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The cooperativity length in models for the glass transition

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Abstract. Kinetic Ising and lattice-gas models with kinetic constraints may serve as models of cooperative dynamics in undercooled liquids near the glass transition. For a class of these models the cooperativity length of a spin/particle is defined and its distribution calculated. It is found that, contrary to an assumption of Adam and Gibbs, there is no simple relation between the cooperativity length and the entropy of these models. For the autocorrelation functions, which exhibit a stretched-exponential time dependence, an approximate sum formula is proposed which contains a relaxation rate depending on cooperativity length. The sum formula is tested for a particular case and found to give good overall agreement with Monte Carlo data.

1. Introduction

In the discussion of the physical mechanism of the enormous slowing down of the diffusive molecular motion in an undercooled liquid near the glass transition the idea of molecules rearranging themselves cooperatively within regions of a characteristic size [1] has been found to be very attractive. The idea had been made quantitative by relating the size of a 'cooperatively rearranging region' to its content of configurational entropy [1]. During the last decade a class of kinetic Ising and lattice-gas models with kinetic constraints were investigated [2–9] which give the idea of cooperativity a concrete meaning. It is the purpose of the present paper to define and calculate the characteristic length of the cooperative process for different models and to relate this length to measurable physical quantities.

The paper is organized as follows. In section 2.1 the cooperativity length of the models is defined according to our intuitive understanding of the term 'cooperative'. Alternative definitions of a characteristic length, which use periodic boundary conditions, are listed for comparison. The results for the probability distribution of the cooperativity length are presented in sections 2.2–2.5. The models investigated are: the (3,2)-Cayley-tree model, the north–east (NE) model, the two-spin facilitated kinetic Ising model and the hard-square lattice-gas model. The first two of these models, which have a directed constraint, exhibit a sharp blocking transition at a critical up-spin concentration. In section 3 an approximate sum formula for the autocorrelation function of the models is proposed, which contains a relaxation rate depending on the cooperativity length. The validity of the sum formula is tested for the NE model in section 3.3. The results of the paper are summarized in section 4.

2. Distribution of cooperativity lengths

2.1. *Definitions*

We first define the cooperativity length l for the two-spin facilitated kinetic Ising model. This definition can be extended to all kinetic Ising models with a kinetic constraint. A

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similar definition applies to lattice-gas models with constrained diffusion dynamics. In the two-spin facilitated kinetic Ising model the lattice sites are occupied by spins which are in the up state with probability c, and in the down state with probability $1-c$. There is no static interaction between the spins. The kinetic constraint allows a spin to flip (in either direction) only if at least two of its four nearest neighbours, no matter which, point in the up direction. We call a spin 'flippable' or 'blocked' depending on whether it is allowed to flip or not. A spin which is initially blocked may be 'mobilized' (≡made flippable) by a certain number of spin flips in its neighbourhood.

We define the cooperativity length l of a particular spin in a particular spin configuration of the infinite lattice as the minimum distance from that spin up to which other spins, which originally are in the down state, need to flip, before the spin considered becomes flippable. The distance is expressed by the neighbour-shell number. Using the intuitive anthropomorphic term, spins up to that distance need to 'cooperate' in order to mobilize the spin considered. p_l is the probability for a spin to have cooperativity length l ($l \geqslant 0$).* The average cooperativity length $\langle l \rangle$ is obtained as

$$\langle l \rangle = \sum_{l=1}^{\infty} l p_l. \tag{2.1}$$

To calculate p_l, a computer algorithm is needed which determines the cooperativity length l for every spin in a random selection of spin configurations. We developed and used such an algorithm for the NE model, the two-spin facilitated kinetic Ising model and the hard-square lattice gas [10]. While the algorithm for the NE model is straightforward, it is fairly involved for the hard-square lattice gas. We shall not describe the algorithms here.

Alternatively, p_l may also be derived from the integrated probability

$$P_l = \sum_{l'=0}^{l} p_{l'}. \tag{2.2}$$

We will outline this second method, as it is more easily explained than the first method of directly calculating p_l. P_l is the probability that the cooperativity length of a spin is not larger than l. If a spin in a particular spin configuration has a cooperativity length not larger than l, it can be mobilized by the flipping of spins on and within the lth shell of neighbours around it. Therefore P_l can be determined as the probability that a spin can be mobilized by a sequence of spin flips which involve only spins on and within the lth neighbour shell. p_l is obtained from P_l as

$$\begin{aligned} p_l &= P_l - P_{l-1} \qquad (l \geqslant 1) \\ p_0 &= P_0. \end{aligned} \tag{2.3}$$

($p_0 = P_0$ is the probability that a spin can flip in the original spin configuration.)

Figure 1 illustrates the calculation of p_l from the integrated probability for the two-spin facilitated kinetic Ising model on the square lattice. The squares drawn mark the different shells of neighbours around the spin considered, which is blocked in the direction shown. The nearest flippable down spins are found on the fourth neighbour shell. Therefore, l is at least four. To test whether l is four or larger, we flip all flippable down spins on and within the fourth-nearest-neighbour shell. This step is repeated until a stable configuration

* In [2], the symbol p_l has a different meaning.

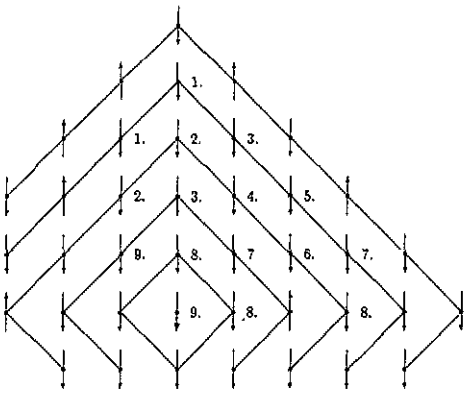

Figure 1. Cooperativity in the two-spin facilitated kinetic Ising model. The blocked spin in the center becomes flippable in the nineth step of the CA. The cooperativity length of the central spin amounts to 4.

is obtained. The sequence of steps defines a cellular automaton (CA). If the spin under consideration is flippable in the final state reached by the CA, l cannot be larger than 4. If, on the other hand, the orientation of that spin is still blocked in the final state of the CA, that spin cannot be made flippable by *any* sequence of spin flips on and within the lth neighbour shell. In this case l is larger than 4. In figure 1 the number of step in which a spin is flipped is marked. The spin in the centre is flipped at the nineth step. Therefore, the first case applies. Since we saw before that l is at least four, $l = 4$ holds for the example shown. For *all* models described in this paper a CA exists by which P_l can be determined. Note that there exist lattice-gas and kinetic Ising models with kinetically constrained dynamics which do not possess this property [11].

