Kinetic Ising Model of the Glass Transition

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A graph theory of single-spin–flip kinetic Ising models is developed and applied to a class of spin models with strongly cooperative dynamics. Self-consistent approximations for the spin time correlation function are presented. One of the dynamical models exhibits a glass transition with no underlying thermodynamic singularity. The approximation for the time correlation function predicts a critical temperature, below which small fluctuations from equilibrium in the thermodynamic limit cannot relax in a finite amount of time.

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The kinetics of structural relaxation in viscous liquids and glasses is a field of much current interest. There are several excellent reviews of relaxation processes in vitreous materials.[1-3] The most commonly used microscopic theories of the dynamics of dense liquids and the glass transition are the free-volume theories[4] and the Gibbs theories.[5] These theories have contributed to our present understanding of relaxation processes in such materials, but they rely on severe mathematical approximations. Montroll and Reiss,[6] Angell and Rao,[7] and Brawer[1] have used simple spin models to investigate the kinetics and development of order in dense fluids. In a recent study, Leutheusser[8] has developed a microscopic model of the glass transition in the hard-sphere fluid. By an approximate analysis of mode-coupling equations, he derived a simple nonlinear equation for the time evolution of the density correlation function that predicts a glass transition.

In this Letter, we introduce a microscopic theory of the glass transition that is based on a kinetic Ising model with very cooperative spin-flip rates. By graphical analysis, we obtain results for the spin system that are very similar to those of Leutheusser for hard spheres. This observation may be a manifestation of some aspect of universality for the glass transition.

The equilibrium properties of our dynamical model are those of the spin-$\frac{1}{2}$ Ising model for N spins on a lattice. (The spin models considered in this paper are standard Ising ferromagnetic models and are not those used to model spin glasses.) The Hamiltonian includes ferromagnetic exchange interactions between all nearest-neighbor pairs of spins and magnetic interaction of each spin with an external field. The state of the jth spin, σ_j, can take the values $+1$ (spin up) or -1 (spin down), and the Hamiltonian is constructed such that a positive field tends to enhance the spin-down configuration.

Following the Glauber construction of a kinetic Ising model,[9] we describe the dynamics of the spin system by a master equation with transition probabilities that satisfy the principle of detailed balance and that allow only a single spin to change state in a differential time increment dt (i.e., a single-spin–flip model). As candidates for models of cooperative relaxation, a class of facilitated kinetic Ising models is considered. An n-spin facilitated model is defined as one for which the flip rate of the jth spin is nonzero only if n or more near neighbors of spin j are in the spin-up state in spin configuration σ.

In this Letter we consider a particular model with $n=1$ and a second model with $n=2$. The one-spin facilitated model is defined by the rate at which the jth spin flips down:

$$W_{j,\mathrm{down}}[\sigma] = m(\sigma)\alpha, \tag{1}$$

where m is the number of near neighbors of spin j that are in the spin-up state in configuration σ and α is a constant that determines the time scale of relaxation at high temperature. The corresponding rate at which the jth spin flips up against the field in spin configuration σ is determined by the condition that $W_{j,\mathrm{up}}$ must satisfy detailed balance with respect to the equilibrium distribution function $p[\sigma]$.[9] The two-spin facilitated model is defined by the down-flip rate

$$W_{j,\mathrm{down}}[\sigma] = \tfrac{1}{2}m(\sigma)[m(\sigma)-1]\alpha. \tag{2}$$

Again the corresponding up-flip rate is determined from detailed balance.

In the present Letter we shall be concerned with the relaxation of small fluctuations from equilibrium. The quantity of interest is the one-spin time correlation function

$$C^s(t) = \langle \sigma_i(t)\sigma_i(0)\rangle - \langle \sigma_i\rangle^2, \tag{3}$$

where $\langle \ldots \rangle$ is an equilibrium ensemble average

over all the 2^N spin configurations and t is the time. We have developed a perturbation expansion for the Laplace transform of the time correlation function,[10] $\hat{C}^2(\epsilon)$ (ϵ is the Laplace variable). The terms in this expansion were assigned a diagrammatic representation and various topological reductions were performed. The time correlation function can be expressed in terms of a single-spin propagator, $\hat{\phi}(\epsilon)$,

$$\hat{C}^s(\epsilon)=4c(1-c)\hat{\phi}(\epsilon)+X[\hat{\phi}(\epsilon)], \tag{4}$$

that has been shown to satisfy the following Dyson equation[10,11]:

$$\hat{\phi}(\epsilon)=\{\epsilon-\Sigma[\hat{\phi}(\epsilon)]\}^{-1}. \tag{5}$$

In Eq. (4), $c=p_1[+1]$ is the exact one-spin equilibrium probability that a spin is up and $X[\hat{\phi}(\epsilon)]$ is a correction to the first term that accounts for correlations between different spins at equilibrium. Because we are interested in spin dynamics in the presence of a field and away from the critical point, such equilibrium correlations will be short ranged. Exact diagrammatic expansions have been derived[10,11] for $X[\hat{\phi}]$ and for the self-energy appearing in Eq. (5), $\Sigma[\hat{\phi}]$.

