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A modified facilitated kinetic Ising model for supercooled liquids

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Abstract. A modification is considered of the well-known Fredrickson–Andersen facilitated kinetic Ising model for studying the glass transition in supercooled liquids. In this modification, which we call the cluster facilitated kinetic Ising model (CluFKI) model, the flip of a spin between the liquid-like regions represented by A or up states and the solid-like regions represented by B or down states can occur (i.e. is facilitated) only if in the cluster containing the spin and those adjacent to it there are at least n spins in the A state. As a result, the transition from a solid-like to a liquid-like region requires more free volume than the reverse transition, which is physically very reasonable. Computer calculations for the $n = 1$ CluFKI model, as well as a qualitative analysis, show that as the temperature T of the system decreases, and so the parameter $x = E/T$ increases, the fraction f_A of spins in state A when the system is in a metastable steady state decreases until it reaches zero for a critical value x_c. Correspondingly, the mean relaxation time $\langle\tau\rangle$ of the system's memory function increases rapidly, and $\langle\tau\rangle \to \infty$ as $x \to x_c$. This behaviour is similar to that for the α-relaxation in supercooled liquids as the glass transition temperature is approached.

1. Introduction

An understanding of the dynamical behaviour of supercooled liquids near the glass transition is an important and as yet unresolved problem of condensed matter physics [1]. There are a number of different types of approach to this problem. On the one hand, one can search for a general framework to describe the problem, just as the Ginzburg–Landau theory provides a general framework for describing phase transitions. For this approach, the most successful candidate so far seems to be mode-coupling theory [2], which accounts for non-linear interactions between density fluctuations and predicts such general properties as a critical temperature well above the glass transition temperature, with associated general forms for the behaviour of various properties. However, such general theories do not attempt to describe the microscopic mechanisms responsible for the glass transition, which have a major effect on the detailed properties of real systems, just as general theories of phase transitions cannot predict the rate at which a new phase will be nucleated and grow. Thus, it is important to consider additional approaches to this problem. Another class of approaches use molecular dynamics simulations. For simple systems, such as atoms interacting with the Lennard-Jones potential, these can certainly be used to test the relevance and accuracy of the predictions of mode-coupling theory, but it is difficult to obtain much more information from them. For more complex systems, such as amorphous silicon [3] or vitreous silica [4], it is possible to obtain more detailed information about these specific systems, but this is at the expense of great computational effort. Moreover, they generally do not provide any indication of the minimum requirements for a system to exhibit the properties common to most glass-forming

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liquids [1]. An alternative class of approaches, which is designed to tackle this last problem, is to consider simple well-defined model systems, the properties of which can readily be analysed or calculated and can often resemble those of real systems. This approach has proved of great value in the investigation of phase transitions and critical phenomena, where the simple models that have been used include the lattice gas models and Ising spin models, and has also been used for the glass transition, and that is the approach used in this paper.

One of the simplest model systems that has been extensively studied in connection with the glass transition is the facilitated kinetic Ising model of Fredrickson and Andersen [5], henceforth referred to as the FA model. In this model, 'spins' are situated at the sites of a lattice, and can be in either an up state with spin $\sigma = 1$, which we refer to as state A, or a down state, state B, with spin $\sigma = -1$. Each spin is assumed to correspond to a region of a supercooled liquid consisting of a group of molecules. An up spin is associated with a liquid-like region, with a higher than average compressibility and lower than average density, and a down spin with a solid-like region or tightly bound cluster having a higher than average density and lower than average compressibility. There are no energetic interactions between the spins, but a spin can only change its state if such a transition is facilitated by the presence of at least n spins in the up state on sites adjacent to it. Physically, this means that a region can only change its state if there are enough low-density regions near it, i.e. if it has enough free volume. The basic motivation for this model is that the glass transition is generally believed to be of dynamic origin, i.e. to result from a slowing down of the dynamics of the system as the glass transition temperature is approached. Since the condition on the neighbours of a given spin for a transition to be facilitated is the same for spins in either orientation, the system has an equilibrium state in which the fractions of spins in orientations A and B, f_A and f_B respectively, are related to the basic transition probabilities in the facilitated state, p_{AB} for transitions from A to B and p_{BA} for transitions from B to A, by the requirements of detailed balance:

