Cooperatively rearranging regions in a two-spin facilitated kinetic Ising model

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Spin-facilitated kinetic Ising models are reasonable models for a study of cooperative dynamics that is assumed in supercooled liquids. The present numerical study of a two-dimensional model confirms the existence of cooperatively rearranging regions by quantitative results. A broad distribution of relevant sizes suggests that the kinetic of spin-facilitated kinetic Ising models can be characterized by a strong pronounced heterogeneity. On the other hand, a characteristic length scale corresponding to a dominant fraction of cooperative regions cannot be supported. Furthermore, the temperature dependence of various quantities of the cooperative regions reflects the typical non-Arrhenius behavior of supercooled liquids.
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In spite of advances in the description of liquids near the glass transition using different approaches[1-4] the phenomenon is generally not completely understood. Supercooled fluids reveal often a non-Arrhenius behavior of the relaxation spectrum such as it is manifested in a stretched exponential decay of the correlation function. In contrast to conventional phase transitions a long-range order is not developed. However, the dynamical glass transition can be described by an increasing cooperativity of local processes with decreasing temperature.[5] The cooperativity leads to the well-known slowing down in the dynamical behavior (non-Arrhenius) that can be illustrated by a strongly curved trajectory in the Arrhenius plot (relaxation time τ versus the inverse temperature T^{-1}). One possible fit of this curve is given by the Williams-Landel-Ferry (WLF) curve[6] with $\ln \tau \propto (T-T_0)^{-1}$ and a finite Vogel temperature T_0. This slowing down is an universal phenomena of the glass transition. There is a general suggestion that these slow processes correspond mainly to the cooperative molecular diffusion, i.e., the self-diffusion coefficient D and the relaxation time τ are often related by $D\tau \simeq 1$.

Mode-coupling theories[1,7,8] (MCT) predict the existence of an ergodic behavior above a critical temperature T_c and a nonergodic behavior below T_c. Note that T_c is in the range between the melting temperature T_m and the glass temperature T_g, i.e., $T_m > T_c > T_g$. At T_c the system undergoes a sharp transition from an ergodic state to a state with partially frozen (density) fluctuations. The slow α-process within the MCT is thought to correspond to the actual dynamic glass transition whereas the fast β-process is often identified with a cage rattling or the boson peak.

Actually, the nonergodic structures obtained from the original MCT below T_c are approximately stable only for a finite time interval. Strongly cooperative processes lead to a slow decay of apparently frozen structures. This slow decay shows the typical properties corresponding usually to the dynamics of the main glass transition (WLF-like behavior of the relaxation time, stretched exponential decay of the correlation function). These effects can be partially described in terms of an extended mode-coupling theory[2,7] introducing additional hopping processes.

There exists also various alternative descriptions[3,9] that explain the cooperative motion of the particles inside a su-percooled liquid below T_c. One of these possibilities is the spin-facilitated kinetic Ising model,[9-12] originally introduced by Fredrickson and Andersen. The basic idea of all these models consists in a coarse graining of space and time scales and simultaneously a reduction of the degrees of freedom. Therefore, the supercooled liquid is separated into cells containing a sufficiently large number of particles that realize a representative number of molecular motions. Thus the many-body system is considered of a virtual lattice with the unit size l. Each cell will be characterized by only one trivial degree of freedom σ_j that characterizes the actual dynamic state of particles inside the cell j. The usual realization is given by the local density ρ_j with $\sigma_j = -1$ (immobile or solidlike state) if $\rho_j > \bar{\rho}$ and $\sigma_j = 1$ (mobile or liquidlike state) if $\rho_j < \bar{\rho}$, where $\bar{\rho}$ is the averaged density of the system. The set of all observables $\sigma = \{\sigma_j\}$ forms a configuration. The evolution of the statistical probability distribution function $P(\sigma, t)$ can be described by a usual master equation: $\partial P(\sigma, t)/\partial t = \Sigma_{\sigma'} L(\sigma, \sigma') P(\sigma, t)$. To make the dynamical matrix $L(\sigma, \sigma')$ and the time evolution of $P(\sigma, t)$ more transparent we use the argumentation following the idea of Fredrickson and Andersen,[9-12] i.e., we suppose that the basic dynamics is a simple (Glauber) process $\sigma_j = +1 \leftrightarrow \sigma_j = -1$ controlled by the thermodynamical Gibb's measure and by self-induced topological restrictions. In particular, an elementary flip at a given cell is allowed only if the number of the nearest neighbored mobile cells ($\sigma_j = +1$) is equal or larger than a restriction number n with $0 < n < z$ (z: coordination number of the lattice). So, elementary flip processes and geometrical restrictions lead to the cooperative rearrangement of the underlying system and therefore to a mesoscopical modeling describing a supercooled liquid below T_c.

