Glassy Dynamics in Icosahedral Systems

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A model for describing the dyanmics of glassy systems is presented. The model incorporates the effects of frustration caused by the imperfect packing of icosahedral clusters in flat three-dimensional space and the presence of non-Abelian defect lines. The model is studied by use of Monte Carlo simulations. The addition of uniform frustration causes the dynamics to be glassy.

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Following the recent discovery[1] of metallic glasses which possess fivefold symmetry, there has been a huge literature[2] devoted to the problems of icosahedral ordering and quasicrystals. Substantial progress has been made in an understanding of the detailed atomic structure of these glasses. There have also been suggestions made about how the sluggish dynamics characteristic of glasses is realized in these materials. The basic idea[3-5] is as follows: Packing spheres in a formation modeled on an icosahedron results in an imperfect fit—a phenomenon called frustration. A preference for local icosahedral order is frustrated on long length scales because of the incompatibility of perfect icosahedral ordering in three-dimensional space. The resulting uniformly frustrated structure is characterized by non-Abelian defect lines, the entanglement of which is believed to lead to slow glassy dynamics. To our knowledge, this crucial idea, while plausible, has not yet been fully tested, although some work in this direction has been done by Straley.[6]

First, we motivate and construct a simple model Hamiltonian which embodies the above idea. We then describe the results of Monte Carlo simulations of the model. We find that incorporating frustration does in fact lead to multiple, metastable states and to sluggish dynamics at low temperatures due to trapping in the local minima.

It is believed that a basic building block of all these systems is the presence of icosahedral clusters of atoms. Once we assume that atoms locally form icosahedra, the important degrees of freedom are the orientations and displacements of the icosahedral clusters. The issue of long-range orientational ordering can be addressed by our ataching to each such cluster an SO(3) operator (matrix) which describes its orientation. This operator is the rotation necessary to reach the orientation of the cluster from some standard orientation. Two orientations, represented by operators A and A', are aligned when an energy of the form

$$\mathrm{Tr}(A'A^{-1})-3 \tag{1}$$

is maximized, where Tr is the trace over the spatial indices for the rotation. This is not the only possible form for such an action, but it is the simplest.

A theory built on Eq. (1) fails to account for two important features of the cluster interaction. If an orientation operator, A, is altered by *first* rotating the standard orientation by a symmetry element of the icosahedron, then nothing should change, because the cluster has not changed. This can be handled simply by replacement of A and $A\phi$ (which is not equivalent to ϕA), so that Eq. (1) becomes

$$\mathrm{Tr}[A'\phi'(A\phi)^{-1}]-3\ , \tag{2}$$

where $\phi,\phi'\in I\subset \mathrm{SO}(3)$ (I is the symmetry group of the icosahedron). The partition function must then include a sum over these "gauge" variables (the ϕ's).

The remaining feature is the fact that one cannot fill flat three-dimensional space with icosahedra, which means that there is frustration. Kléman and Sadoc[3] have argued that the frustration can be removed by a packing of the icosahedra on the surface of a hypersphere in four dimensions. Nelson[4] and Sethna[5] have used this idea to show that as we move through flat three-dimensional space, the energy is minimized by the requirement that the orientations not be identically aligned. We model this effect by replacing Eq. (2) by

$$\mathrm{Tr}[A'\phi' g(A\phi)^{-1}]-3\ , \tag{3}$$

where, for simplicity, g is chosen to be a rotation by an angle θ about the axis defined by the line joining the cluster with orientation A to the cluster with orientation A'. The angle θ causes frustration because the system is unable to satisfy fully all bonds simultaneously. At last this can be all put together to form

$$-H_{\mathrm{bonds}}\equiv\sum_{\langle ij\rangle}\{\mathrm{Tr}[A_i\phi_{i,\hat{n}_{ij}}g(\hat{n}_{ij})(A_j\phi_{j,\hat{n}_{ij}})^{-1}]-3\}. \tag{4}$$

Here $\langle ij\rangle$ denotes nearest-neighbor sites i and j; $\phi_{i,\hat{n}_{ij}}\in I$ is the symmetry element for site i for the interaction with the site j, displaced from site i by $\hat{n}_{ij}$. For our calculations we have chosen the sites to lie on a cubic lattice. The notation is illustrated in Fig. 1(a).

