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Evidence of a dynamical length scale in the 'f-spin frustrated kinetic Ising model'

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Abstract. In this paper we study the connection between the equilibrium relaxation properties of glass-forming systems and the spatial organization of cooperative processes which govern their dynamics. This study has been performed by Monte Carlo simulations of f-spin frustrated kinetic lsing models for different local kinetic constraints f. Both the equilibrium dynamics of these systems and the topological properties of their cooperative processes were investigated through the calculation of autocorrelation functions and the distribution of cooperativity lengths. The results show that the different local kinetic constraints induce very different spatial organizations of the cooperative processes and thus heterogeneous dynamics of different natures. On the other hand, whatever their spatial organization, the average spatial extent of the cooperative processes acts as a dynamical length scale which governs the dynamics of the system.

1. Introduction

A most striking feature of the dynamics of glasses is the effective increase of the activation energy detected in undercooled liquids as the glass transition is approached [1]. This behaviour gives rise to the characteristic non-Arrhenian dynamics of glasses and is generally attributed to the increasing cooperativity of the molecular motions upon cooling. This interpretation is, for instance, the framework of the Adam and Gibbs theory [2] which assumes the existence of 'cooperatively rearranging regions' whose size is expected to be inversely proportional to the configurational entropy of the system. However, up to now this assumption could not be confirmed by any direct experimental observation of cooperative processes. The recent finding of heterogeneous dynamics [3–5] in some undercooled liquids and glasses is the only experimental fact which infers the existence of cooperative molecular motions. Two fundamental questions arise from this which we are interested in here:

- Does the increasing spatial extent of the cooperative processes on approaching the glass transition provide a 'dynamical length scale' which governs the dynamics of the system [6]?
- Is there a connection between the temperature evolution of this characteristic length for the dynamics and the static structural correlation length which is suspected to develop in the undercooled liquids?

These attractive open questions [7, 8] are, however, very difficult to address in glass-forming liquids for which such dynamical and structural characteristic lengths are extremely difficult to determine experimentally:

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- A dynamical characteristic length can only be measured indirectly by the analysis of size effects which occur, for instance, when the liquid is confined in small pores [9, 10]. In that case, the linear dimension of the pores must be chosen to compete with that of the spatial extent of the cooperative process.
- A structural characteristic length can hardly be derived from a spatially average structure factor $S(|\vec{Q}|)$ which only gives poor structural information about a possible short-range order developing in the undercooled liquid [2, 7]. Accordingly, no sign of structural ordering could be detected in many glass-forming liquids in their route to the glassy state, even in those which develop a strongly non-Arrhenian dynamics (i.e. in so-called fragile liquids [1]).

All these difficulties partially disappear in computer experiments which allow detailed investigation of both the structure and the dynamics. This advantage is even more effective when studying suitable spin models whose simplicity allows us to selectively study some specific fundamental mechanisms possibly involved in the complex vitrification process. One of these models is the 'f-spin frustrated kinetic Ising model' (f-SFKI model) which has been developed by Fredrickson [11] to test whether the concept of cooperativity can be invoked to explain the dramatic changes of the dynamics on approaching the glass transition. The main feature of this model (described below) is a local kinetic frustration whose strength f can be varied to produce more or less cooperative dynamics. This model has been shown to induce many phenomenological characters of glasses such as, for example, nonexponential relaxations [12], non-Arrhenian dynamics [13], and secondary relaxations [14]. Moreover, because of the simplicity of the model, the cooperative processes which govern the relaxation of the system can be fully characterized. In particular, a cooperativity length L_c can be unambiguously defined [15] and exactly computed for each spin giving a detailed picture of the cooperative processes in the system.

In this paper we use this concept of cooperativity length to study the cooperativity patterns generated by various local kinetic constraints (f) of the f-SFKI model. We will show in particular that different local kinetic constraints f lead to very different spatial organizations of the cooperative processes and thus to heterogeneous dynamics of a different nature. The main goal of this paper is to test whether or not there exists a dynamical length scale which governs the relaxation of the system independently of the spatial organization of cooperative processes.

