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LETTER TO THE EDITOR

A cluster facilitated kinetic Ising model for supercooled liquids

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Abstract. A fundamental modification is considered of the well-known Fredrickson–Andersen (FA) n-spin facilitated kinetic Ising model for studying the glass transition in supercooled liquids, in which the up spins correspond to a liquid-like state A and the down states to a solid-like state B. In our general model, which we call the n-spin cluster facilitated kinetic Ising model, a spin can flip from one state to the other (i.e. is facilitated) only if in the cluster containing the spin and those adjacent to it there are at least n up spins. Thus, in contrast to the FA model, it is easier for an up spin to flip than for one in the down state, which is the physically reasonable motivation for considering this class of models and leads to very different properties. In this communication, we consider the simplest case, namely $n = 1$, for which both a qualitative analysis and computer simulations show that as the temperature of the system decreases, the fraction f_A of spins in state A when the system is in a metastable steady state decreases until it reaches zero at a critical temperature T_c, and the mean relaxation time of the system's memory function increases rapidly as T_c is approached.

The dynamical behaviour of a supercooled liquid near the glass transition temperature is generally assumed to involve some type of frustration that is responsible for the slowing down of the dynamics as the temperature is reduced [1]. There are two main types of approach (apart from molecular dynamic simulations of simple systems) in attempts to understand this behaviour. In one of these, it is postulated that a certain mechanism is operative, such as non-linear interactions between density fluctuations in the popular mode-coupling theory [2], time-dependent interactions in Ngai's coupling model [3], or entropy-driven excitation to the top of a potential energy landscape [4], while in the other, which is the one used in this communication, a simple model system is studied which has features similar to those expected of a supercooled liquid or a glass, and its properties are compared to those of these materials.

The class of model systems that we consider is a modification of the well-known class of n-spin facilitated kinetic Ising (nFKI) models for various values of n proposed by Fredrickson and Andersen (FA) [5]. As in their model, the system consists of two types of region, each corresponding to a group of molecules, which are represented by spins that can be in one of two orientations. The up spin, or orientation A, corresponds to a liquid-like region with a higher-than-average compressibility and lower-than-average density, while the down spin, or orientation B, corresponds to a solid-like region or tightly bound cluster with higher-than-average density and lower-than-average compressibility. The energy of the solid-like regions B is lower than that of the liquid-like regions A, by the amount E, so at low temperatures there is a tendency for spins to adopt the down orientation B. In our modification, which we call the n-spin cluster facilitated kinetic Ising (nCFKI) model, a given spin can only change its orientation, or flip, if this change is facilitated by the presence of a minimum critical number n of up spins in the cluster consisting of a given site and all the sites adjacent to it. This seemingly small modification to the nFKI model, in which transitions are facilitated by the

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presence of n up spins on the sites adjacent to the given site, introduces an asymmetry between the facilitation required for up and down spins which is the fundamental difference between our model and the usual one. In our model, an up spin on a given site only requires $n-1$ adjacent spins to be up for a flip to be permitted, while a down spin requires n such adjacent spins. This is physically quite reasonable, since a region of higher density should require more free volume near it in order to expand than does a low-density region in order to contract. In contrast to the nFKI model, where in the equilibrium state at temperature T the fraction of spins f_A and f_B in states A and B respectively are related by $f_A p_{AB} = f_B p_{BA}$, the only possible steady states of the nCFKI model are those in which all the spins are frozen, with only clusters of $n-1$ up spins present. However, for sufficiently small values of the parameter $x = E/T$, i.e. for sufficiently high temperatures, one expects quasi-steady unfrozen states to be able to exist for very long times, and these will be metastable states of the system. The results of the computer simulations reported below confirm that this is the case for $n = 1$. Such a situation is reminiscent of that in real supercooled liquids, the states of which are by definition metastable [6], and is to be contrasted with the nFKI model where no metastable states exist and there are never any permanently blocked states [7]. In an extension of this model which is more relevant to glasses and will not be considered here, less facilitated flips are also allowed to occur, but with much higher activation energies.

