. Thus, cooling rates needed to observe such a collapse are presumably computationally inaccessible.

Some time ago Anderson proposed [11] that the glassy transition, which is a kinetic phenomenon, might be related in the limit of small cooling rate with a certain thermodynamic transition. The results of the present paper show that the Ising model with a plaquette interactions provides an interesting realization of this idea: the peak in the specific heat of the liquid occurs exactly at the temperature where the internal energy jumps under very slow cooling.

Anderson's idea has had a rather limited experimental support [12]. The main problem is that under slow [13] cooling real liquids do not get trapped in the glassy phase but instead
crystallize. The reason for that is that when liquid is cooled below the melting point it becomes metastable and within a finite time due to heterogeneous or homogeneous crystal nucleation \[14\] it crystallizes. Only under sufficiently fast cooling can the crystal nucleation be avoided and the liquid be trapped in the glassy state. In this context, the model with plaquette interactions corresponds to an almost ideal liquid with an extremely large lifetime of a metastable state. Although such strong metastability allows us to examine the interesting regime of slow cooling, it is also inhibits the crystallization of supercooled liquid. To study the competition of crystallization and glass formation within computationally accessible times we enhanced the former effect by fixing a certain fraction of spins. We observe that due to such heterogeneous crystallization seeds the final state of the system indeed strongly depends on the cooling rate. Namely, only for sufficiently fast cooling can the system beat the crystallization trap and end up in a glassy state. When the cooling is slow, similarly to real liquids, the system crystalizes. Thus, in agreement with experiments, the glassy transition appears to be a kinetic phenomenon with the cooling rate determining the final state of the system. These results appear to indicate that the three-dimensional Ising model with plaquette interactions is a very promising candidate for a lattice model of glasses.

In section 2 we introduce the model and briefly describe its already reported, rather unusual, properties. In section 3 we study the behaviour of our model under continuous cooling. The analysis of the results in presence of crystallization seeds is done in section 4. Final discussion of our results, including the relation with the ideal glassy transition, is presented in section 5. In this section we also argue why our model, being in some sense fine-tuned, might shed some light on the apparent robustness of glasses.

§ 2. Model and its basic properties

In the present paper we study the three-dimensional Ising model with a four-spin interaction. Models with multi-spin interactions have frequently been used, for example, in the context of random surfaces \[15\] or lattice field theory \[16, 17, 18\]. There are also some reports of glassy behaviour in such systems \[19, 20\]. Our model is defined by the following Hamiltonian

\[
H = - \sum S_i S_j S_k S_l,
\]

where the summation is over elementary plaquettes of the cubic lattice and \( S_i = \pm 1 \). This model was recently studied in the context of lattice field theory \[21\]. Moreover, the glassy behaviour was studied for the random version of model \(2.1\) \[22\]. Clearly, a ferromagnetic configuration minimizes the Hamiltonian \(2.1\). It is also easy to realize that flipping coplanar spins does not change the energy. Thus any configuration obtained from the ferromagnetic configuration by flipping coplanar spins is also a ground-state configuration. Also any combination of such coplanar flippings (even for crossing planes) does not increase the energy. Simple analysis along these lines shows that for the model on the lattice of the linear size \( L \) the degeneracy of the ground state is equal to \( 2^{3L} \). Although the ground state of this model is strongly degenerate, its ground-state entropy is zero.

All the results reported in this paper were obtained using a standard Monte Carlo method with random sequential update using Metropolis algorithm \[23\]. Some other details concerning these simulations can be found elsewhere \[10\].

2.1 Thermodynamics and metastability

Upon heating an arbitrary ground-state configuration, the model undergoes a sharp transition at the temperature \( T \sim 3.9 \), where we have put the Boltzmann constant \( k_B \) to unity \[3, 21\]. This transition is accompanied by a pronounced peak in the specific heat. The system sizes \( L = 24 \) and
40 used in these simulations were rather large and the location of this peak is almost independent on \( L \). These results suggest that the model undergoes a thermodynamic transition around \( T = 3.9 \).