2. Model and simulation techniques

2.1. The model

Basically, the f-SFKI model is a classical Ising model whose dynamics is made cooperative by a local dynamical frustration rule [11]. We consider the case where the N spins ($S_i = \pm 1$) of the system do not interact together. They only interact with an external magnetic field (h) so that the Hamiltonian of the system is simply:

$$H = h \sum_{i=1}^{N} S_i \qquad (h = \pm 1). \tag{1}$$

The magnetic field h can be settled to $h = -1$ or $h = +1$ to produce equilibrium spin-up concentrations (c^+) respectively greater or smaller than $\frac{1}{2}$. By varying the temperature, it is thus possible to produce any spin-up concentration which is the parameter governing the cooperative effects in the system.

The dynamical frustration rule prevents a spin from flipping if it is not surrounded by at least f spins up. f is called the order of the frustration. Such a rule does not break the detailed balance condition so that the equilibrium properties of the system are those of the well known paramagnetic Ising model as long as the system remains ergodic. On the other hand, the dynamic of the system is strongly affected by this rule since many spins are dynamically blocked and need the cooperation of less frustrated surrounding spins to be unlocked and allowed to relax. This effect is particularly sensitive for the low spin-up concentration for which the frustration rule becomes increasingly difficult to fulfil. Such a situation occurs at low temperature when the system is submitted to a positive magnetic field ($h = +1$).

In this paper, we have investigated different orders of frustration: $f = 1.5$, 2 and 3. The non-integer value $f = 1.5$ simply corresponds to a system where spins with order of frustration $f = 1$ and $f = 2$ are equally and randomly distributed in the lattice. In that case, half of the spins need at least one spin-up among its first neighbours to be mobile while the other half need at least two spins up. This situation could correspond experimentally to that of mixed compounds made of molecules with different sizes and shapes: the largest and the less spherical being the most frustrated.

2.2. The simulation techniques

We have calculated the equilibrium dynamical properties of the f-SFKI model at different temperatures using the conventional Monte Carlo simulation technique. The simulations were performed on a square lattices with $N = L \times L$ sites subject to periodic boundary conditions. The equilibrium situations corresponding to a given temperature have been generated from the all spin-up configuration ($S_i = +1, \forall\, i = 1, N$) which is insensitive to the frustration rule. In each case, several thousands of Monte Carlo steps (MCS) have been discarded at the beginning of the simulation to settle a perfect equilibration of the system at the investigated temperature.

At each temperature, the relaxation of the system was probed by monitoring the equilibrium autocorrelation function:

$$\phi_{eq}(t) = \frac{\langle S_i(O)S_i(t)\rangle_{eq} - M_{eq}^2}{1 - M_{eq}^2} \qquad S_i = \pm 1 \qquad M_{eq} = \langle S_i\rangle_{eq}. \tag{2}$$

In the Monte Carlo process the spins were randomly updated using the individual transition probabilities $W(S_i \to -S_i)$ proposed by Glauber [16]:

$$W(S_i \to -S_i) = \frac{1}{2}\left(1 + th\left(\frac{S_i h}{T}\right)\right). \tag{3}$$

These probabilities have the advantage over those proposed by Metropolis [17] of providing a relaxation time τ independent of the temperature for the non-frustrated system ($\tau =$ 1 MCS, $\forall T$ for $f = 0$). The modifications of the dynamics which will appear for $f \neq 0$ will thus be interpreted as a direct consequence of the frustration.

We have also calculated the equilibrium distribution of the cooperativity lengths of the individual spins. The cooperativity length L_c of a spin was initially defined by Sappelt and Jäckle [15] and it can be determined in three steps:

(1) We consider a spin dynamically blocked according to the frustration rule.
(2) We determine the shortest sequence of flip satisfying the frustration rule, necessary to mobilize the initially blocked spin.
(3) The neighbour's shell number of the farthest spin in this sequence defines the cooperativity length of the considered blocked spin.