The definition of the cooperativity length given above and used in this paper expresses the intuitive idea of cooperativity in a most direct way. However, alternative definitions, which were used previously, are more convenient for computation. To calculate the integrated probability P_l as described above, a CA needs to be run for every spin and configuration separately. However, if periodic boundary conditions are introduced for all spins of a finite lattice of size $L \times L$, a CA needs to be run only once. It is therefore convenient to define a CA which in a repeated process flips all flippable down spins in a $L \times L$ lattice with periodic boundary conditions. Let f_L denote the fraction of spins which remain blocked in the final state of this CA, averaged over many spin configurations. Then $q_L = f_{L-1} - f_L$ represents the probability that a spin in a lattice of linear dimension $L - 1$ is permanently blocked, but not in one of linear dimension L ($L \geqslant 1$, $f_0 = 1$). (If $f_\infty > 0$, which is the case in the NE model and Cayley-tree model below the critical up-spin concentration, q_L needs to be normalized by a factor $(1 - f_\infty)^{-1}$.)

From q_L we derive the average length

$$\langle l \rangle_R = \sum_{l=1}^{\infty} l q_l \tag{2.4}$$

which is the average size that a lattice with periodic boundary conditions must have for a spin not to be permanently blocked [2]. Although the situation is somewhat obscured by the use of periodic boundary conditions, $\langle l \rangle_R$ may also be interpreted as a characteristic length of cooperativity.

For the average cooperativity length, a second alternative definition is obtained as follows. Again the CA for a $L \times L$ lattice with periodic boundary conditions is used. Let $w_L(c)$ denote the probability that the final configuration of the automaton is the all-up spin state, i. e. the probability that no permanently blocked spins exist. In lattice-gas terms, $w_L(c)$ can be expressed as the probability that all particles on the lattice are culled, for a culling rule which translates the spin CA into lattice-gas language. In this way $w_L(c)$ is related to a problem of bootstrap percolation [12]. From $w_L(c)$ a characteristic length can be derived in two different ways. First, putting $w_L(c) = w$, with, say, $w = 50\%$ defines the characteristic length $L = \xi_w(c)$ [3, 13, 14]. In the second way a characteristic length is obtained via a critical L-dependent up-spin concentration $c_p(L)$, which is defined by

$$c_p(L) = \int_0^1 c \frac{\mathrm{d}w_L(c)}{\mathrm{d}c} \mathrm{d}c. \tag{2.5}$$

Inversion of the function $c_p(L)$ yields the characteristic length $\xi_p(c)$ [15]. Because of their relation to bootstrap percolation, we refer to the characteristic lengths ξ_w and ξ_p as 'percolation lengths'.

The cooperativity lengths defined above are obtained either from effectively infinite systems ($\langle l \rangle$) or from finite systems with periodic boundary conditions in both lattice directions ($\langle l \rangle_R, \xi_w, \xi_p$). An alternative method, which exploits the difference of relaxation times occurring for *different* types of boundary conditions, has been used by Butler and Harrowell [16]. These authors derive a correlation length of cooperative motion from the distance from a boundary over which the relaxation time of a spin depends on whether the boundary condition is blocking or free.

2.2. (3,2)-Cayley-tree model [2]

Ising spins occupy the sites of a Cayley tree, where every site except the site at the base has three next neighbours, two above and one below. The spins are randomly oriented, with up-spin probability c. The kinetic constraint of the model allows a spin to flip only if both its upper neighbours are in the up state. The model exhibits a sharp blocking transition at a critical up-spin concentration $c^* = 1/2$. For concentrations $c < c^*$ a finite fraction f of spins is permanently blocked on the infinite tree. f plays the role of an order parameter for the dynamical phase transition. The phase transition is of second order.

Every site of the Cayley tree is at the base of a new tree and by the kinetic constraint every spin is coupled to all spins belonging to the tree above it. The cooperativity length l is defined as the minimum height up to which spins have to be flipped to render the spin at the base flippable.

Reiter, Mauch and Jäckle [2] have presented an approximate analytical calculation of the probability f_l that a spin at the base of a Cayley tree of height l is permanently blocked. Since the spins on the highest level are blocked, f_l is connected with the distribution of cooperativity lengths p_l by

$$f_l = \sum_{l'=l}^{\infty} p_{l'} \tag{2.6}$$

whence

$$p_l = f_l - f_{l+1}. \tag{2.7}$$

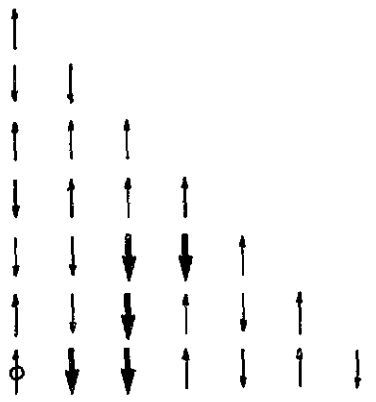

Figure 2. Directed path of down spins in the NE model. The blocked spin in the corner has cooperativity length $l = 5$.

For concentrations c close to $c^*(|c - c^*|/c^* \ll 1)$ two regions $l < l_0$ and $l > l_0$ ($l_0 \approx 1/(2\epsilon)$, $\epsilon = |c - c^*|$) may be distinguished. Using the results of [2], we obtain

$$p_l \approx \frac{1}{(1-c)^2} \frac{1}{(l+4)(l+5)} \qquad \text{for } l < l_0 \tag{2.8}$$

and

$$p_l \approx \frac{4\epsilon^2}{(1-c)^2} \exp(1 - 2\epsilon l) \qquad \text{for } l > l_0. \tag{2.9}$$

This yields for the average cooperativity length

$$\langle l \rangle \approx -B - 4 \ln |c - c^*| \tag{2.10}$$

where B is a positive constant.