It is useful to consider the ordering of the plaquettes, which are defined as the elementary loops of bonds. In our case they are squares as illustrated in Fig. 1(b). Choosing site indices 1, 2, 3, and 4 to correspond to a given plaquette (P), we can define an interaction $W(P)$ by

$$W(P)\equiv \mathrm{Tr}(\phi_{1,\hat{n}_{1,2}}\phi^{-1}_{2,\hat{n}_{2,1}}\phi_{2,\hat{n}_{2,3}}\phi^{-1}_{3,\hat{n}_{3,2}}\phi_{3,\hat{n}_{3,4}}\phi^{-1}_{4,\hat{n}_{4,3}}\phi_{4,\hat{n}_{4,1}}\phi^{-1}_{1,\hat{n}_{1,4}})-3. \tag{5}$$

In the absence of frustration, this term is maximized if the orientations of the sites in the plaquette are all equal up to a gauge choice, and thus serves as a mechanism for controlling the density of vortexlike defects. Furthermore, this term is required by symmetry in a complete theory. We therefore include an additional term in the Hamiltonian of the form

$$-H_{\text{plaquette}}\equiv\alpha\sum_{\text{plaquettes } P} W(P). \tag{6}$$

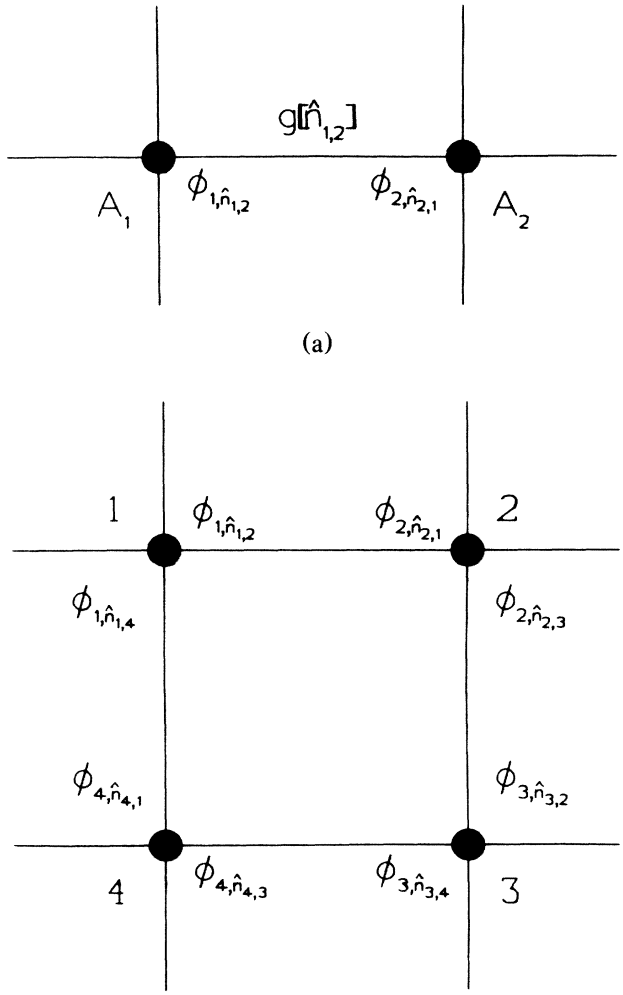

FIG. 1. The notation used for the operators in the text. (a) The variables associated with the pair interactions in H_{bonds}: The A's are SO(3) rotations describing the orientation of the cluster, the ϕ's are gauge variables which maintain the cluster symmetry, and g is a fixed frustration matrix. (b) The gauge variables associated with the sites of a plaquette. Note that the properties of the trace allows cyclic permutation of the site indices so that $W(P)$ is uniquely defined.

The model presented is characterized by no randomness and translational invariance, but with the frustration providing the mechanism for glassy orientational ordering, somewhat reminiscent of glassy plastic crystals.[7] We have ignored the randomness in the positional degrees of freedom by freezing the sites on a cubic lattice. This is because the essential physics behind the slow dynamics is believed to result from the noncommutativity of the orientations making it difficult to untangle defects and should therefore be present whether the system is translatinally invariant or not. One could, in principle, construct a lattice version of the full Nelson-Sethna theory [$A\in$ SO(4)], but the additional variables would make this system computationally prohibitive.

One way of describing the disordering processes is to give an enumeration of the possible topological defects.[8] Defect lines in a theory with spins in symmetry group O are characterized by the first homotopy group $H=\pi_1(O)$. In our case $O=\mathrm{SO}(3)/I$ and hence $H=I'$, where I' is the icosahedral subgroup of SU(2), including possible 2π rotations (see Nelson and Widom[9] for more details). Aside from the additional sign ambiguity, defects are characterized simply by elements of the icosahedral group and hence are *non*-Abelian. Thus the defects have difficulty disentangling themselves because they cannot pass through each other. When this is combined with frustration ($\theta\neq 0$) and its complex energy contours, the result is that the dynamics of the problem may become *very* slow, to the point of becoming glassy.