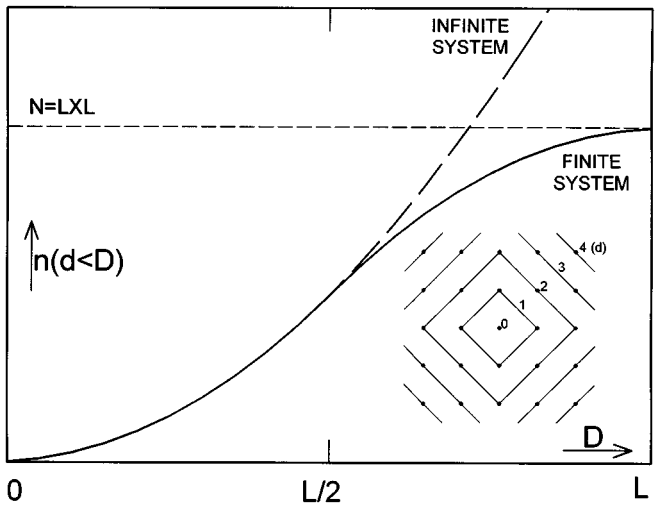

Figure 1. Evolution of the number $n(d < D)$ of different spins whose distance d to a given spin is smaller than D in a square lattice and for a metric of Manahttan. In an infinite system (- - - -) this number diverges like $2D(D+1)$ while in a finite system (——), this evolution slows down for distances D greater than the half lattice size $L/2$. This effect gives rise to an artificial increase of the cooperativity lengths greater than $L/2$ and thus to an overestimation of the relaxation time τ. To avoid this effect we have taken care to use systematically lattices whose size L is at least two times that of the largest individual cooperativity length provided by the frustration.

The cooperativity length of one given spin thus represents the smallest distance over which the spin's reorganization has to occur to unlock a given spin. The cooperativity length of a mobile spin is set equal to zero. The algorithm used to determine the cooperativity length of a blocked spin is briefly described in [15] and in the appendix of this paper.

Strong size effects are expected to occur in finite systems when the largest individual cooperativity length in the system exceed the half lattice size $(L/2)$. This happens at low temperature since the decrease of the spin-up concentration causes the increase of the cooperativity lengths. To avoid this problem we have taken care to use large lattices (up to 300×300) whose size is at least two times that of the largest individual cooperativity length measured in the system. As shown in figure 1, smaller lattices lead unavoidably to overestimate cooperativity lengths greater than the half lattice size $L/2$ and thus artificially slow down the linear dynamics of the system.

3. Results

In order to characterize the spatial organization of the cooperative processes in the f-SFKI model, we have determined the distribution of the cooperativity lengths at different temperatures and for different orders of frustration f. Our results show that for a given average spatial extent of the cooperativity, its spatial organization is strongly dependent on the details of the local frustration rule.

This is clearly shown in figure 2 where we have reported three equilibrium distributions of cooperativity lengths corresponding to three different orders of frustration ($f = 1.5$, $f = 2$ and $f = 3$). These distributions have been obtained at different temperatures (and thus correspond to different spin-up concentrations) suitably chosen to provide the same average cooperativity length ($\langle L_c \rangle = 8$). While these three distributions have the same centre of mass they have