$$f_A p_{AB} = f_B p_{BA}. \tag{1}$$

The ratio of these transition probabilities at temperature T is a function only of the combination (in the appropriate units) $x = E/T$, namely

$$p_{BA}/p_{AB} = \exp(-E/T) \equiv \exp(-x). \tag{2}$$

It follows from equations (1) and (2) that f_A decreases as the temperature decreases, and so the facilitation requirement becomes more difficult to satisfy, and this leads to a slowing down of the dynamics of the system as the temperature is lowered or x increases [6], but with no evidence of any sudden change in the system's behaviour at any stage [7]. This can be a disadvantage for a modelling of the glass transition, where after a rapid change in the system's properties over a small temperature range the system essentially freezes below the glass transition temperature.

In view of this, we examine in this paper a modification of the FA model which we call the cluster facilitated kinetic Ising (CluFKI) model, the properties of which have previously been described briefly [8]. In this model, we replace the requirement for permitting a flip at a given site of n up spins on the sites adjacent to it by the requirement that the cluster of spins containing that site and all the sites adjacent to it contain at least n spins in the up state. This seemingly small change to the FA model has quite drastic consequences, since it introduces an asymmetry between the facilitation required for up and down spins. An up spin on a given site only requires $n - 1$ adjacent spins to be up for there to be n up spins in the cluster so that a transition is permitted, while a down spin requires n adjacent spins to be in the up state for a transition to be permitted. The physical motivation for such an asymmetry is that, for instance, a region of higher density, as represented by a spin in orientation B, i.e. a

down spin, requires more free volume near it in order to expand and so make a transition to the lower-density orientation A represented by an up spin than does a low-density region to contract and so make a transition to a higher-density one. The model is presented in detail in section 2, and its general properties are discussed. In section 3 we examine which quantities are in general the most useful for characterizing the dynamic properties of a system such as ours, before presenting and discussing the results of our calculations in section 4. Finally our conclusions are presented in section 5.

2. Description and analysis of the model

In the n-spin cluster facilitated kinetic Ising (n-CluFKI) model, as in the FA model, the system consists of two types of region, which are represented by spins that can be in either the up, or A, orientation or in the down, or B, orientation, and the transitions between them will be referred to as flips of the spin. As discussed in the introduction, for a flip to be facilitated, so that a transition is possible, we require that the number of up spins in the cluster consisting of a given site and all the sites adjacent to it must reach a critical number n. This model can be presented in terms of Fock space and second quantization just like the standard FA model [9], but we will not pursue this further here. For the sake of simplicity and convenience, we follow Graham *et al* [10], and let the rates for a facilitated transition be independent of the number of up spins in the cluster. The simplest possible model for such a system is the $n = 1$ model, in which a down spin requires just one adjacent up spin in order to flip, but an up spin can flip without any restrictions. In this case, the only possible equilibrium state of the system is the unique state in which all the spins are down, a state that can always be entered and can never be left, so no transitions from it are possible. However, as we now show from qualitative arguments and as was found in our calculations, the results of which are presented in section 4, at sufficiently high temperatures quasi-steady metastable states exist, with dynamical equilibrium, in which a finite number of spins are in the up state.

For the $n = 1$ model, the probability p_{AB} of transition from state A to state B is a constant, independent of the orientations of the adjacent spins, since a spin in state A is automatically in a cluster containing such a spin. Physically, this corresponds to a liquid-like region being able to change into a solid-like one without requiring any extra free volume, which is not unreasonable. The transition probability p_{BA} is given by equation (2) if there is an up spin adjacent to the spin in orientation B and otherwise is zero. 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 Z spins adjacent to a given down spin is in the up state, with the result that its flip is facilitated, is