2.3. North-east model [2]

On a square lattice non-interacting Ising spins point upward with probability c and downward with probability $1 - c$. A spin is allowed to flip only if its two nearest neighbours to the north and to the east both are up spins. Like the (3,2)-Cayley model the north–east model exhibits a sharp blocking transition which is of second order. The critical concentration is $c^* = 0.294$ [2]. By the kinetic constraint a spin is kinetically coupled to the spins north–east of it, i. e. to the spins in the upper right quadrant, of which it occupies a corner. It is independent of all other spins. Therefore, for the calculation of the cooperativity length of a particular spin, only the spins in this quadrant have to be considered.

A spin has cooperativity length l if down spins up to the lth neighbour shell in the upper right quadrant from this spin need to be flipped in order to make this spin flippable. The minimum number of down spins which need to be flipped form a directed path which starts from a blocking down spin neighbour of the spin considered. The directed paths contain only steps going in the north or the east direction. Therefore, the cooperativity length l is also the maximum length of directed paths of down spins which start from the blocking down spin neighbours north or east of the spin considered (for $l \geqslant 1$). The path length is measured by the maximum distance reached in the north–east direction. Figure 2 shows an illustrating example with $l = 5$.

Figure 3 shows a semi-log plot of the distribution p_l of cooperativity lengths for various concentrations for the lattice size 128 × 128. Note that there is a qualitative similarity between p_l in the (3,2)-Cayley model and in the north–east model. For great lengths p_l decreases exponentially, whereas for lengths which are shorter than a concentration-dependent threshold the decrease is non-exponential.

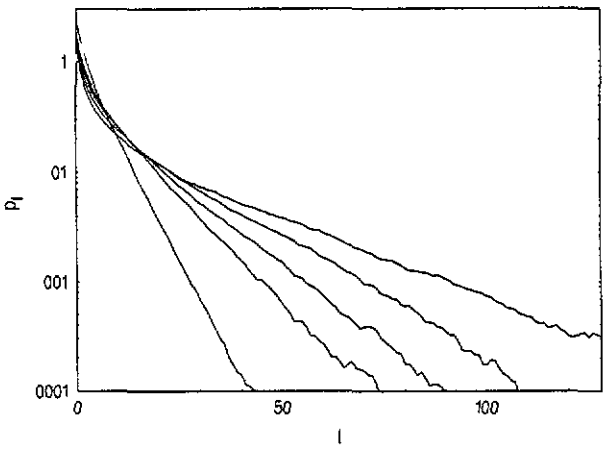

Figure 3. Distribution of cooperativity lengths p_l for the NE model for the concentrations $c = 0.50$, 0.43, 0.41, 0.39 and 0.37 (from below). Lattice size is 128 × 128.

The average cooperativity length $\langle l \rangle$ diverges at the critical concentration c^*. Our results for $\langle l \rangle$ obtained for the lattice size 128 × 128 can be fitted by $\langle l \rangle \propto (c - c^*)^{-\nu}$ with a critical exponent $\nu = 1.43$ in the concentration range $0.37 \leqslant c \leqslant 0.46$. One should expect that $\langle l \rangle$ diverges like the longitudinal correlation length $\xi_{\|}$ of the directed site percolation problem on a square lattice. However, the critical exponent for $\xi_{\|}$ is $\nu_{\|} = 1.73$ [17]. The origin of this discrepancy is not clear. One possibility is that we have not reached the asymptotic critical region in our calculation of the average cooperativity length. (The same situation occurs for the characteristic length $\langle l \rangle_R$ of [2], for which a critical exponent $\nu = 1.37$ was derived.)

2.4. Two-spin facilitated kinetic Ising model

The two-spin facilitated kinetic Ising model has already been introduced in section 1.1. As opposed to the models with a directed kinetic constraint, this model has no blocking transition at a finite up-spin concentration in the thermodynamic limit $L \to \infty$ [7, 18].

As the kinetic constraint is isotropic, the distributions of cooperativity lengths for up spins and for down spins are different. If a spin points upward, the probability of being flippable for the spins in the first-neighbour shell around it is enhanced, since only one additional up spin is required on the second-neighbour shell. Therefore, the probability $p_l^{\uparrow}$ for a spin to point upward and have cooperativity length l exhibits a maximum at $l = 1$ (figure 4a). Conversely, if a spin points downward, the nearest-neighbour spins around it are less likely to be flippable than on average, since two up spins are required on the second-neighbour shell. Therefore the probability $p_l^{\downarrow}$ for a spin to point downward and have cooperativity length l exhibits a minimum at $l = 1$ (figure 4b). The strong maximum