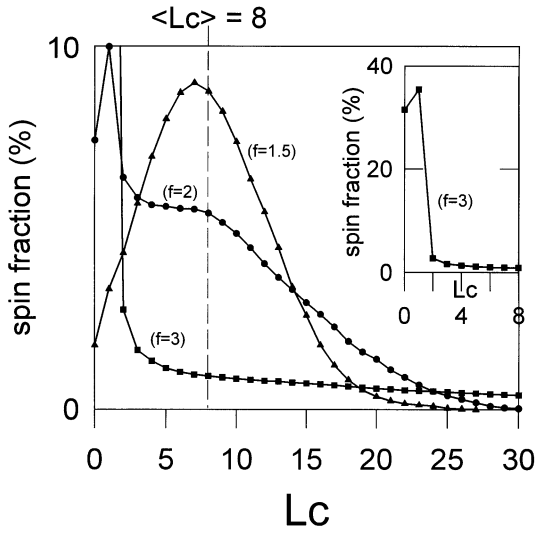

Figure 2. Equilibrium distributions of the cooperativity lengths in systems with different orders of frustration ($f = 1.5$, 2 and 3). These distributions were obtained at different temperatures and thus, for different spin-up concentrations, in order to provide the same average cooperativity length ($\langle L_c \rangle = 8$). For $f = 3$, the beginning of the distribution is shown in the inset while the end of the distribution which slowly decreases to zero for $L_c = 140$ is not shown. All the data are drawn from simulations of a large system (300×300 spins) for which size effects are avoided.

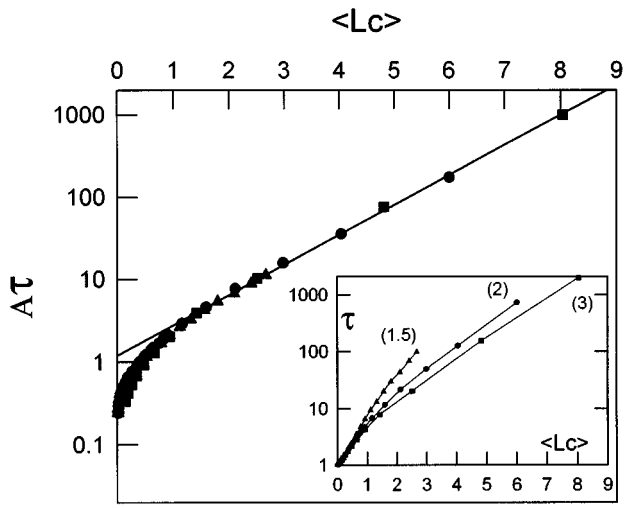

Figure 3. Relaxation time τ rescaled by the spin flip frequency A (4, 5, 6) of the mobile spins versus the average cooperativity length $\langle L_c \rangle$. The three curves correspond to different orders of frustration: $f = 1.5$(▲), $f = 2$(●), and $f = 3$(■). A view of the data before rescaling is shown in the inset.

strongly different structures. For $f = 1.5$, the distribution shows a maximum whose position is close to the average cooperativity length marked by the dashed line. For $f = 2$, the distribution runs to higher values while the maximum of the distribution is strongly shifted towards the small cooperativity lengths. Note, also, a shouldering at a position where the previous distribution

($f = 1.5$) has its maximum. For $f = 3$, the maximum of the distribution is much more pronounced as shown by the very sharp peak localized around $L_c = 1$ (inset of figure 2). The shouldering observed for $f = 2$ has disappeared and is replaced by a very long tail slowly decreasing towards cooperativity lengths as large as $L_c = 140$.

For $f = 1.5$ or $f = 2$, the SFKI model is known to be ergodic [11]. Since there is no interaction between the spins, the spins +1 and −1 are randomly distributed in the lattice in proportions fixed by the detailed balance. The major differences seen in the spatial organization of the cooperative processes (figure 3) thus cannot be attributed to some differences in the local ordering of the spins. These differences are, in fact, directly generated by the dynamical local frustration rule itself and appear to depend strongly on the order of the frustration. However, the previous remarks do not hold for orders of frustration f greater than 2. In that case the frustration rule makes the system non-ergodic and induces some structural ordering. A detailed study of the equilibrium thermodynamics properties of these highly frustrated systems will be published elsewhere [18].