The Hamiltonian constructed above is perhaps the simplest one that captures the essential physics of non-Abelian defect lines and uniform frustration. The partition function is given by

$$Z\equiv\sum_{\{A_i,\phi_{i,\hat{n}}\}} e^{-\beta(H_{\text{bonds}}+H_{\text{plaquettes}})}, \tag{7}$$

where $\beta=J_0/(k_BT)$, J_0 is a constant energy included here to make H_{bonds} and $H_{\text{plaquettes}}$ dimensionless, and T is the temperature. The g's are fixed matrixes once the frustration θ is chosen. With this formalism the dynamics of such a system is then analyzed by performing standard Monte Carlo calculations[10] at specified values of T, α, and θ.

Although the physically most interesting case is the icosahedral problem, other symmetry groups (such as

tetrahedral, with $\phi \in T$, the tetrahedral symmetry group) can be treated in the same way with similar results. In fact we have performed most of our calculations for the tetrahedral group because the lower entropy causes the transition to occur at a higher, more accessible temperature. Since the results are indeed qualitatively similar for both the icosahedral and tetrahedral cases, we will restrict ourselves to a discussion of the latter results.

Most of our calculations were carried out on a $6\times6\times6$ sample, with periodic boundary conditions. Larger sizes could not be studied in detail because of the relatively long central processing unit time per Monte Carlo step, which results from the extreme complexity of the Hamiltonian.

If glassiness is present, the model is expected to exhibit a large number of metastable energetic minima in any of which the system can be trapped. It is therefore important to study whether, on cooling, the Monte Carlo runs achieve a unique final state. Unless otherwise stated, the energies quoted below are total energies of the $6\times6\times6$ lattice.

The specific heat of the system was calculated while it was being gradually cooled. Figure 2 shows the results with $\alpha=0.05$ for both $\theta=0$ and $\theta=1$. In both cases β was initialized at 0.3 and increased by steps of 0.04. At each β, the first 200 Monte Carlo steps were discarded and the next 400 Monte Carlo steps were used for calculation of the themodynamic quantities. The specific heat was then evaluated at each β from

$$C \equiv \beta^2\{\langle E^2\rangle - \langle E\rangle^2\},$$

where E is the observed energy per site of a configuration and angular brackets denote the thermal (Monte Carlo) average. There is a sharp qualitative difference in the specific-heat data between the two cases. The unfrustrated case appears to be much sharper and smoother than the frustrated case. This distinction is somewhat similar to that observed by Halsey[11] in a model for Josephson-junction arrays. The principal difference between Halsey's model and ours is that our model incorporates non-Abelian defects. The frustrated case is also characterized by a significant increase in the noise in the low-temperature phase. This noise is probably due to the small size of our system. In both the $\theta=0$ and $\theta=1$ cases the transition is around $\beta\sim1$. We have also monitored the density of fully ordered plaquettes having $W(P)=0$. At the lowest temperatures for $\theta=0$, virtually all the plaquettes are fully ordered, whereas for $\theta=1$ only about a third of the plaquettes have $W(P)=0$.

We have also performed slow cooling runs at $\theta=1$, $\alpha=0.05$, starting at a high temperature ($\beta=0.3$) in a totally random initial state. The temperature was dropped by a factor of 0.7 until β reached about 250. At each β, 600 Monte Carlo steps were done. The lowest energy (about 202 with changes of order 0.001) state was