It is thus surprising that upon cooling a high-temperature (liquid) sample the model does not undergo any change at \( T = 3.9 \). Instead, it is only when cooled below \( T = T_g \) \( \sim 3.4 \) that the liquid looses its stability and evolves toward the low-temperature phase. We observed that for \( 3.4 < T < 3.9 \) it is virtually impossible to direct the evolution of a liquid sample toward a low-temperature phase. The transition at \( T = T_g \) is also accompanied by a peak in the specific heat and for the examined system sizes, \( L = 24 \) and \( 40 \), the location of this peak is also almost independent of \( L \). The behaviour of the specific heat in the vicinity of \( T_g \) is shown in Fig. 1.

Using thermodynamic integration we calculated the free energy of both liquid and crystal phases of the model \([10]\) which show that the crossing point of these free energies is around \( T = 3.6 \). However, no changes were observed at that temperature during the heating or cooling. The above described thermodynamic properties suggests that at computationally accessible time scale, model \((2.1)\) undergoes two transitions depending whether the system is being cooled or heated. These transitions seem to screen the 'true' first-order thermodynamic transition which presumably takes place around \( T = 3.6 \) i.e., at the crossing point of the free energies.

Such behaviour of model \((2.1)\) resembles hysteresis and metastability effects, which frequently occur in ordinary first-order transitions. However, it is believed \([24]\) that for short-range interacting systems such effects are only quantitative and longer simulation time decreases the hysteresis range and eventually pinpoint the temperature of the first-order transition. On the other hand, our simulations \([10]\) suggest that in model \((2.1)\) squeezing the hysteresis into the temperature range smaller than \((3.4, 3.9)\) is almost impossible \([25]\). The only way to overcome the very strong metastability of model \((2.1)\) is to start simulations from inhomogeneous initial configurations, i.e., containing both phases of the system. Indeed one observes \([10]\) that evolution of such a system depends on whether temperature is above or below the expected thermodynamic transition \( T = T_c \approx 3.6 \) \([26]\).

In the last section we suggest that the metastability of model \((2.1)\), which is probably strongly related with its glassy properties, is caused by energy and entropy barriers. However, more precise understanding of the mechanism generating such a strong metastability is clearly desirable.

### 2.2 Domain coarsening and energy barriers

When cooled below its critical point, a macroscopic system undergoes the interesting phenomenon of domain coarsening \([27]\). Various theoretical and numerical techniques predict that for systems with a scalar order parameter and nonconserved dynamics, as is the case here, the characteristic length \( l \) (which approximately corresponds to the average size of domains) should increase with time \( t \) as

\[
l \sim t^{1/2}.
\]  

(2.2)

However, as shown by Shore et al. \([7]\), for certain models of this kind the increase of \( l \) can be much slower. Namely, they have shown that for the SS model and sufficiently low temperature the characteristic length \( l \) increases only logarithmically in time \( (l \sim \ln t) \) \([28]\). Such a slow increase is compatible with the widely accepted conception of glasses.

Recently we have noted that for model \((2.1)\) the characteristic length also increases very slowly in time, presumably also logarithmically. An additional support to the fact that \( l \) might increase in the same way as in the SS model comes from the fact that both models at low temperature generate energy barriers in the same manner.

To see how these barriers arise in model \((2.1)\), let us consider first its two-dimensional (square lattice) version. In particular, let us consider a square domain of ‘\(^{-}\)’ spins of linear size...
surrounded by ‘+’ spins (see Fig. 3a). Elementary counting immediately shows that the energy excess of such a domain is independent of its size $M$ and depends only on the number of corners in this domain (i.e., four). Such a dependence of energy of excitation on its size should be contrasted with the ordinary (two-spin) Ising model, where this excess energy is proportional to the perimeter of the excitation (i.e., $4M$). Next, let us observe that to remove such an excitation the system has to flip some of the ‘–’ spins, but this will inevitably increase the number of corners in the resulting domain and thus the energy (see Fig. 3b). This argument easily generalizes to three dimensions: for the cubic-like domain the excess energy is proportional to the total length of boundary edges (i.e., $12M$). Similarly to the two-dimensional case, to remove such an excitation the system has to climb some energy barriers, which this time will increase linearly with $M$. At low temperature such barriers make the process of removing such excitations extremely slow. Similar arguments were more thoroughly elaborated for the SS model.