The above results show that the spatial organization of the cooperative processes which lead to a given average cooperativity length $\langle L_c \rangle$ are very different according to the order of the frustration. This indicates that different local frustration mechanisms produce heterogeneous dynamics of different natures. It is not thus obvious, *a priori*, that there exists a universal relation between the relaxation time of the system and its average cooperativity length. To test that point we have calculated the relaxation time τ of the f-SFKI model in a wide range of temperatures and for different orders of frustration. This relaxation time was determined from the equilibrium autocorrelation function which was previously reported [11–13] to be non-exponential for $f = 2$, but correctly described by the Kohlrausch–Williams–Watts (KWW) law. We have found this behaviour to hold also for $f = 1.5$ and $f = 3$ over many decades in time.

The relaxation times obtained from a fit to the autocorrelation functions with the KWW law are plotted in the inset of figure 3 against the corresponding average cooperativity lengths. Note that whatever the order of the frustration, the relaxation times converges towards $\tau = 1$ MCS for the small cooperativity lengths. This situation simply corresponds to that of a non-frustrated system effectively obtained for $\langle L_c \rangle = 0$. On the other hand, we observe a strong increasing dispersion of the data for the high cooperativity lengths so that the three curves do not collapse together onto a single master curve.

As indicated before, the distributions of cooperativity lengths leading to the same value of $\langle L_c \rangle$ for different orders of frustration are obtained for different spin-up concentrations c^+ and thus for different temperatures. For the same reasons, the relaxation times in figure 3 related to a given value of $\langle L_c \rangle$ were also obtained at different temperatures, and are, therefore, expected to differ slightly from each other. This difference is due to the temperature dependence of the spin flip frequency A of the mobile spins which can simply be written as

$$A = c^+ W(+1 \to -1) + (1 - c^+) W(-1 \to +1) \tag{4}$$

and expressed against the temperature

$$A = \frac{1}{2}\left(1 - th^2\left(\frac{h}{T}\right)\right) \qquad (\forall f = 0, 4) \tag{5}$$

or expressed against the spin-up concentration in the ergodic situations, i.e. for $f \leqslant 2$:

$$A = 2c^+(1 - c^+) \qquad (\forall f \leqslant 2). \tag{6}$$

The cooperativity and the temperature thus interplay to give the effective relaxation times displayed in the inset of figure 3. To get rid of this interplay and to determine the effect of cooperativity on the dynamics only, we have systematically rescaled the effective relaxation

times by their corresponding spin flip frequency $A(T)$ of the mobile spins (5), (6). The results are shown in figure 3. Note that the three curves corresponding to three different orders of frustration superimpose perfectly onto a single master curve. This means that the average cooperativity length fully characterizes the cooperative dynamics of the f-SFKI model whatever the order of frustration. Moreover, figure 3 also shows an asymptotic exponential behaviour of the relaxation time for cooperativity lengths greater than one. A sharp blocking transition of the dynamics for a finite average cooperativity length is thus not expected, even for orders of frustration greater than two for which the system is non-ergodic.

4. Conclusion

To explain the particular dynamics of glass-forming systems, Adam and Gibbs [2] have postulated the existence of cooperatively rearranging regions whose sizes govern the relaxation of the system. The spatial extent of the cooperative processes is thus expected to provide a characteristic length for the dynamics.

To test the universal aspect of this characteristic length we have investigated in detail the cooperativity pattern which governs the dynamics of the f-SFKI model developed by Fredrickson [11]. Different orders of frustration f were studied ($f = 1.5$, 2 and 3) for a large range of temperatures.

Our results reveal a universal connection between the relaxation time of the system and the average spatial extent of the cooperative processes. This universality holds in the whole investigated temperature range and for miscellaneous frustration mechanisms. In particular, this universality holds despite the facts that:

- the spatial organization of the cooperativity is found to be strongly dependent on the details of the frustration rule;
- no local structural ordering develops for $f = 1.5$ and 2 while it does for $f = 3$ [18];
- the dynamics is ergodic for $f = 1.5$ and 2 while it is non-ergodic for $f = 3$ [18].