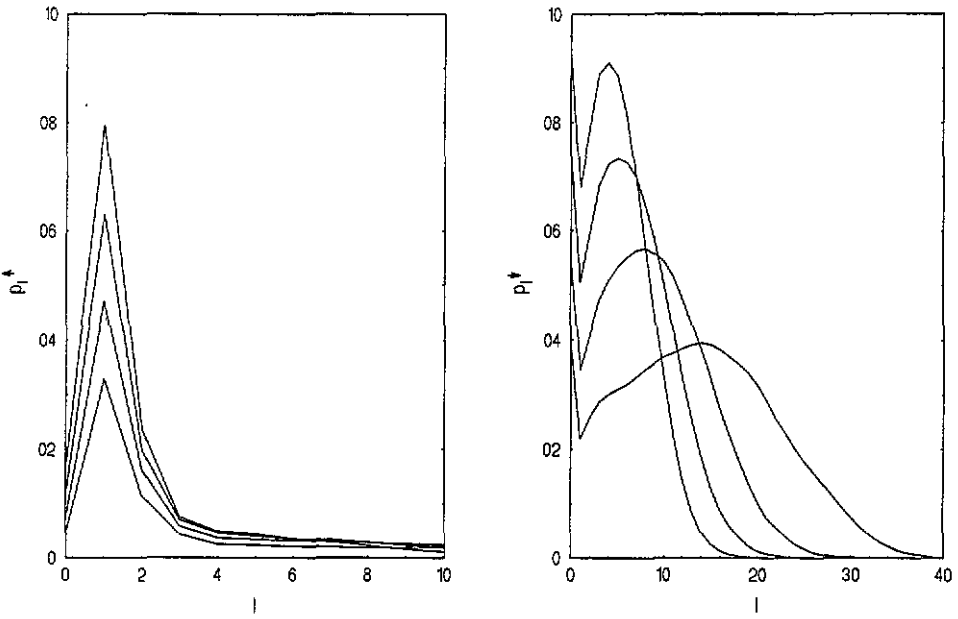

Figure 4. Probability $p_l^{\uparrow}$ for a spin to point upwards and have the cooperativity length l (left) and probability $p_l^{\downarrow}$ for a spin to point downwards and have the cooperativity length l (right) for the two-spin facilitated kinetic Ising model. Concentrations (from above) are $c = 0.15$, 0.13, 0.11 and 0.08. Lattice size is 128×128.

in $p_l^{\uparrow}$ survives in the total probability p_l of cooperativity length l, which is the sum of $p_l^{\uparrow}$ and $p_l^{\downarrow}$. p_l is plotted in figure 5 for various concentrations for lattice size 128×128. The most important feature of the p_l-curves is the broad maximum occurring near the average cooperativity length $\langle l \rangle$ (cf equation (2.13)). This feature is explained qualitatively by the existence of 'critical droplets' [18] in a growth process for all-up spin clusters. The argument is as follows. A growth process is considered by which square all-up spin clusters grow layer by layer around a central up spin. (Alternatively, one may also consider the growth from a corner [18].) In accord with the kinetic constraint of the model, an $l \times l$ all-up spin cluster grows to size $(l+2) \times (l+2)$, if on each of the four edges of the $(l+2)$th layer at least one up spin exists [18]. Since for up-spin concentration c the average separation between up spins is $1/c$, an all-up spin cluster of size $l_c \times l_c$ with $l_c \gg 1/c$ will almost certainly grow arbitrarily large. Such a cluster may be called a 'critical droplet' [18], by analogy with classical nucleation theory. Let p_c denote the probability for a particular cell of size $l_c \times l_c$ of the lattice to contain such a critical droplet. If we divide a large lattice of size $L \times L$ into $(L/l_c)^2$ cells of this size,

$$\overline{w}_L \equiv 1 - (1 - p_c)^{(L/l_c)^2} \tag{2.11}$$

is the probability for at least one of the cells to contain a critical droplet. Since $p_c \ll 1$ for small $c \ll 1$, we may write

$$\overline{w}_L = 1 - \exp\bigl(-p_c(L/l_c)^2\bigr). \tag{2.12}$$

$\overline{w}_L$ is an approximation for the probability w_L (section 1.1) that the all-up spin state can be reached from an arbitrary spin configuration of the $L \times L$ lattice. Since many paths of

growth are neglected in the growth process considered, $\overline{w}_L$ is a lower bound to w_L. $d\overline{w}_L/dL$ increases linearly with L for small L and has a broad maximum at $L_{max} = l_c/\sqrt{2p_c}$. We expect the length dependence of the distribution of cooperativity lengths p_l to be similar to that of dw_L/dL and its approximation $d\overline{w}_L/dL$. This is what we observe in figure 5.

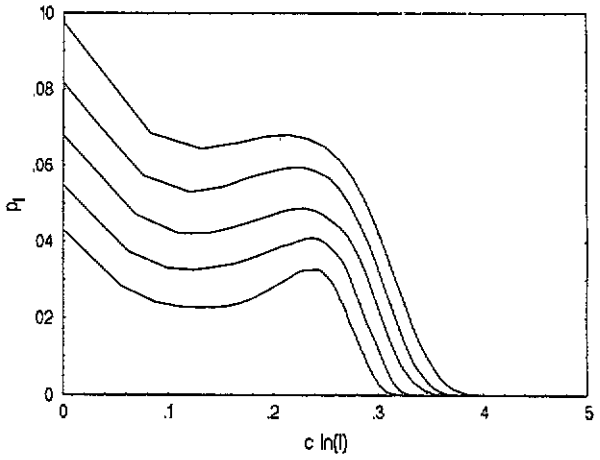

Figure 5. Distribution of cooperativity lengths p_l for the two-spin facilitated kinetic Ising model. Concentrations (from above) are $c = 0.12$, 0.11, 0.10, 0.09 and 0.08 (lattice size is 128×128).

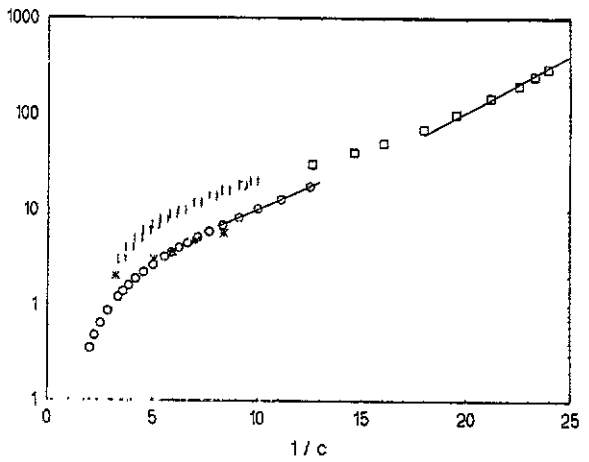

Figure 6. Concentration dependence of the average cooperativity length $\langle l \rangle$ (○), the percolation length ξ_p (□) and the correlation length ξ (⋆) of Butler and Harrowell [16] for the two-spin facilitated kinetic Ising model (data for ξ_p from [15]). The lines represent the exponential fits for large lengths.