However, to show that such barriers are relevant in the process of coarsening one has to show that the system spontaneously generates such cubic configurations. Snapshot configurations for the SS model clearly show that the system indeed generates such configurations. However, due to strong degeneracy of the ground state, the situation is more complicated for model (2.1). Firstly, let us notice that low-energy domain walls, as between ‘+’ and ‘–’ domains, are not the only possibility. For example, a cubic-like antiferromagnetic domain (antiferromagnetic configuration is also one of the ground states) surrounded by ‘+’ spins, as in Fig. 3c, has an excess energy proportional to the area of the boundary (i.e., like in the ordinary Ising model). There are also some other ground states, for which energy of domain walls in some sense interpolates between these low- and high-energy examples. The extent to which these different domains will appear in the late-time configurations is determined by a very complicated dynamic process. In general, however, for high-energy domain walls the energy barriers are much smaller or even non-existent and we expect that they will be relatively quickly eliminated and the late-time evolution will be dominated by dynamics of low-energy (and high-barrier) domains. To some extent this is confirmed in Fig. 2 which shows a zero-temperature snapshot configuration obtained during a cooling process, which is described in more details in the next section. Although we would need the whole three-dimensional structure to draw domain boundaries, we can see that indeed a lot of relatively large cubic-like (flat) ferromagnetic domains exist and they are presumably the principal reason for the slow dynamics of model (2.1). This argument will be also used in the next section to relate the energy excess and the characteristic length.

To summarize this subsection, our simulations suggest that the low-temperature (i.e., at $T < T_g$) coarsening in model (2.1) is very slow, which is presumably related with energy barriers which the model can spontaneously generate during such a process. An independent confirmation of the model’s slow dynamics is presented in the next section.

§ 3. Cooling

A glassy transition is essentially a kinetic phenomenon, which appears when a physical system is being cooled. Usually one prepares the system at a certain temperature above the glassy transition and then lowers the temperature e.g., at a constant cooling rate $r = \frac{dT}{dt}$. One of the important quantities describing this process is a zero-temperature characteristic length $l_0$ which can be regarded as an average size of domains at the end of the cooling process (i.e., at $T = 0$). Of course the slower the cooling the larger the characteristic length $l_0$, since the system has more time to build some local order. However, for glasses the growth of domains is very slow. More precisely, on phenomenological grounds, one expects that in glasses $l_0$ increases only
logarithmically with the inverse cooling rate, namely
\[ l_0 \sim \ln(1/r). \] (3.1)

Such a slow growth of \( l_0 \) might be contrasted with a much faster one,
\[ l_0 \sim r^{-1/2}, \] (3.2)

which appears in an ordinary Ising model. Actually, it is conjectured that the exponents entering asymptotic expressions (3.2) are the same also for other types of dynamics. With this conjecture, the relation (3.1) is simply a consequence of the fact that for glasses the characteristic length \( l \) is expected to grow logarithmically in time.

However, from the fact that the model has a slow low-temperature dynamics does not follow that \( l_0 \) also slowly increases as function of inverse cooling rate. This is clearly the case of the SS model: when prepared at a temperature above the critical temperature and submitted to some cooling, the model inevitably has to pass through the fast-dynamics temperature range. For the small cooling rate the growth of order in this temperature range is dominant and thus \( l_0 \sim r^{-1/2} \) follows. Such a rapid increase of \( l_0 \) is the main reason why SS is not yet a satisfactory model of glasses. In the following we present some numerical data which show that in model (2.1) \( l_0 \) increases much slower than in the SS model and we believe that the growth might be even consistent with (3.1).

We simulated model (2.1) under continuous cooling with a constant cooling rate \( r \) and initial temperature \( T_0 = 4.2 \) (\( T_0 > T_g \)). This means that temperature as a function of time is given by \( T = T_0 - rt \). The temperature dependence of internal energy is shown in Fig. 4. We performed calculations for several system sizes \( L \) in order to ensure that \( L \) was sufficiently large. For example for \( r = 0.02 \) the system size \( L = 30 \) is sufficient to obtain size-independent results but for \( r = 0.00002 \) we had to take \( L = 70 \). One can see that although \( r \) decreases by three decades, the zero-temperature energy \( U_0(r) \) very slowly approaches the ground-state energy \( U_{gs} = -3 \).