The self-energy, $\Sigma[\hat{\phi}]$, depends on the fraction of up spins, c, and on the quantity $\alpha\hat{\phi}(\epsilon)$ for the one- and two-spin facilitated models. An approximation to $\Sigma[\hat{\phi}]$ for the one-spin (two-spin) facilitated model that should be accurate at both high and low temperatures (hence, large and small c) can be obtained by summing the infinite set of self-energy diagrams that are first (second) order in c, but that include all orders in $\hat{\phi}(\epsilon)$. For small values of c this approximation should be accurate, because all diagrams not included in the approximation that are nth order in $\hat{\phi}(\epsilon)$ contain at least one more power of c than the nth-order diagrams included in the approximation. For large values of c, $|\alpha\hat{\phi}(\epsilon)|<1$, so that the single diagram in the self-energy series that is zeroth order in $\hat{\phi}(\epsilon)$ provides the dominant contribution to $\Sigma[\hat{\phi}]$. This diagram, however, is included in the approximation described above. Thus, the approximation should be accurate for both large and small values of c, and is expected to be realistic for intermediate values as well. The structure of the diagrams neglected suggests that this approximation for an n-spin facilitated model will be best when n/z is small. A similar analysis of the $X[\hat{\phi}]$ diagrams indicates that $X[\hat{\phi}]$ is negligible in comparsion with the first term in Eq. (4) at both high and low temperatures.

In time units of α^{-1}, the above approximation for the one-spin facilitated model can be written

$$\Sigma_1[\hat{\phi}(\epsilon)]=\frac{-zc\{1+2\hat{\phi}_2(\epsilon)+[\hat{\phi}_2(\epsilon)]^2\}}{(1-c)[1+\hat{\phi}_2(\epsilon)][1+2\hat{\phi}_2(\epsilon)]}, \tag{6}$$

where $\hat{\phi}_n(\epsilon)$ is the Laplace transform of $[\phi(t)]^n$ and z is the coordination number of the lattice. The corresponding approximation for the two-spin facilitated model is given by

$$\Sigma_2[\hat{\phi}(\epsilon)]=\frac{-\frac{1}{2}z(z-1)c^2}{(1-c)[1+(1-c)\hat{\phi}_3(\epsilon)]}. \tag{7}$$

When Eqs. (6) and (7) are substituted into Eq. (5) for Σ, closed equations for $\hat{\phi}(\epsilon)$ are obtained that provide approximations to the time correlation function for the one- and two-spin facilitated models. These equations can be expressed as nonlinear integral equations for $\phi(t)$. They can be solved numerically and analyzed by using the asymptotic techniques developed by Leutheusser.[8]

It is convenient to define an average structural relaxation time for the models, τ, as the area under $\phi(t)$, $\tau=\hat{\phi}(0)$. For the one-spin model, the above equation predicts that $\tau\cong(1-c)/zc$ for large c, and for small values of c the asymptotic behavior of τ is given by $\tau\cong 2/zc$. These results for the relaxation time yield Arrhenius temperature dependence for τ at both high and low temperatures, with the respective activation enthalpies given by $2H$ and $2H+2zJ$. H is defined as the field strength and J is the exchange-coupling parameter between near-neighbor spins.

The low-temperature behavior of the one-spin model is consistent with a defect diffusion picture. Under such conditions the dominant configuration of the spin system will be a large connected region of down spins in which a small number of isolated spin-up "defects" are imbedded. In the one-spin model each such defect can facilitate one of its neighboring down spins to flip up, after which the original defect spin can flip down. Hence, at low temperatures defects have a nonzero diffusion constant and can migrate. The activation enthalpy for the resulting structural relaxation is governed by the activation barrier for a single step in the diffusion process, $2H+2(z-2)J$. To leading order in $1/z$ this agrees with the prediction of Eqs. (5) and (6).

For the two-spin facilitated model, the approximate equation for $\hat{\phi}(\epsilon)$ is very similar to that for the density correlation function in Leutheusser's model of the glass transition [Eq. (3) of Ref. 8]. The self-consistent equation for the two-spin facili-

tated model has the following properties. For $c > c^*$, where

$$c^* = (\tfrac{2}{3})^{3/2}/[z^{1/2}(z-1)^{1/2} + (\tfrac{2}{3})^{3/2}],$$

the approximation for $\phi(t)$ decays to zero at long times. At c^*, the approximation predicts that $\phi(t)$ decays to the nonzero value of $\frac{2}{3}$. For $c < c^*$ we find that $\phi(t)$ decays to a nonzero value $f(c)$, where $f(c)$ is the largest positive real root of the equation

$$f^2(f-1) + \tfrac{1}{2}z(z-1)c^2/(1-c)^2 = 0. \quad (8)$$

Thus, the approximation for the two-spin facilitated model predicts that the spin system will fall out of equilibrium, for $c \leq c^*$.