Figure 6 shows our data for the average cooperativity length $\langle l \rangle$ together with the results of Nakanishi and Takano [15] for the percolation length ξ_p. Following the concept

of critical droplets, we can conclude [18, 19] that the asymptotic concentration dependence of the percolation length $\xi_p(c)$ is of the form

$$\xi_p(c) = a \exp(b/c). \tag{2.13}$$

The data of Nakanishi and Takano show this form (with $a = 0.48$ and $b = 0.27$) for higher concentrations where $\xi_p \gtrsim 70$. Our data for $\langle l \rangle$ can be fitted to the same formula for concentrations $0.08 \leqslant c \leqslant 0.12$ with different fit parameters $a = 1.13$ and $b = 0.219$. We have probably not reached the region of asymptotic concentration dependence of $\langle l \rangle$. Rather we expect the curves for $\langle l \rangle$ and ξ_p to merge asymptotically for low concentrations. Also included in the figure are data for an alternative definition of a correlation length ξ of cooperative motion calculated by Butler and Harrowell [16]. ξ appears to increase more slowly with decreasing up-spin concentration than $\langle l \rangle$ and ξ_p.

2.5. Hard-square lattice-gas model [3]

The hard-square lattice-gas model is a lattice gas with diffusion dynamics (Kawasaki dynamics) on a square lattice in two dimensions. The particles have an extended-hard-core interaction which forbids the simultaneous occupation of nearest-neighbour sites on the lattice. As a consequence, particles behave like hard squares, which are allowed to touch one another at corners but not to overlap. A particle can jump to a nearest-neighbour site only if the nearest-neighbour sites of the new site are vacant. Besides this kinetic contraint, the hard-core interaction also causes an order–disorder phase transition, which occurs at the critical particle concentration $c^* = 0.3677$. For concentrations higher than c^* one of the two sublattices is preferentially occupied. The model has no blocking transition below the maximum concentration $c_{\max} = 1/2$.

We call a particle 'blocked' if it cannot jump in any of the four directions, and 'mobile' otherwise. For a blocked particle to become mobile a sequence of jumps of other particles has to take place first (cf figure 1 for the spin model). The cooperativity length l of a particle in a certain lattice configuration is defined as the minimum distance up to which particles are involved in such a sequence. A particle can be blocked only by particles on sites of the same sublattice, since the nearest-neighbour sites around a particle, which belong to the other sublattice, are always empty. Therefore, only particles on the same sublattice need be considered in a sequence of jumps. For this reason we measure the distance up to which such a sequence extends by the numbers of neighbour shells on one sublattice.

The distribution p_l of cooperativity lengths and the average cooperativity length $\langle l \rangle$ were calculated for a selection of lattice-gas configurations, which were prepared by computer simulation. To prepare a configuration we start with a lattice of maximum concentration ($c_{\max} = 1/2$) and let the system equilibrate for a certain length of time, typically 4000 Monte Carlo steps per site (MCS). For the equilibration we use Glauber dynamics, whereby particles are randomly condensed on and evaporated from the sites of the lattice according to a given activity z. This procedure is necessary because it is impossible to obtain configurations with a density higher than 0.3641 by placing particles randomly on an empty lattice [3, 20]. For the calculation of the cooperativity length a computer algorithm was developed which is not reproduced here. For every configuration prepared by the equilibration process this algorithm is run to determine the cooperativity length of every particle.

The results for p_l for lattice size 128×128 and for various concentrations are shown in figure 7. The length dependence of p_l resembles the behaviour of p_l for the two-spin facilitated kinetic Ising model. For concentrations higher than $c \approx 0.38$, p_l exhibits a

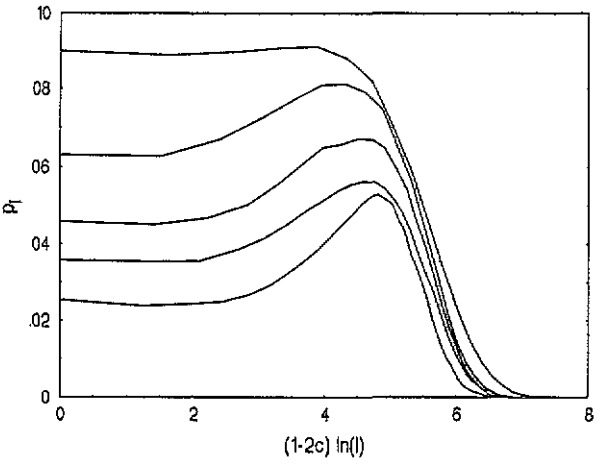

Figure 7. Distribution of cooperativity lengths p_l for the hard-square lattice-gas. Concentrations (from above) $c \approx 0.378$, 0.389, 0.397, 0.404 and 0.411 (lattice size 128×128).

broad maximum near the average cooperativity length. This maximum can be explained by the existence of critical droplets in a growth process for vacancy clusters on the majority sublattice [14], using similar ideas as for the two-spin facilitated kinetic Ising model.

The concentration dependence of the average cooperativity length is shown in figure 8, where $2\langle l\rangle + 1$ is plotted semi-logarithmically versus $1/c_h$. $c_h = 1 - 2c$ is the hole concentration on the majority sublattice in the ordered phase well above c^*; $2\langle l\rangle + 1$ rather than $\langle l\rangle$ is plotted for comparison with the percolation length $\xi_{0.5}$ [14], since the lth neighbour shell is contained in a square of width $2l + 1$. (All lengths are in units of the lattice constant of a sublattice.) According to figure 8, for high particle concentrations the two lengths $2\langle l\rangle + 1$ and $\xi_{0.5}$ become identical, with an exponential dependence on the hole concentration proportional to $\exp(b/c_h)$ ($b > 0$ is a constant). However, as for the other models, we have not reached the asymptotic behaviour for $c \to 0.5$, which, according to Froböse [14] does not start below $c \approx 0.475$. Froböse's results indicate that the asymptotic dependence of the characteristic lengths on $1/c_h$ may be more rapid than exponential.