In this communication, we examine only the simplest nCFKI model, namely that for which $n = 1$, in which case the equilibrium state is the unique state in which all the spins are down, i.e. in which $f_A = 0$. Following Graham *et al* [8], we let the rates for a facilitated transition be independent of the number of up spins in the cluster. Thus the basic transition probabilities p_{AB} and p_{BA} for transitions from A to B and from B to A respectively are given by $p_{AB} = h$, a constant, independent of the orientations of the adjacent spins (since $n - 1 = 0$), while if there is an up spin adjacent to the spin in orientation B $p_{BA} = h\exp(-E/T)$, and otherwise $p_{BA} = 0$. For this case, the following simple argument shows that metastable states of the system with $f_A > 0$ are expected to exist up to a critical value x_c of x. Let $f_B = 1 - f_A$ denote the probability that a spin is in a down state. Then the probability that at least one of the spins adjacent to a given down spin is in the up state, with the result that its flip is facilitated, is

$$P_A = 1 - f_B^Z \tag{1}$$

and a steady state should in principle be possible in which

$$\mathrm{d}f_B/\mathrm{d}t = P_A h\exp(-x) f_B - h(1 - f_B) = 0 \tag{2}$$

an equation which has solutions with $f_B < 1$, i.e. non-zero values of f_A, if x is sufficiently small. An upper limit for x_c can be found by considering the following extreme case. If the system is in a state with just one up spin, then if the probability of its flipping to the down orientation B is greater than that of at least one of its Z neighbours flipping to the up orientation A the system will probably freeze into the state with all spins down. The condition for this to occur is

$$h > 1 - (1 - h\mathrm{e}^{-x})^Z \tag{3}$$

and if h is small enough for terms of order $h^2\mathrm{e}^{-2x}$ to be ignored this condition becomes $Z\mathrm{e}^{-x} < 1$. Thus when $x > \ln(Z)$ the system is certainly expected to freeze. However, in practice fluctuations from the most probable events will lead to f_A becoming zero for much lower values of x. While such fluctuations are of course possible for any value of x, the likelihood of their occurring is infinitesimal for small values of x, and extensive calculations show that there is a quite well-defined value x_c of x at which they occur within a reasonable time.

We now present and discuss the results of simulations in which the spins are located on the sites of two-dimensional square lattices and three-dimensional simple cubic lattices. Our calculations were performed for square lattices with sides of length 100, 150 and 200 lattice sites, and for cubic lattices with sides 20, 30 and 40 sites in length. For both types of lattice it was found that the intermediate size, containing 22 500 and 27 000 spins respectively, was large enough to give reliable results. In all our calculations, we used transition rates per Monte Carlo step of $h = 0.03$, since trial calculations showed that smaller values of h did not have an appreciable effect on the results. The maximum number of Monte Carlo steps used in any given run was 8×10^4. The initial state of the system was always that used by FA [5], in which all spins were up, i.e. in orientation A, and the system was allowed to reach a state of dynamic equilibrium before its steady-state isothermal properties were studied.

The first property of the system that we discuss is the average concentration $\langle f_A \rangle$ of up spins. For both the square and cubic lattices, the steady-state value of $\langle f_A \rangle$ was found for any given value of x to be virtually independent of the lattice size for lattices of a given type, and to decrease steadily as x increased, until it became zero for a critical value x_c. The values of x_c that we found were between 0.75 and 0.76 for the square lattices and between 1.38 and 1.40 for the cubic lattices, which are much less than those predicted by equation (3), as expected. In addition the steady-state values of $\langle f_A \rangle$ were much less than those predicted by equation (2), which is also not surprising, since even for the usual FA model mean-field theory does not provide a good approximation [9].

In order to study the dynamic properties of the system, we consider the spin memory function $S(t)$, which measures the fraction of spins that have not changed their orientation by time t in any given run. This is more convenient to use than the spin correlation function $\varphi(t)$ used by FA [5] since it fluctuates less between different simulations, while other workers have found it to be at least as useful as $\varphi(t)$ [10]. We found that $S(t)$ always reached zero after a sufficient number of steps, i.e. no spin was permanently frozen for $x < x_c$. In figure 1, we show, for $x = 0.7, 1.0$ and 1.3, $\log(-\log[S(t)])$ as a function of $\log(t)$ for the simple cubic lattice. In this representation, a stretched-exponential form $S(t) = \exp(-[t/\tau_{SE}]^{\beta})$ [11] is represented by a straight line with slope β. As can be seen from the figure, the stretched exponential is a reasonable approximation for the highest temperature, $x = 0.7$, but becomes