Such models[9-12] are denoted as n-spin-facilitated Ising models on a d-dimensional lattice SFM[n,d]. The SFM[n,d] can be classified as an Ising-like model the kinetics of which is confined by restrictions of the ordering of nearest neighbors to a given lattice cell. These self-adapting environments influence in particular the long-time behavior of the spin-spin and therefore of the corresponding density-density correlation functions. These models were studied numerically[13-16] (SFM[2,2]) and recently also analytically[17] (SFM[1,1]).

In the present paper we will give on the basis of the SFM[2,2] a numerical approach to the size of the cooperative regions. Cooperative regions or cooperatively rearranging regions[5] are regions with a kinetic correlation of the particle motion. Recently, numerical investigations[18–20] are performed that demonstrate the existence of such regions for the SFM[2,2]. The short-time evolution of the SFM[2,2] shows typical pocketlike structures of spins that are flipped since a given initial time[18] and that suggest qualitatively the cooperative motion of the spin-facilitated kinetic Ising model. Furthermore, it was demonstrated[19,20] that the average cooperative length l (this length is defined as the distance from a particular spin to other spins needed to flip before the selected spin becomes flippable) shows a strong dependence on the temperature. On the other hand, up to now there is no quantitative information about the size distribution of cooperative regions.

The above introduced definition of cooperatively rearranging regions[5] is too imprecise for a well-defined mathematical investigation.

Therefore, we use a technique that is capable of being extended to other model systems like Lennard-Jones or hard-core liquids. We define that there exist in the environment of each cell j a time- and temperature-dependent cooperative region $R_j(t,T)$ containing the minimum number of another cell that must change at least one time their state, before the state of the chosen cell j can be changed. All cells of a cooperative region $R_j(t,T)$ form a connected cluster.

The numerical simulation bases on two procedures: (1) creation of equilibrium configurations for the SFM[2,2] on a two-dimensional lattice and (2) determination of the cooperative regions of all cells.

The aim of the simulation is the determination of the temperature-dependent distribution function $\Phi(N,T)$ that de-

scribes the probability of finding a cooperative region consisting of N cells at temperature T.

The creation of equilibrium configurations is based on the following steps. Starting from a regular (square) lattice we introduce at each lattice point a spin variable σ_i with the two possible states $\sigma_i = \pm 1$ and the initial configuration $\sigma = \{\sigma_i = +1$ for all $i\}$. We allow the elementary steps: $\sigma_i = -1 \rightleftharpoons \sigma_i = +1$. Such flips are realized with a transition probability 1 for $+1 \rightarrow -1$ and $\exp\{-\varepsilon/T\}$ for $-1 \rightarrow +1$ (ε is the energy difference between the solid and liquidlike state). In addition to this thermodynamic flip rate we have the topological restriction that a flip of this type is only possible if the following condition is satisfied: $\Sigma_{j(i)}(1-\sigma_j) \leq 4$. [$j(i)$ means all z neighbors of the lattice point i.] As mentioned above, this restriction is the central idea of each SFM[n,d] and leads to the characteristic hindrance effects. Using these elementary steps it is easy to create an equilibrium configuration. The equilibrium is reached if the ratio N_-/N_+ ($N_\pm$ are the numbers of spin state $\sigma = +1$ and $\sigma = -1$, respectively) becomes

$$N_+/(N_- + N_+) = 1/(1 + \exp \varepsilon/T). \tag{1}$$

It should be denoted that the principle of detailed balance is always fulfilled, i.e., the equilibrium state is realized for each spin and each elementary process.