3. A sum formula for the autocorrelation function

It is a central idea of the theory of dynamic critical phenomena to relate a characteristic relaxation time to the correlation length of order-parameter fluctuations. If a similar relation between the characteristic length and time exists for our models, the only candidate for the characteristic length is the average cooperativity length $\langle l\rangle$, or one of its alternatives. Comparing the average cooperativity length in our models with the correlation length of critical fluctuations, one notices an important difference: $\langle l\rangle$ is *not* the correlation length for the space-dependent fluctuations of some measurable quantity, but needs to be extracted from the puzzle of cooperative spin or particle dynamics. We found that the individual cooperativity length l is given by the length of a directed path of down spins for the NE model. For the two-spin facilitated kinetic Ising model and the hard-square lattice gas l must be determined by means of a cellular automaton, which derives from the kinetic rule, or by a related algorithm.

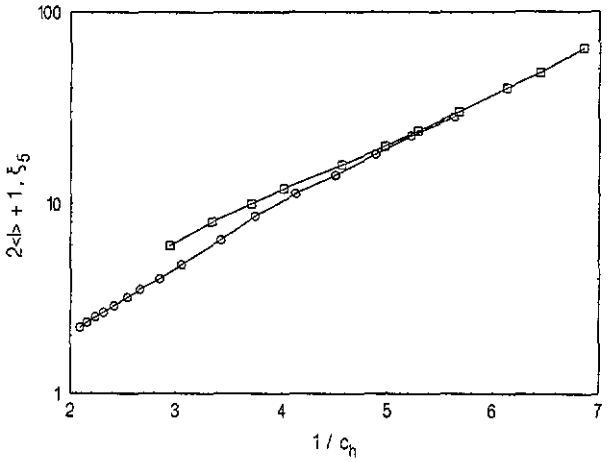

Figure 8. Concentration dependence of the percolation length $\xi_{0.5}$ (□) and of $2\langle l\rangle + 1$ (○) for the hard-square lattice-gas (data for $\xi_{0.5}$ from [14]). Lattice size 128×128 ($c_h = 1 - 2c$).

Adam and Gibbs [1] had assumed the size of a cooperatively rearranging region to be inversely proportional to the configurational entropy per molecule. We note that an analogous relation between the average cooperativity length and the entropy of the models considered above does *not* exist. In fact, the cooperativity length of the models is not related in any simple way to their entropy. For the models with a sharp blocking transition the entropy is continuous where the cooperativity length diverges. For the two-spin facilitated kinetic Ising model $\langle l\rangle$ diverges for $c \to 0$ with an essential singularity (equation 2.13), whereas the inverse of the entropy per spin diverges only as $[c(1 - \ln c)]^{-1}$. A similar difference exists for the hard-square lattice gas. The assumption of inverse proportionality between the size of the cooperatively rearranging regions and the configurational entropy is a crucial point in the derivation of the Adam–Gibbs relation

$$\langle\tau\rangle \propto \exp(a/S_c) \qquad (a > 0, \text{ constant}) \tag{3.1}$$

between the average relaxation rate $\langle\tau\rangle$ and the molar configurational entropy. For our models, therefore, the Adam–Gibbs formula (3.1) seems to have no justification in terms of cooperativity. Nevertheless, Fredrickson [21, 22] found the formula to hold with good accuracy in a wide range for the two-spin facilitated kinetic Ising model. There is no consistent explanation of this agreement.

Here we leave the path of Adam and Gibbs and search for a direct relation between the distribution of cooperativity lengths and the dynamic properties of the models. We propose an expression for the autocorrelation function in terms of relaxation rates γ_l associated with cooperativity lengths l. From the autocorrelation function the average relaxation time can be calculated. Our search was stimulated by figure 2 of [9] for the hierarchically constrained kinetic Ising chain, which shows that the autocorrelation function for the infinite chain can be obtained as the envelope function of the autocorrelation functions for finite chains with blocking boundary. A mathematical expression of similar type was proposed by Palmer, Stein, Abrahams and Anderson [23], who ascribed the origin of the Kohlrausch–Williams–Watts stretched exponential form $\exp[-(t/\tau)^\beta]$ of relaxation functions for glassy materials to the hierarchical coupling of a series of relaxation processes.

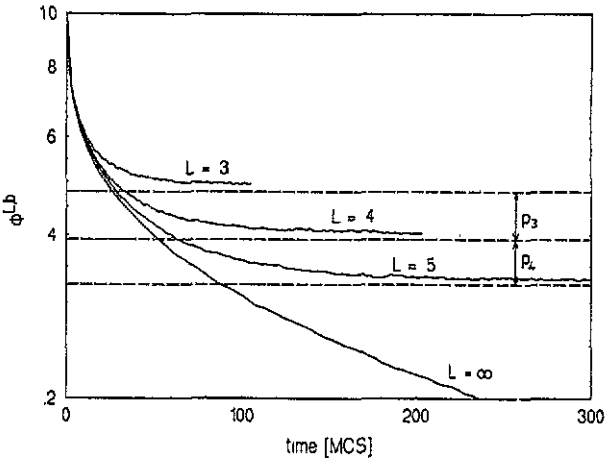

Figure 9. Monte Carlo data for $\phi^{L,b}(t)$, $L = 3, 4$ and 5 and for the autocorrelation function of the infinite system (undermost curve) for the NE model. The horizontal lines mark the asymptotic values $\phi^{L,b}(\infty)$. Concentration $c = 0.50$.