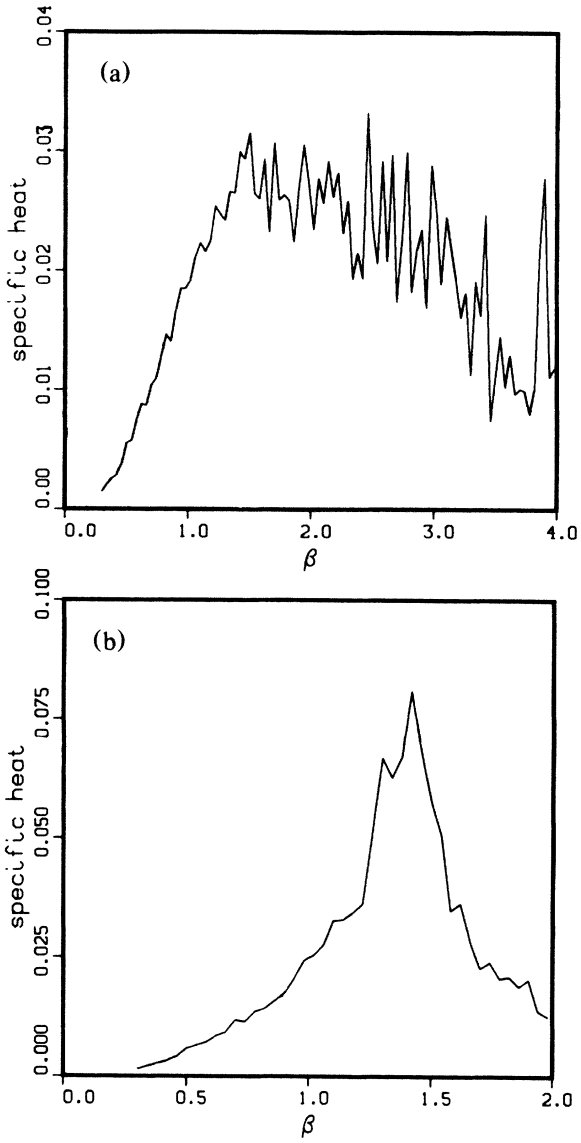

FIG. 2. The specific heat vs β for $\alpha=0.05$ with (a) $\theta=1$ and (b) $\theta=0$.

reached with such a run. The system remains stable after a few thousand Monte Carlo steps, strongly suggesting it has reached a local minimum.

We have also performed several zero-temperature quenches from different initial random configurations at $\theta=1$, $\alpha=0.05$. The system reached different local minima after 600 Monte Carlo steps. The final energies obtained were around 300 with occasional changes occurring in a given run of the size $\gtrsim0.01$. We calculated overlaps for three distinct minima and found the overlap index to be around 0.8 (an overlap index of 1 implies perfect match whereas two random configurations have an overlap of ~0.74), indicating that the local minima did in fact correspond to widely separated points in

phase space. The Monte Carlo results do indicate metastabiltiy with large energetic differences between the local minima.

We have also carried out a low-temperature run ($\beta=10$) with $\alpha=0.05$ while slowly increasing the frustration from $\theta=0$ to $\theta=1$ in steps of 0.025, starting with a uniformly aligned configuration (the ground state for $\theta=0$). At each θ, 150 Monte Carlo steps were performed to watch the evolution of the energy. As θ increases, at some point, the ϕ's will have to start changing. This discrete change produces an energy barrier too high to cross at such low temperatures, resulting in states much more energetic (finally reaching aout 600 at $\theta=1$) than found in the runs at fixed θ. Performing similar runs at a higher temperature ($\beta=3$) allows some of the barriers to be crossed and the final energy reached at $\theta=0.9$ fluctuated between about 360 and 380.

Is the model we have constructed more like a spin-glass than a glass? The key difference between a spin-glass and a glass is that the lattice has a well defined crystalline ground state that the system is unable to reach while it is being rapidly cooled from the liquid state, whereas the spin-glass is not characterized by any obvious ordering. We do not believe that we have located the ground state for $\theta=1$, because we expect the true ground state to have some sort of periodicity analogous to the Frank-Kasper[12] phases in metallic glasses. Perhaps this is not true, but it seems to be a reasonable guess for a uniform system with no disorder. It is conceivable that the inability to find a ground state is related to the incommensurability of the lattice with the preferred structure of the Hamiltonian. This might produce a complex ground-state structure which would require a very long time to reach. To test this, it would be necessary to choose θ so as to become commensurate. We have not done this. Also, it is not clear that it is possible to do this in any nontrivial way, because of the non-Abelian nature of the g's for the three distinct directions. In particular we have looked at $W(P)$ for the plaquettes and found no obvious periodicity even in the lowest energy state. Our inability to find the ground state is consistent with the glassy nature that we are suggesting.

It should be noted that all the runs performed at $\theta=0$ reach an almost fully aligned state as they are cooled, because there is no frustration.

One might wonder whether the above results are an artifact of the small system size considered. We do not believe that this is the case, since larger systems should only have more local minima and even more complicated energy contours.

To conclude, we have argued for the existence of glassy behavior in systems with icosahedral (or tetrahedral) symmetry. This has been illustrated by explicit Monte Carlo calculations which show a complicated low-temperature phase characterized by many local minima and associated metastability in the dynamics.

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