After reaching the equilibrium, the flip processes of all cells will be stopped. The actual configuration may be σ^*. In a subsequent step we choose randomly an available cell k of σ^*. Only this cell receives the possibility for a further motion under consideration of the above-mentioned elementary steps and kinetic restrictions. If the cell k changes its state after a sufficiently long simulation time, then the cooperative region has the size $\tilde{N}_{\text{coop}}^{(k)} = 1$. If not, a second cell of σ^*
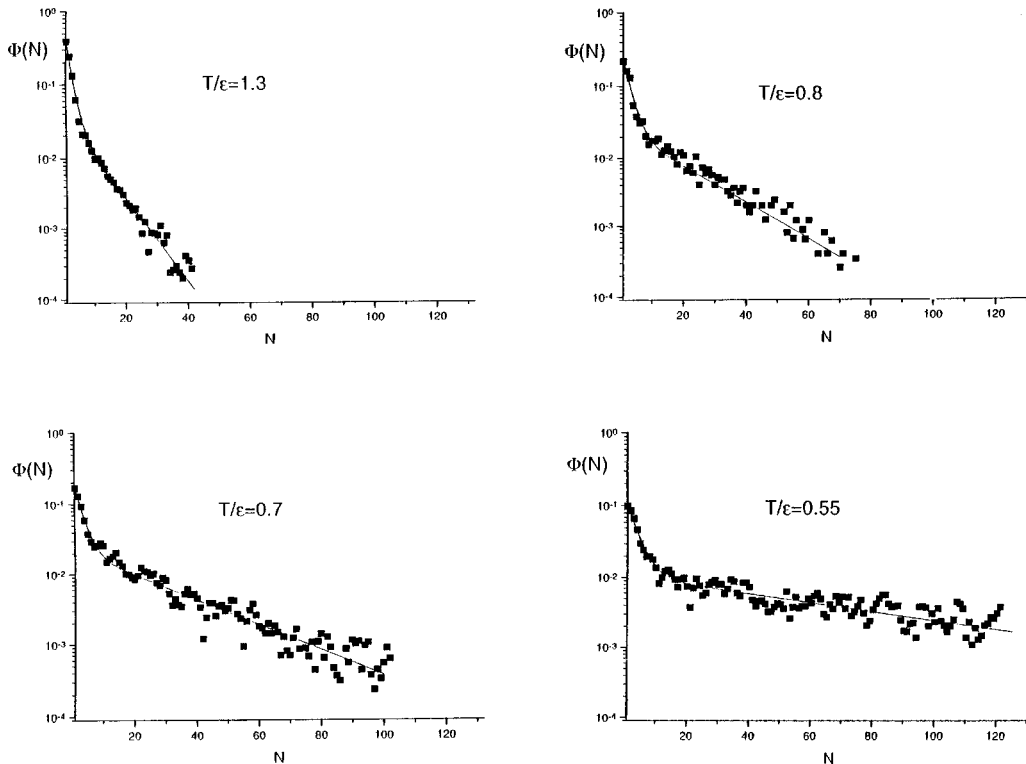

FIG. 1. Distribution function $\Phi(N,T)$ for different temperatures. The solid lines correspond to a fit using Eq. (2).
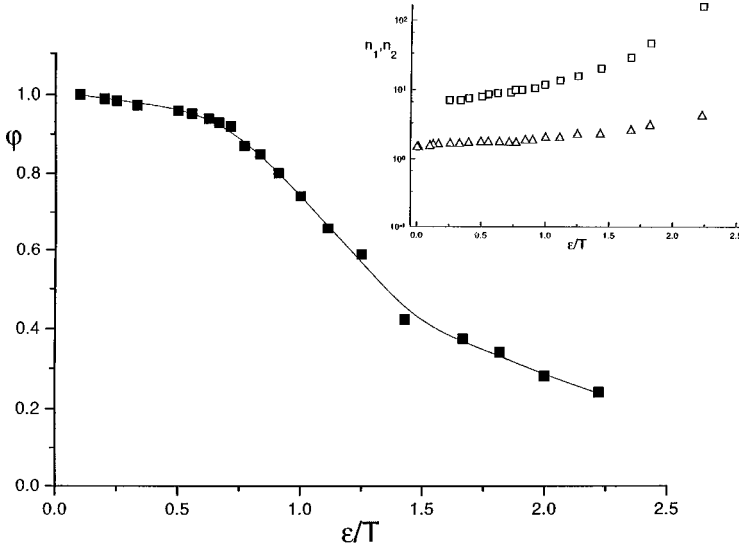
FIG. 2. Fraction $\varphi(T)$ of relatively movable regions as a function of ε/T. The inset shows the temperature dependence of n_1 (triangles) and n_2 (squares).