$$P_A = 1 - f_B^Z \tag{3}$$

and a steady state should in principle be possible in which

$$\mathrm{d}f_B/\mathrm{d}t = P_A p_{BA} f_B - p_{AB}(1 - f_B) = 0. \tag{4}$$

This is an equation which can readily be solved numerically in conjunction with equation (2). For the simple cubic lattice, where $Z = 6$, this leads to solutions with $f_B < 1$, i.e. to non-zero values of f_A, if $x < 1.791$. However, in practice fluctuations from this average will lead to the system freezing for much lower values of x. While such fluctuations are of course possible for any value of x, the likelihood of their occurring is very small for values of x close to zero, and extensive calculations show that there is a quite well-defined value x_c of x at which they occur. Such a situation is reminiscent of that in real supercooled liquids, which are in metastable states and which effectively freeze before the system reaches the Kauzmann temperature T_K at which their entropy would vanish [11], and suggests that fluctuations from the most probable state at a given temperature could be involved in the glass transition.

In the n-CluFKI model with $n > 1$, similar arguments show that the only possible steady states of the system are those in which all the spins are frozen because only clusters of $n - 1$ adjacent up spins are present. For $n = 2$, for instance, these are the states in which no cluster contains more than one up spin. Because of the large number of such states, which can be regarded as corresponding to a high entropy, it is very easy for parts of the system to enter one of them, and this is why our calculations showed that at any finite temperature most of the spins were frozen and only a small fraction of them underwent transitions for a long period of time. While such a system could correspond physically to an amorphous solid in the glassy state, in which at any instant structural changes will only occur in those regions in which the bonds between molecules are weaker, it is difficult to obtain much useful information from our model without a detailed analysis of the locations of the unfrozen regions which we have not yet performed, and so in the rest of this paper we restrict our attention to the $n = 1$ model.

3. Analysis of the dynamic properties of an Ising spin system

Before we present the results of our computations in section 4, it is worthwhile to discuss how to characterize the dynamic properties of an Ising spin system. This discussion consists of two parts. First of all, we consider which function to use to describe these properties, and then we discuss and compare two ways of characterizing non-exponential relaxation.

There are two types of dynamical property that can be studied for systems possessing states of dynamical equilibrium, namely the rate at which a system initially far from such an equilibrium state approaches it and the properties of the system when it is in dynamic equilibrium. These correspond, respectively, to the response of the system following a rapid change in temperature and to its properties at a given temperature. The physical motivation for our model suggests that it should correspond more to a supercooled liquid at a fixed temperature than to how it responds to a sudden cooling, and so we consider only the properties in the equilibrium state. Since the equilibrium is dynamic, the spin at any given site will fluctuate with time, and in such a case there are two basic dynamic properties of interest. The first of these is the spin memory function $S(t)$, which measures the fraction of spins that have not changed their orientation by time t, and the other is the spin correlation function

$$\phi(t) = [\langle\sigma_i(t)\sigma_i(0)\rangle - \langle\sigma_i\rangle^2]/[1 - \langle\sigma_i\rangle^2]. \tag{5}$$

For a system in which no spin is frozen, both of these functions will tend to zero as $t \to \infty$, but while $S(t)$ is a monotonically decreasing function of the time t for systems of any size, $\phi(t)$ will tend to oscillate for large values of t, especially for systems of a finite size, and this makes it more difficult to analyse and describe its behaviour as a function of t. Moreover, in our system one does not know in advance the equilibrium value of f_A and hence of $\langle\sigma_i\rangle$, and these have to be replaced by their values at time $t = 0$ for any given run. Thus, although in practice we calculated both $S(t)$ and $\phi(t)$, and found that their behaviour was qualitatively quite similar, we will only present the results for the memory function $S(t)$. Incidentally, even for the usual FA model, in which the equilibrium value of $\langle\sigma_i\rangle$ at any given temperature is determined by equations (1) and (2), there has been a discussion in the literature as to which function is the more useful for describing the system's dynamic properties [6].