3.1. Blocking boundary conditions and cooperativity length

To decompose the autocorrelation function for the infinite system into contributions from different cooperativity lengths, it is useful to consider finite systems with blocking boundary. We formulate the case of Ising models with single-spin flip (Glauber) dynamics. An analogous formulation applies to the case of lattice-gas models with diffusion (Kawasaki) dynamics. Let

$$\phi^{L,b}(t) = \langle \sigma(t)\sigma(0)\rangle_{L,b}/\big(4c(1-c)\big) \tag{3.2}$$

denote the normalized autocorrelation function for the spin at the origin if the spins on the Lth neighbour shell are fixed in their initial directions. Under this condition only spins up to the $(L-1)$th neighbour shell can flip, provided that the kinetic rule is obeyed. Therefore, the spin at the origin is permanently blocked unless its cooperativity length is not larger than $L-1$. Since the probability that the spin at the origin is not permanently blocked is given by the total decay $1-\phi^{L,b}(\infty)$ of the autocorrelation function, the equation

$$1-\phi^{L,b}(\infty) = \sum_{l=0}^{L-1} p_l = P_{L-1} \tag{3.3}$$

follows. Taking the difference between L and $L+1$ we obtain

$$\phi^{L,b}(\infty) - \phi^{L+1,b}(\infty) = p_L \qquad \text{for } L \geqslant 1 \tag{3.4}$$

and

$$1-\phi^{1,b}(\infty) = p_0. \tag{3.5}$$

With these relations we have expressed the probability for cooperativity length L via the difference between the infinite-time limits of the autocorrelation function for blocking boundary at L and $L+1$. The relation is illustrated in figure 9. Here and in the following the unit of time is defined as the inverse of a spin-flip attempt frequency, so that the flip rate of flippable up and down spins is given by $(1-c)$ and c, respectively.

3.2. Sum formula

We propose an approximate sum formula which expresses the normalized spin-autocorrelation function $\phi(t)$ of the infinite system by a sum of exponentials. We arrive at this formula in the following way.

Since $\phi(t)$ is the limit of the autocorrelation functions $\phi^{L,b}(t)$ of finite systems with blocking boundary conditions for $L \to \infty$, it can be expressed as a sum over the differences of the latter. The expression reads

$$\phi(t) = 1 - \sum_{L=0}^{\infty} \left(\phi^{L,b}(t) - \phi^{L+1,b}(t)\right) \tag{3.6}$$

where we put $\phi^{0,b}(t) = 1$. We approximate each difference in the simplest possible way as

$$\phi^{L,b}(t) - \phi^{L+1,b}(t) = p_L(1 - \mathrm{e}^{-\gamma_L t}) \tag{3.7}$$

with a single L-dependent relaxation rate γ_L. We choose γ_L to be the smallest relaxation rate occurring in the expression for $\phi^{L+1,b}(t) - \phi^{L+1,b}(\infty)$, i. e. the rate which determines the asymptotic decay of the function $\phi^{L+1,b}(t)$ towards its infinite-time limit:

$$\phi^{L+1,b}(t) - \phi^{L+1,b}(\infty) \sim \exp(-\gamma_L t) \qquad \text{for } t \to \infty. \tag{3.8}$$

Inserting (3.7) in the sum (3.6) yields a sum formula for an approximation $\overline{\phi}(t)$ of $\phi(t)$:

$$\overline{\phi}(t) - \phi(\infty) = \sum_{L=0}^{\infty} p_L \mathrm{e}^{-\gamma_L t}. \tag{3.9}$$

(For ergodic systems we have $P_\infty = 1$ and $\phi(\infty) = 0$.)

Note that (3.7) is in accord with (3.4). However, the approximation (3.7) is fairly crude, since the time dependence of $\phi^{L,b}(t) - \phi^{L+1,b}(t)$ is generally non-exponential too. It can be shown that this difference grows at least like t^{L+1} for short times, in contrast to the linear growth with t which follows from (3.7). Nevertheless, with this approximation formula (3.9) reproduces characteristic features of the autocorrelation function $\phi(t)$, as is shown now for an example of the NE model. We mention that formula (3.9) was applied already to the special case of the hierarchically constrained kinetic Ising chain by Eisinger [8].

3.3. Test of approximation formula for the NE model

We tested the accuracy of formula (3.9) for the NE model at concentration $c = 0.5$. The distribution p_L of cooperativity lengths was calculated by computer simulation (see section 1.3). To evaluate the relaxation rates γ_L we also used simulations. Following the definition (3.8) we have to simulate $\phi^{L,b}(t)$ for different values of L. Then γ_L should be obtained by measuring the slope of $\ln(\phi^{L+1,b}(t) - \phi^{L+1,b}(\infty))$ for long times. Unfortunately, the relaxation rates γ_L could not be determined with sufficient accuracy by this procedure. Instead, we derived the relaxation rate γ_L from the asymptotic decay of a modified autocorrelation function $\phi_L(t)$, in which the contribution of the smallest relaxation rate is more pronounced. $\phi_L(t)$ is defined as the autocorrelation function of a spin with cooperativity length L which is at the centre of a system of size $L + 1$ with blocking boundary. Here we assume that the smallest relaxation rate occurring in $\phi_L(t)$ and $\phi^{L+1,b}(t)$ is the same, so that $\phi_L(t)$ also decays with relaxation rate γ_L for $t \to \infty$. This assumption

is very plausible since a spin contributing to $\phi_L(t)$ also contributes to $\phi^{L+1,b}(t)$, and L is the longest possible cooperativity length in a system of size $L+1$ with blocking boundary. Figure 10 shows a Kohlrausch plot of the Monte Carlo results for $\phi_L(t)$ for lengths $L = 1$ to $L = 12$ at up-spin concentration $c = 0.5$. The asymptotic exponential behaviour yields a straight line with unity slope. The relaxation rate γ_L can be obtained from the intersection point of this line with the ordinate axis (figure 11). Because of the slowing down of the relaxation with increasing length, the procedure of obtaining the relaxation rates γ_L from the asymptotic behaviour of the autocorrelation function $\phi_L(t)$ requires a huge amount of computation time for large lengths L. Therefore for lengths $L > 12$ we extrapolated the power-law behaviour of γ_L, which is observed for L ranging from 6 to 12, to larger L values (dashed line in figure 11). The relaxation rates obtained by extrapolation affect $\bar{\phi}(t)$ appreciably only for long times $t \gg 10^2$.