Such a behaviour provides a qualitative confirmation of the glassy dynamics of our model. For a quantitative comparison we have to relate the excess energy \( \delta U(r) = U_0(r) - U_{gs} \) with the characteristic length \( l_0 \). Although it is not a rigorously established relation, one can assume that these quantities are related in the following way
\[ \delta U(r) \sim \frac{1}{l_0^2}. \] (3.3)

To find how \( l_0 \) increases with the inverse cooling rate, we plot \( \delta U(r) \) as a function of \( r \) in the double-logarithmic scale and the graph is shown in Fig. 5. From this plot one can infer that approximately \( \delta U(r) \sim r^{0.2} \) which, using (3.3), becomes \( l_0 \sim r^{-0.2} \). However, the data in Fig. 5 have positive curvature and the asymptotic increase of \( l_0 \) might be even slower. In addition to that we want to argue that relation (3.3) might not hold for model (2.1) and a modified relation will lead to even slower increase of \( l_0 \).

First let us briefly review arguments leading to relation (3.3). Let us consider an ordinary Ising model on the three-dimensional lattice of linear size \( L \). If characteristic length is equal to \( l \), then the number of domains in this system scale as \( (L/l)^3 \). Since the energy associated with each domain scales as \( l^2 \) (i.e., like the area of the surface of domains), thus the total excess energy per site in the system scales as \( l^2(L/l)^3/L^3 = 1/l \) and (3.3) follows. However, as we have mentioned in the previous section, model (2.1) might generate low-energy interfaces whose energy scales as \( l \). Repeating the above arguments for such interfaces immediately implies
\[ \delta U(r) \sim \frac{1}{l_0^2}. \] (3.4)
instead of (3.3). Although it is difficult to provide convincing arguments, we would like to argue in favour of relation (3.4) rather than (3.3). Namely, we suggest that at the end of the cooling process (i.e., at $T = 0$), the interfaces in the system will be mainly of low-energy and high-barrier type similar to those shown in Fig. 3a. Indeed, as we have already noticed at the end of the previous section, the high-energy interfaces are those with the lowest (or even zero) energy barriers and thus their removal is likely to be the fastest process in the course of cooling the system. Moreover, as one can see in Fig. 2, the substantial portion of our system is indeed occupied by relatively large and ferromagnetic segments and, as we already mentioned, interfaces between such domains have low energy (and high barriers).

Inverting (3.4) we obtain $l_0 \sim (\delta U(r))^{1/2}$ and thus the increase of $l_0$ would be given by half of the slope in Fig. 5. This would imply that $l_0$ increases like $r^{-0.1}$ or, taking into account the positive curvature in Fig. 5, even slower. But even with (3.3) rather than (3.4) holding, the increase of $l_0$ ($\sim r^{-0.2}$ or slower) is very slow and equally likely one can expect that the asymptotic increase is only logarithmic with $r$. However, much more extensive simulations would be needed to definitely resolve this issue.

§ 4. Crystallization versus glass formation

Although interesting on theoretical grounds, the slow-cooling regime is very difficult to examine experimentally. As we already mentioned in the Introduction, this is because under slow cooling liquids have sufficient amount of time to nucleate `crystal seeds' which divert the evolution toward crystal phase. To beat the crystallization trap and transform the liquid into glass one has to cool the system sufficiently fast, which sometimes requires a very sophisticated technique [14].

As we already mentioned, the free energies of crystal and liquid phases of model (2.1) crosses around $T = T_c \sim 3.6$ which means that for $T_g < T < T_c$ liquid is in the metastable state. On the other hand the present calculations show (see Fig. 4) that in this temperature range even under the slowest, computationally accessible, cooling the crystallization never happens. In order to study the competition of crystallization and glass formation we have to enhance the former process. We did it by fixing a certain fraction of spins in the 'up' state. Numerical results for cooling of such a system are shown in Fig. 6. One can see that for fast cooling ($r = 0.2, 0.002$) liquid becomes trapped in the (high-energy) glassy state. On the other hand, slow cooling enables the system to reach the (low-energy) crystal state. Let us also note that in the limit $r \to 0$ the jump in the internal energy seems to converge to $T = 3.6$ i.e., the crossing point of the free energies of the crystal and the liquid phases. Such a behaviour is consistent with the fact that for $T_g < T < 3.6$ the liquid is metastable and when sufficiently enhanced, the crystallization might take place.