The two main properties that characterize the behaviour of a relaxation function $f(t)$ for which $f(0) = 1$ and $f(\infty) = 0$ are the timescale of its decrease, which can generally be characterized by a relaxation time τ, and how the relaxation rate changes with time, i.e. the functional form of $f(t)$ as a function of t/τ. A relaxation time for $f(t)$ can be defined in a number of ways. If $f(t)$ is described in terms of a distribution of relaxation times

(DRT) $g(\tau)$ [12]

$$f(t) = \int g(\tau) \exp(-t/\tau)\, \mathrm{d}\tau \tag{6}$$

then the mean value of τ^α is given by

$$\langle \tau^\alpha \rangle = \int_0^\infty t^{\alpha-1} f(t)\, \mathrm{d}t \tag{7}$$

and $\langle \tau \rangle$ is the natural choice for the characteristic relaxation time. Alternatively, if $f(t)$ is fitted to a stretched-exponential form [13]

$$f(t) = \exp(-[t/\tau_{SE}]^\beta) \tag{8}$$

then the time τ_{SE} can be treated as the function's relaxation time. If the fit to a stretched exponential is exact, it is trivial to show that

$$\langle \tau^\alpha \rangle = (\tau_{SE}^\alpha/\beta)\Gamma(\alpha/\beta), . \tag{9}$$

where $\Gamma(x)$ is the gamma function. However, this relationship assumes an exact fit, while in practice the fit to a stretched-exponential function is usually only made for values of $f(t)$ greater than 0.01, while smaller values of $f(t)$ can have an appreciable effect on $\langle \tau \rangle$, especially if $f(t)$ decays algebraically slowly, rather than exponentially slowly, at long times.

For a function $f(t)$ that fits the stretched exponential, the manner in which the relaxation changes with time is obviously described by the stretching exponent β, but no such simple description exists for one described by a DRT. Moreover, the distribution function $g(\tau)$ is usually not readily available from experiment or from the results of computer simulations. However, the standard deviation of τ can readily be calculated, and so can that of $\sqrt{\tau}$, from equation (7). While it would seem more natural to calculate the standard deviation of τ, this involves $\langle \tau^2 \rangle$ and so $tf(t)$, which is very strongly affected by the values of $f(t)$ at long times, where the small values of $f(t)$ are subject to strong statistical fluctuations. The standard deviation of $\sqrt{\tau}$, which involves only $\langle \sqrt{\tau} \rangle$ and $\langle \tau \rangle$, is much less affected by these small values of $f(t)$, and so is a much more convenient measure of the width of the dispersion of τ. For the stretched-exponential function, one readily finds that the normalized standard deviation of $\sqrt{\tau}$:

$$\sigma_N = \sqrt{[(\langle \tau \rangle - \langle \sqrt{\tau} \rangle^2)/\langle \tau \rangle]} \tag{10}$$

is given by

$$\sigma_N = \sqrt{[1 - \Gamma(1/2\beta)^2/\beta\Gamma(1/\beta)]}. \tag{11}$$

This increases monotonically as β decreases from zero for $\beta = 1$ to unity when $\beta \to 0$. Some typical values of σ_N are 0.143 for $\beta = 0.95$, 0.207 for $\beta = 0.9$ and 0.261 for $\beta = 0.85$.

4. Results and discussion

For our CluFKI model it is not possible to find *a priori* the steady state of the system, or even whether such a state exists for a given value of x, and so one has to rely exclusively on the results of numerical calculations in order to study these systems. We report and discuss here only the results of calculations for the $n = 1$ model for three-dimensional simple cubic lattices, since as reported elsewhere [8] the results for the two-dimensional square lattice are qualitatively very similar. Our calculations were performed for cubic lattices of size $20 \times 20 \times 20$, $30 \times 30 \times 30$ and $40 \times 40 \times 40$, and it was found that the intermediate size, containing 27 000 spins, was large enough to give reliable results. In most of our calculations, we used transition rates per

Monte Carlo step of $p_{AB} = 0.03$, since trial calculations showed that smaller values of p_{AB} did not have an appreciable effect on the results for $\langle\tau\rangle$ and $\langle\sqrt{\tau}\rangle$, but for the fitting to the stretched-exponential function we found it preferable to use a value of $p_{AB} = 0.01$. The initial state of the system was that used by FA [5], in which all spins were up, i.e. in orientation A, and for each value of x $(=E/T)$ the system was allowed to reach a state of dynamic equilibrium before several successive runs were performed to determine its steady-state or 'isothermal' properties.