neighbored to k will be chosen randomly. Both cells form a simple cluster. The cells of this cluster receive again the possibility for a motion whereas the state of all other cells is completely frozen. If now the cell k changes its state after a sufficiently long time, then the cooperative region has the size $\widetilde{N}_{\text{coop}}^{(k)} = 2$. If one observes no change of the state of cell k, an additional cell of σ^* neighbored to the previous cluster is randomly determined and the same procedure will be repeated. The cluster size will be increased up to the case that the original cell k changes its state. Thus, the apparent size of the cooperative region is $\widetilde{N}_{\text{coop}}^{(k)}$.

The same procedure, starting from the old configuration σ^* and the original cell k will be realized sufficiently often (only the growing of the cluster is always changed). The aim is the determination of a minimum number $N_{\text{coop}}^{(k)} = \min(\widetilde{N}_{\text{coop}}^{(k)})$. Thus, $N_{\text{coop}}^{(k)}$ is the size of the cooperative region of the cell k for a given configuration σ^*.

Now, one can start the same procedure for another cell of the same configuration σ^* or also for another equilibrium configuration. The repetition will be realized over a sufficiently long computation time up to the moment that one has a relatively smooth distribution function $\Phi(N,T)$ describing the probability of finding a cooperative region consisting of N cells.

The numerical simulation of the kinetics of the SFM[2,2] is possible by using a simple spin-flip dynamics realized by a usual Monte Carlo simulation with the elementary steps and thermodynamic transition probabilities discussed above. We do not expect a long-range structure in contrast to the behavior of typical critical phenomena; see Refs. 1 and 16) and therefore the volume can be chosen relatively small. In the following considerations in two-dimensional space we use a square lattice with L^2 sites ($L=50$) and periodic boundary conditions.

The size N of cooperative regions, determined by the above-mentioned procedure, has a probability distribution $\Phi(N,T)$ that decreases monotonously with increasing N. Figure 1 shows these probability distributions $\Phi(N,T)$ for various temperatures. Obviously, it is easy to see that there is no characteristic value N_{char} at which an extremum of $\Phi(N,T)$ occurs. Therefore, the motivation of a characteristic

length scale becomes questionable. Of course one can determine an averaged size of the cooperative regions and therefore an averaged length scale of these objects, but this is not a usual characteristic length corresponding to a dominant fraction of cooperative regions with a size close to N_{char}. We conclude that cooperative regions at a given temperature are not at all relatively similar objects, and especially at low temperatures these objects have a broad spectrum. The assumption of some authors[21] that cooperative regions form a relatively regular ''kinetic pattern'' cannot be confirmed at least by the present investigations of the SFM[2,2].

On the other hand, the present analysis of the SFM[2,2] signalized that there occurs an increasing kinetic heterogeneity with decreasing temperature. This behavior was observed also by other numerical simulations[22,23] and by various experimental techniques.[24,25]

The probability distribution $\Phi(N,T)$ can be empirically approximated by the superposition of two exponential functions; see Fig. 1:

$$\Phi(N,T) = \varphi(T)(\exp\{n_1^{-1}(T)\} - 1)\exp\left\{-\frac{N}{n_1(T)}\right\}$$
$$+ [1 - \varphi(T)](\exp\{n_2^{-1}(T)\} - 1)\exp\left\{-\frac{N}{n_2(T)}\right\}$$