§ 5. Discussion

The main goal of the present paper was to examine the behaviour of the Ising model with a four-spin interaction under cooling. We have shown that the zero-temperature characteristic length increases very slowly as a function of inverse cooling rate. Moreover we have shown that when nucleation seeds are introduced and the cooling is slow enough, the system ends up in the crystal phase. Thus in agreement with many experiments, the glassy transition becomes a kinetic phenomenon driven by the cooling rate. These results, together with the fact that the model possesses a slow coarsening dynamics, is a very strong indication that model (2.1) might capture the essence of the glassy transition in realistic systems. In this section we discuss some other implications of our results.
(i) **Ideal glassy transition**

Some time ago it was proposed by Anderson that in the limit of vanishing cooling rate the glassy transition might be related with a certain thermodynamic transition. This idea has only limited experimental confirmation [12]: the excess entropy of the supercooled liquid extrapolates to zero at a temperature, which seems to be close to the temperature of the singularity of the viscosity, when fitted using the so-called Vogel-Tammann-Fulcher formula. However, experimental difficulties lead to very ambiguous results and even the very existence of this hypothetical thermodynamical transition is still not certain.

More generally, Anderson’s idea expresses the expectation that changes of dynamical and thermodynamical properties should be related. Indeed, there are some reports supporting this statement. For example, some works on frustrated and/or disordered systems indicate that the appearance of nonexponentially decaying correlation functions might be induced by a certain thermodynamical [30] or percolative transition [31]. Another example is the frequently referred to in our paper SS model, where the appearance of the slow-dynamics regime is induced by the corner-rounding transition, which is a well-defined equilibrium transition [32].

In our opinion, the comparison of Fig. 1 and Fig. 4 shows that model (2.1) conforms Anderson’s idea. The specific heat shown in Fig. 1 is a thermodynamic quantity. It was calculated in a (standard) quasi-equilibrium manner: after fixing a temperature we relaxed the system and then measured the variance of the internal energy. The sharp peak seen in Fig. 1 indicates a thermodynamic-like singularity in this model. On the other hand an almost vertical drop of the internal energy under continuous cooling, shown in Fig. 4, indicates the proper (i.e., dynamic) glassy transition. One can see in Fig. 4 that the lower the cooling rate \( r \) the sharper the transition. At first sight one might expect that in the limit \( r \to 0 \) the transition becomes infinitely sharp and coincides with thermodynamic singularities, as e.g., the peak of the specific heat. However, as we already mentioned, our previous results [10] suggest that metastability of the liquid is only a finite time/size effect and neither the peak nor the internal energy drop can be made perfectly sharp. Such a scenario, is in agreement with experimental description of the glassy transition [1].

(ii) **Mechanism of the glassy transition**

Which properties of our model are responsible for the glassy behaviour? The mechanism which we would like to suggest is based on the presence of both entropy and energy barriers. The latter ones were already discussed in this paper and it is likely that they are the source of the slow low-temperature dynamics of model (2.1) and also of the SS model. But they are not sufficient for the model to be glassy: in the SS model these barriers vanish below the critical point and as a result the model orders too quickly.

Measurements of a certain characteristic time suggest that energy barriers in model (2.1) exist even above the glassy transition [10]. When this property is combined with the ability of the liquid to persist down to \( T_g \), it leads to a remarkable consequence: when cooled below \( T_g \), the liquid looses stability and the domain coarsening starts. But the strong energy barriers, which exist between certain types of domains hampers the process and trap the system in the glassy phase. Consequently, there is no fast-dynamics regime in the low-temperature phase and upon cooling the system orders very slowly. The second crucial property is thus the ability of the liquid to persist (for some time) in the metastable state. Since the liquid state is highly disordered, we expect that it is supported by some entropy barriers [33]. The only argument which we can provide to justify this claim is that these entropy barriers are presumably related with the strong degeneracy of the ground state of model (2.1), which leads to many different types of small domains in the liquid phase. In the SS model the ground state is only double degenerate and apparently such barriers are absent.