At large values of c ($\sim \frac{1}{2}$) the decay of $\phi(t)$ is exponential with a relaxation time $\tau \cong 2(1-c)/z(z-1)c^2$. As c^* is approached from above, the spectrum of relaxation times for the two-spin model becomes very broad {consistent with a Williams-Watts function $\sim \exp[-(t/\tau)^\beta]$, $\beta < 1$}. Such nonexponential decays are observed in real materials in the vicinity of the glass transition and are believed to arise from cooperativity of relaxation.[1,8,9]

The approximation for the average structural relaxation time for the two-spin facilitated model on a simple-cubic lattice ($z = 6$) and $c \geq c^*$ is shown in Fig. 1. In the limit of both high and low temperature $-\ln c$ is proportional to $1/T$, so that the figure is similar to an Arrhenius plot for the temperature dependence of τ. The qualitative features of Fig. 1 are in agreement with experiment.[1-5] At high temperature (or large c) the approximation exhibits Arrhenius behavior with a temperature-independent activation enthalpy, but the activation enthalpy becomes strongly temperature dependent as c is decreased towards c^*. The average relaxation time in the present approximation diverges at c^* according to $\tau \sim (c-c^*)^{-1.765}$. This divergence is weaker than in the Vogel-Fulcher expression {$\tau \sim \exp[A/(c-c^*)]$}, which is often used to fit relaxation and viscosity data, but it is known that the Vogel-Fulcher equation does not accurately describe experiments very near the "ideal" glass transition at c^*.[1]

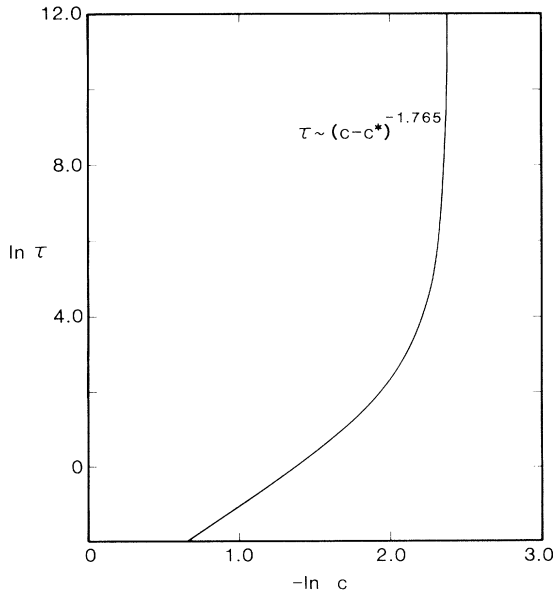

FIG. 1. An Arrhenius-type plot of the average relaxation time, τ, vs the fraction of up spins, c, for the two-spin facilitated model and a simple-cubic lattice. τ diverges like $(c-c^*)^{-1.765}$ at $c^* = 0.0904$.

In Ref. 11 we present an argument that in the thermodynamic limit ($N \to \infty$) for the two-spin facilitated model, the master equation dynamics constitute an irreducible Markov chain on the full manifold of 2^N spin states (with the exception of a set of states with negligible weight). Hence, the equilibrium properties of the two-spin model must correspond to the equilibrium properties of the full manifold of states, i.e., the properties of the equilibrium Ising model. Because the Ising model has no thermodynamic singularities for nonzero field, *the glass transition predicted by the above approximation for the two-spin model has no underlying thermodynamic singularity.* Hence, the transition is a purely kinetic effect resulting from dramatically increased cooperativity of relaxation at low temperatures.

To discuss the nature of this cooperativity, let us consider the case of a simple-cubic lattice in three dimensions. In the two-spin facilitated model at low temperatures, unlike the one-spin facilitated model, there are no defects involving a finite number of up spins that are mobile in the sense that they can cause a propagation of spin-up defects over large distances in a "sea" of down spins. Any collection of defects that is surrounded by a cubic surface of down spins cannot, by itself, cause the down spins in that surface (or outside) to flip up, since each spin in the surface has at most one neighbor in the interior of the surface. The defects are trapped, and the surface spins can relax only by defects propagating in from the outside. However, at low temperatures most defects on the outside are themselves trapped by similar surfaces. In the present approximation, the relaxation time and the activation enthalpy diverge at some critical concentration c^* in the thermodynamic limit. We believe that this divergence is real, but the present approxi-

mation is probably not accurate enough to characterize properly the nature of the singularity.

Other facilitated spin models may exhibit qualitatively different dynamical behavior. In particular, the three-spin facilitated model constructed in the same manner as the models discussed here may exhibit a glass transition that has an underlying thermodynamic singularity. Such a singularity would correspond to a transition in which, as c is decreased by lowering the temperature, at some point only a subset of the entire manifold of Ising spin states is accessible to the system.

A detailed treatment of the theory and results described in this Letter will be published elsewhere.[10,11]

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