The properties of the system, as functions of x, that are of most interest are the average concentration $\langle f_A\rangle$ of up spins, which we discuss first, and the dynamics of the system, as discussed in the previous section. 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, and to decrease steadily as x increased, until it became zero for a critical value x_c that was approximately 1.385 for the $30\times30\times30$ lattice on which most of our calculations were performed, 1.38 for the $20\times20\times20$ lattice and between 1.39 and 1.40 for the $40\times40\times40$ lattice. These values are much less than the value of 1.79 predicted by equation (4), as is to be expected since if as a result of a fluctuation the system reaches a state in which $f_A = 0$ it will be unable to leave this state. Moreover, as shown in figure 1, we found that the steady-state values of $\langle f_A\rangle$, were appreciably less than those given by equation (4), especially as x approaches x_c. This is not too surprising, since even for the usual FA model mean-field theory does not provide a very good approximation [14]. In contrast to the steady-state value of $\langle f_A\rangle$, the fluctuations $\delta f_A = |f_A - \langle f_A\rangle|$ in f_A were found to depend quite strongly on the lattice size, and to increase somewhat in magnitude as x approached x_c, while their relative magnitude increases rapidly because of the decrease in $\langle f_A\rangle$. This is to be expected, since as the absolute number of up spins (which is given by Nf_A for a system of N spins) decreases, the number of permitted transitions per step decreases and so the probability of relatively large fluctuations from the average steady state increases. For the lattice of 27 000 spins, the relative fluctuations in f_A were about $\pm5\%$ for $x = 1$, where $\langle f_A\rangle = 0.2$, but $\pm18\%$ for $x = 1.30$, where $\langle f_A\rangle = 0.07$, and $\pm38\%$ for $x = 1.36$, where $\langle f_A\rangle = 0.033$.

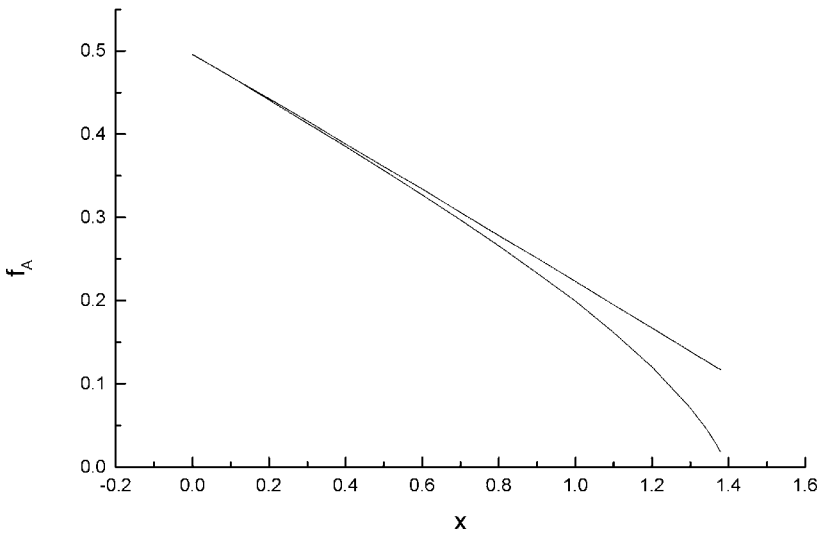

Figure 1. $\langle f_A\rangle$ as a function of $x = E/T$. The upper line is the value predicted by equation (4) for the simple cubic lattice and the lower curve the result found in our calculations.