We have to emphasize, however, that the very concept of energy and entropy barrier is only
approximate. At finite temperature it is more appropriate to consider rather free-energy barriers but then the whole mechanism becomes much more difficult to comprehend. We hope that further studies will explain properties of this model in a more rigorous way.

(iii) Model (2.1) and robustness of glasses
It is sometimes claimed that virtually every liquid can be transformed into glass, provided that the cooling rate is fast enough [14] and any model of glasses should explain such robustness of glasses. As we already mentioned, the glassy behaviour in our model results from the presence of both entropy and energy barriers. How robust might such properties be in real systems? Firstly let us consider the energy barriers. The SS model contains competing nearest- and next-nearest neighbour interactions and model (2.1) contains only multiple interactions. Since both types of interactions are quite common in real systems we expect that such barriers might be a rule rather than an exception. In our opinion, it is the absence of energy barriers (as in two-spin Ising model) which is unlikely to exist in real systems. As for the entropy barriers they are also likely to be common in real systems [13]. However, when model (2.1) is perturbed, for example, by adding a two-spin interaction, then the ground state becomes double degenerate (as the SS model) and entropy barriers will presumably disappear. Such a fragile nature of entropy barriers in model (2.1) might be a consequence of the discreteness of the model. Thus, retaining plaquette interactions only in model (2.1) does not mean that we expect that only systems with such fine-tuned interactions exhibit glassy behaviour. Such a choice is needed only to generate entropy barriers in lattice models. In off-lattice models such barriers are likely to be more generic.

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Although we could overcome metastability of this model in direct simulations, we observed that the droplet nucleation mechanism must be effective. Namely, when we start the simulations with the thermodynamically unstable phase with a sufficiently large droplet of a stable phase injected 'artificially' at the beginning then this droplet might divert the evolution toward the stable phase. Without such a droplet the unstable phase remains in its state virtually forever. Moreover, the minimal size of such droplets is rather large which suggests that their spontaneous nucleation is an extremely unlikely event.

With such a choice of the initial configuration the system does not have to nucleate the stable phase and the evolution is greatly enhanced toward the thermodynamically stable phase.

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Figure captions

Fig. 1: The specific heat $C$ as a function of temperature $T$ calculated from the variance of the internal energy for $L = 24$ (○) and $L = 40$ (+). At each temperature we relaxed the system for $10^3$ Monte Carlo steps and measurement was done during $10^4$ Monte Carlo steps.

Fig. 2: An example of zero-temperature single-layer configuration obtained during the cooling of model (2.1) at the rate $r = 0.0002$ and for the system size $L = 50$. Up and down spins are denoted by ◦ and dots, respectively.

Fig. 3: (a) An example of low-energy interface in the two-dimensional version of model (2.1). An excess energy (i.e., the number of ‘unsatisfied’ plaquettes) comes from the four corner plaquettes. To remove such a configuration the system is likely to proceed through configurations like those shown in (b). The excess energy is higher in this case. (c) An example of high-energy interface (ferromagnetic and antiferromagnetic states are ground states of model (2.1)). One can easily see that the excess energy increases linearly with the size of this excitation. However, to remove this excitation the system does not have to increase its energy (there are no energy barriers in this case). The process of removal of such excitations should be much faster and basically such as in the two-spin Ising model.

Fig. 4: The internal energy $U$ as a function of temperature for (from the top) $r = 0.02$, 0.002, 0.0005, 0.00002, 0.00005 and 0.000002.

Fig. 5: The excess energy $\delta U(r)$ as a function of $r$ in the double-logarithmic scale. The dotted line has slope 0.2.

Fig. 6: The internal energy $U$ as a function of temperature for (from the least to the most steep) $r = 0.02$, 0.002, 0.0005, 0.0002, 0.00005, 0.00002, 0.000001 and 0.000002. Calculations were done for $L = 50$ and with 5% of spins fixed in the ‘up’ state. The dotted line corresponds to heating the ferromagnetic state ($L=40$) without any spins fixed. The slow-cooling results ($r < 0.0005$) in the low-temperature regime are indistinguishable from those corresponding to heating.
\[ \log\delta U(r) \frac{1}{3} \]