Acknowledgments

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Appendix. Computational details

The algorithm used to determine the cooperativity length L_c of a blocked spin S_i is presented in figure A1. The main procedure of this algorithm consists in flipping up systematically all the flippable down spins on and inside the nth neighbour shell of the considered spin S_i until a stable configuration is reached. Starting from the first neighbour shell ($n = 1$), the previous procedure is reiterated for increasing neighbour shell number n, until the initially blocked spin S_i becomes mobile. The neighbour shell number for which this condition is met for the first time then provides the cooperativity length L_c of the blocked spin S_i.

All the simulations presented in this paper were performed using a DEC Alfaserver (1000A) computer. The simplicity of the frustration rule makes the spin-up updating quite rapid (3×10^{-7} s for a single spin flip). On the other hand, the measurement of the cooperativity length L_c of one given spin S_i is much more time consuming since it requires to visit many times all the $2L_c(L_c + 1)$ spins located on and inside its L_cth neighbour shell.

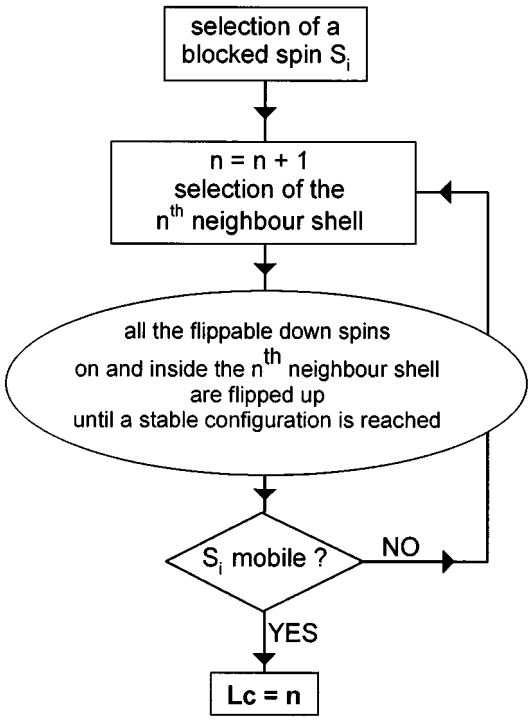

Figure A1. Schematic algorithm used to determine the cooperativity length L_c of a spin S_i dynamically blocked.

References

[1] Angell C A 1991 *J. Non-Cryst. Solids* **131–133** 13
[2] Adam G and Gibbs J H 1964 *J. Chem. Phys.* **43** 139
[3] Smith-Rohr K and Spiess H W 1991 *Phys. Rev. Lett.* **66** 3020
[4] Heuer A, Wilhelm M, Zimmermann H and Spiess H W 1995 *Phys. Rev. Lett.* **75** 2851
[5] Cicerone M T, Blackburn F R and Ediger M D 1995 *J. Chem. Phys.* **102** 471
[6] Ray P and Binder K 1994 *Europhys. Lett.* **27** 53
[7] Jäckle J 1986 *Rep. Prog. Phys.* **49** 171
[8] Buttler S and Harowell P 1991 *J. Chem. Phys.* **95** 4454
[9] Fischer E W, Donth E and Steffen W 1992 *Phys. Rev. Lett.* **68** 2344
[10] Richert R 1996 *Phys. Rev.* B **54** 15 762
[11] Fredrickson G H and Andersen H C 1984 *Phys. Rev. Lett.* **53** 1244
[12] Fredrickson G H and Andersen H C 1985 *J. Chem. Phys.* **83** 5822
[13] Fredrickson G H and Brawer S A 1986 *J. Chem. Phys.* **84** 3351
[14] Harrowell P 1993 *Phys. Rev.* E **48** 4359
[15] Sappelt D and Jäckle J 1993 *J. Phys. A: Math. Gen.* **26** 7325
[16] Glauber R J 1963 *J. Math. Phys.* **4** 294
[17] Metropolis N, Rosenbluth A, Rosenbluth M, Teller A and Teller E 1953 *J. Chem. Phys.* **21** 1087
[18] Tetaert M and Willart J F to be published