The first point to note about the dynamic properties of the system is that $S(t)$ always reached zero after a sufficiently large number of steps for $x < x_c$, i.e. no spin was found to be permanently frozen, but $S(t)$ could not usually be fitted to a simple exponential relaxation i.e. $S(t) \neq S(0)\exp(-t/\tau)$. For $x > x_c$ the system is, of course, frozen in the state where all the spins are in the down orientation or solid-like configuration B. Such a freezing could be avoided if one allowed unfacilitated transitions from B to A with a much lower probability, which could correspond physically to the creation of a vacancy and an interstitial in a solid, but this case will not be discussed here.

With regard to the timescale of the relaxation, we found that the mean relaxation time $\langle\tau\rangle$ for several runs and the relaxation time τ_{SE} for a fit of the average results of these runs to the stretched-exponential function differed by not more than 5%, and in figure 2 we show, on a logarithmic scale, $\langle\tau\rangle$ as a function of x, together with the corresponding values of $\langle f_A\rangle$. As can be seen, $\langle\tau\rangle$ increases monotonically with increasing x and decreasing $\langle f_A\rangle$, just as in the FA model [6] and the rapid increase in $\langle\tau\rangle$ as $x \to x_c$ is correlated with the rapid decrease in $\langle f_A\rangle$. The relative fluctuations in $\langle\tau\rangle$ between different runs from its mean value were typically less than $\pm 1\%$ for $x \leqslant 1$, but reached $\pm 4\%$ for $x = 1.30$ and $\pm 20\%$ for $x = 1.36$, so while $\langle\tau\rangle$ tends to increase without limit as $x \to x_c$ the results shown in this figure are not too reliable in this limit. This increase in the relative fluctuations is related to that for $\langle f_A\rangle$ mentioned above, since when most of the spins are in state B the relaxation of the memory function is determined primarily by the flips of the spins in this state, which requires the presence of an A spin on an adjacent site and so is approximately proportional to f_A.

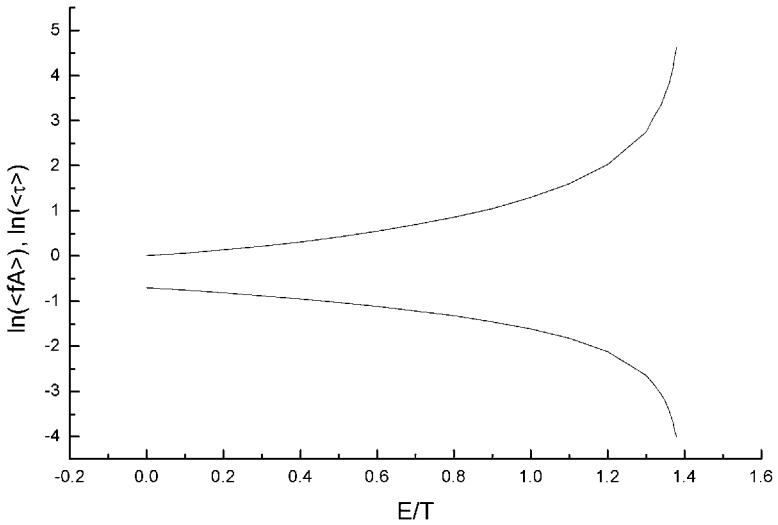

Figure 2. The upper curve shows $\langle\tau\rangle$ and the lower curve $\langle f_A\rangle$, on a logarithmic scale, as functions of $x = E/T$.

Finally, we report the results for the time dependence of $S(t)$. As discussed in section 3, this can be described in terms of either the stretching exponent β of the stretched-exponential function or the normalized standard deviation σ_N of $\langle\sqrt{\tau}\rangle$. The value of β was found to decrease gradually from 0.995 for $x = 0$ to 0.89 for $x = 0.8$, after which it remained steady as x increased up to $x = 1.2$, and then increased and started to fluctuate. According to equation (11), this would correspond to σ_N increasing steadily from 0.04 for $x = 0$ to 0.22 for $x = 0.8$, and then remaining steady up to $x = 1.2$, after which it tends to decrease. By

contrast, our calculations showed that σ_N increased steadily from 0.03 for $x = 0$ to 0.28 for $x = 1.2$, after which it fluctuated and tended to decrease somewhat with increasing x. Both sets of results are shown in figure 3, where the continuous curve connects the points obtained directly from our computer calculations and the isolated points the values derived from the fit to the stretched exponential and equation (11). The differences between the two sets of results are partly because $S(t)$ is not described exactly by a stretched-exponential function and partly because the fit to the stretched exponential was only performed for $S(t) > 0.01$, while the value of $\langle\tau\rangle$ is derived from the behaviour of $S(t)$ at all times. The increase in σ_N with increasing x represents an increase in the dispersion of the relaxation times τ in the DRT model with decreasing f_A, which is physically very reasonable.