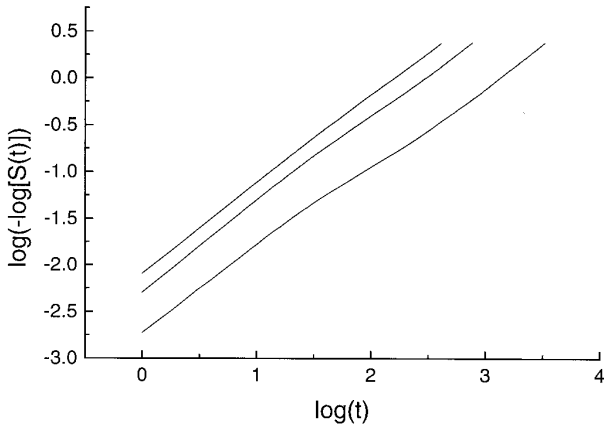

Figure 1. The spin memory function $S(t)$ as a function of the time t, for $x = 0.7$ (the uppermost curve), 1.0 (the middle curve) and 1.3 (the lowest curve).

a poorer approximation as the temperature decreases, i.e. as x increases.

A relaxation time for $S(t)$ can be defined in a number of ways. Two of the simplest of these are either as the mean relaxation time $\langle\tau_s\rangle$ if $S(t)$ is described in terms of a distribution of relaxation times [12] $S(t) = \int g(\tau)\exp(-t/\tau)\,\mathrm{d}\tau$, or as the time τ_{SE} if $S(t)$ is fitted to the stretched-exponential form given above. In view of the results shown in figure 1, it is obviously more useful for our system to use the mean relaxation time $\langle\tau_s\rangle$ to characterize its dynamics. For both the square and the cubic lattices, the values of $\langle\tau_s\rangle$ for different runs were found to be essentially independent of the system size, and also did not fluctuate too strongly between different runs until x approached x_c. Quite remarkably, we found that the mean relaxation time $\langle\tau_s\rangle$ was essentially the same function of x/x_c for the square and the cubic lattices. This is not true for the behaviour of $\langle f_A\rangle$, the value of which is strongly influenced by the topology and so differs for the two types of system, with the result that $\langle\tau_s\rangle$ is not a unique function of $\langle f_A\rangle$. In figure 2, we show $\langle\tau_s\rangle$ for the cubic lattice as a function of x on a semi-logarithmic scale, so that a simple thermally activated process would be represented by a straight line with a slope corresponding to the activation energy. As can be seen from this figure, $\langle\tau_s\rangle$ tends to increase without limit as $x \to x_c$, and certainly does not follow an Arrhenius law, i.e. the dynamics of the system slows down very rapidly as x approaches x_c, just as does the dynamics of a supercooled liquid as the glass transition temperature is approached.

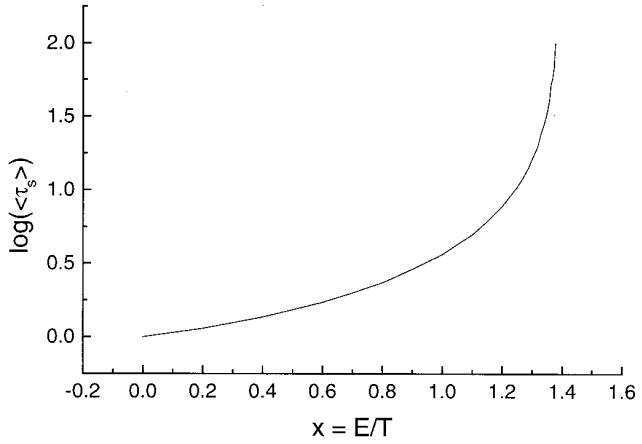

Figure 2. The mean relaxation time $\langle\tau_s\rangle$ of the spin memory function $S(t)$ as a function of $x = E/T$.

We conclude that, at least for $n = 1$, the nCFKI models have a number of properties that differ fundamentally from those of the usual FA nFKI models, and which suggest that they may be an interesting new class of models for a supercooled liquid near its glass transition. In particular, while the only stable state for $n = 1$ is that for which $f_A = 0$, the system exists in metastable states, just as do supercooled liquids, when the temperature is not too low. Our main findings are: that the mean concentration f_A of up spins in the metastable state decreases steadily with increasing values of the parameter $x = E/T$ up to a critical value x_c beyond which $f_A = 0$ and all the spins are frozen in the down orientation; that the mean relaxation time $\langle\tau_s\rangle$ for the spin memory function $S(t)$ increases slowly for small values of x but then very rapidly as x approaches x_c; and that $S(t)$ shows a complicated decay with t which can be well approximated by a stretched-exponential function only when x is not too close to x_c. The first two of these properties, at least, are quite similar to those of the α-relaxation in glasses [1].

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