$$(2)$$

with $n_1(T) < n_2(T)$. This representation fulfills always the normalization condition $\Sigma_{N=1}^{\infty}\Phi(N,T) = 1$. The value of $n_1(T)$ is relative small (one obtains $n_1 \approx 5$ at the lowest temperature of the present simulation). On the other hand, $n_2(T)$ is of an order of magnitude of the averaged size of cooperative regions; see Fig. 3. The first term of Eq. (2) can be roughly interpreted as a fraction of relatively small and movable cooperatively rearranging regions. This part consists mainly in regions with a very small size, i.e., this fraction appears on a coarse-grained length scale as a homogeneous fraction. The second term corresponds to the fraction of relatively strong disabled cooperative regions with a broad distribution of relevant sizes and consequently a pronounced heterogeneity. The fraction of these relatively large cooperatively rearranging regions is given by $1 - \varphi(T)$ whereas the
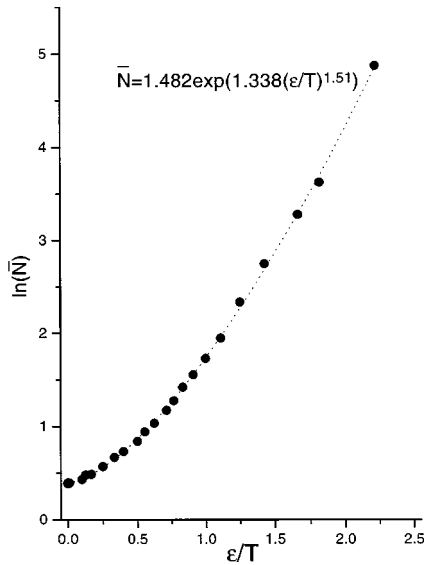
FIG. 3. Averaged size $\bar{N}$ of the cooperative regions as a function of ε/T. The dotted line corresponds to a fit using $\ln\bar{N}=A+B(\varepsilon/T)^{\gamma}$.

fraction of the relatively small and movable regions is given by $\varphi(T)$. As expected, $\varphi(T)$ decreases with decreasing temperature; see Fig. 2. Furthermore, it can be confirmed in a more quantitative way that the heterogeneity of the kinetics increases with decreasing temperature because both the fraction of the large cooperatively rearranging regions and the width of the corresponding probability distribution function increase with decreasing temperature. This behavior is a characteristic property of a supercooled liquid below T_c that supported the above-mentioned assumption that the SFM[2,2] is a reasonable description for the slow dynamical processes at $T<T_c$.

The knowledge of the distribution function allows the determination of thermodynamical averages. Here we discuss the average size $\bar{N}$ of the cooperative regions. Figure 3 shows the relatively strong dependence of $\bar{N}$ on temperature. As expected, the averaged size of the cooperatively rearranging regions is not Arrhenius activated. A rough fit leads to the representation $\ln\bar{N}=A+B(\varepsilon/T)^{\gamma}$ with $A=0.394\pm0.005$, $B=1.34\pm0.01$, and $\gamma=1.51\pm0.02$ but a WLF fit with $\ln\tau=A'+B'(T-T_0)^{-1}$ is also possible with a slightly less accuracy. It should be denoted that $\sqrt{\bar{N}}$ is proportional to the average size l defined by Sappelt and Jäckle.[20]

The important message of our simulations using the SFM[2,2] is that this model can be used as a reasonable model for the slow kinetics of a supercooled liquid below T_c. The old assumption of the existence of cooperatively rearranging regions[5] in such a liquid can be confirmed by quantitative results. Furthermore, the broad distribution of relevant sizes suggests on the one hand that the kinetic of the SFM[2,2] is characterized by a strong pronounced heterogeneity that can be observed also for other models of supercooled liquids and for real glasses. On the other hand, the present results suggest that there is no characteristic length scale corresponding to a dominant fraction of cooperative regions. This statement is also supported by various experimental data[26,27] that confirm the absence of a length scale near the glass transition. However, one should not definitively exclude the existence of such a length scale, e.g., there is the possibility that the analyzed cluster-size distribution is not the appropriate quantity that may reveal a characteristic length. Finally, the temperature dependence of characteristic quantities of the cooperative regions (e.g., the averaged size $\bar{N}$) reflects the typical non-Arrhenius behavior of glassy systems.

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