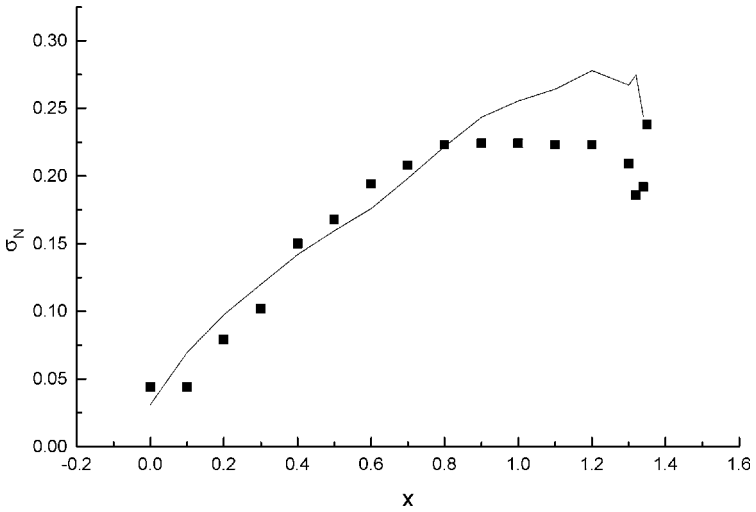

Figure 3. The normalized standard deviation σ_N of $\sqrt{\tau}$ as a function of x. The continuous curve shows the results of our calculations and the points the values obtained from fitting $S(t)$ to a stretched exponential and using equation (11).

From all these results, we see that the CluFKI model with $n = 1$ has two interesting properties, differing from those of the standard FA model, which may be relevant to the behaviour of glasses. Firstly, while the FA systems at a given temperature are always in thermal equilibrium, with f_A given by equations (1) and (2), the CluFKI systems for $x < x_c$ are in metastable states, with fluctuating values of f_A and appreciably lower values of $\langle f_A\rangle$ than those predicted by mean-field theory. This reproduces some of the features of supercooled liquids and glasses [1], which are believed to be in metastable states, the transitions between which can correspond to the fluctuations of f_A in our model, even though their origins in the two cases are somewhat different. Secondly, while in the standard FA model the decrease in $\langle f_A\rangle$ and corresponding increase in $\langle\tau\rangle$ as x increases is gradual and continuous, in the CluFKI model these trends accelerate rapidly as $x \to x_c$, at which point f_A becomes zero and $\langle\tau\rangle$ becomes infinite, i.e. the system freezes, a behaviour reminiscent of that found for the α-relaxation in supercooled liquids as the glass transition temperature is approached.

5. Conclusions

We conclude that the $n = 1$ cluster facilitated kinetic Ising (CluFKI) model, in which only the transition from a high-density solid-like to a lower-density liquid-like region requires

facilitation by the presence of an adjacent lower-density liquid-like region, has a number of properties that suggest it may be an interesting model for a supercooled liquid near its glass transition. For this model, the concentration f_A of up spins decreases monotonically with increasing values of the parameter x, which can be regarded as corresponding to an inverse temperature, up to a critical value x_c beyond which all the spins are frozen in the down orientation, and the mean relaxation time $\langle\tau\rangle$ increases slowly for small values of x but then very rapidly as x approaches x_c. These properties are quite similar to those of the α-relaxation in glasses [1], which is effectively frozen out at temperatures below the glass transition temperature T_g, and for which the relaxation time increases rapidly as the temperature approaches T_g from above.

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