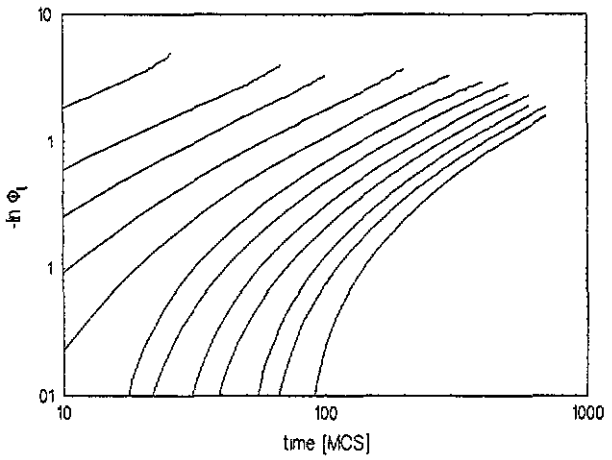

Figure 10. Kohlrausch plot of the Monte Carlo results for $\phi_L(t)$, for L from 1 to 12 (from the left) for the NE model. Concentration $c = 0.50$.

Figure 12 shows a Kohlrausch plot of the result for the sum formula (3.9) in comparison with the Monte Carlo curve for $\phi(t)$ at the same up-spin concentration $c = 0.5$. Although the agreement is not quantitative, the sum formula reproduces the main characteristics of $\phi(t)$ at short and intermediate times remarkably well. The slope in the intermediate time region ($5 < t < 500$), which corresponds to a fractional exponent $\beta_m = 0.36$, is reproduced rather accurately. We note that for long times the exponential decrease of p_L together with a power-law dependence $\gamma_L \propto L^{-\alpha}$ of the relaxation rate for large L yields, by the method of steepest descent, a Kohlrausch–Williams–Watts-like dependence of $\bar{\phi}(t)$ with fractional exponent $\beta = (1+\alpha)^{-1}$. $\beta = 0.36$ is obtained for $\alpha = 1.78$, which is close to the average slope ($= 1.73$) of γ_L in the log–log plot of figure 11.

The result of the sum formula for the asymptotic long-time regime must remain open, since the relaxation rates γ_L for large L ($L \gg 12$) could not be determined. The Kohlrausch plot of the available Monte Carlo data in figure 11 shows that the effective fractional exponent increases to about 0.5 at the longest times, but an exponential asymptotic decay of $\phi(t)$ cannot be ruled out.

Monte Carlo data of $\phi(t)$ for other concentrations look qualitatively similar to the result for $c = 0.5$. However, the fractional exponent β_m, which characterizes the time dependence

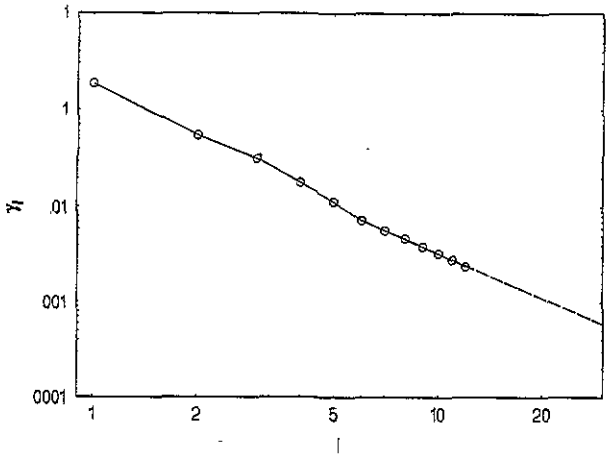

Figure 11. Relaxation rates γ_L which are obtained from the asymptotic exponential decay of $\phi_L(t)$ (see figure 10). The dashed line extrapolates the power-law fit $\gamma_L \propto L^{-1.57}$ obtained for $6 \leqslant L \leqslant 12$.

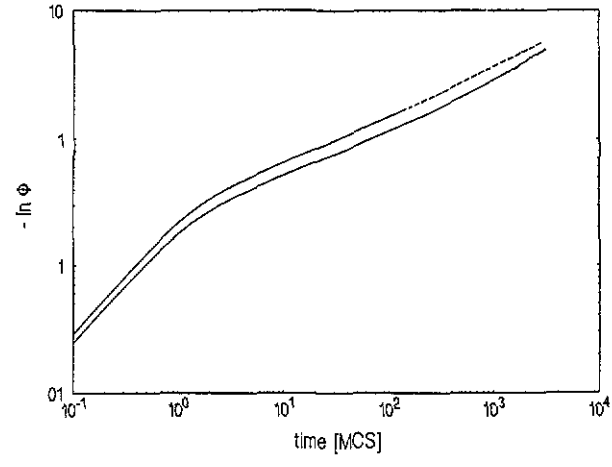

Figure 12. Kohlrausch plot of the result for the sum formula (upper curve) and the Monte Carlo curve (lower curve) for the autocorrelation function $\phi(t)$ for the NE model. Concentration $c = 0.50$.

of $\phi(t)$ in the intermediate time regime, is found to vary. For example, for $c = 0.44$ we obtain $\beta_m = 0.30$. We anticipate from this result that the form of the L-dependence of the relaxation rate γ_L, i.e. its approximate power-law dependence, also varies with c.

4. Conclusion

Regarding the relevance of the cooperativity length to measurable physical quantities, its most obvious consequence is the existence of size effects. In systems of linear dimension smaller than the average cooperativity length, most of the spins (or particles) are permanently blocked and no longer contribute to the response of the system to external perturbations.

Similar effects are to be expected for real undercooled liquids in confined geometries if the average cooperativity length of the liquid becomes comparable to or larger than the confining length. The experimental observation of such a size effect would yield the average cooperativity length most directly. Systems of interest are glass-forming liquids filled in porous inorganic crystals or glasses [24], or the amorphous regions of semicrystalline polymers [25]. The glass transition of such confined liquids could be probed by a variety of experimental techniques, the most common being the differential scanning calorimetry. The suppression of cooperative motion due to confinement should lead to a broadening and shift to lower temperature of the glass transition. So far only a broadening has been observed, but not a shift to lower temperatures [24, 25]. The difficulty lies in the smallness of the cooperativity length of glass-forming liquids, which has been estimated to be of the order of 20 Å [26]. In systems of comparable linear dimensions the size effect due to the suppression of cooperative motion may be masked by effects of liquid–wall interactions.

As a second consequence of the concept of a cooperativity length, we explored a possible connection between the autocorrelation function and the distribution of cooperativity lengths, assuming a relation between cooperativity length and relaxation rate. Introducing blocking boundary conditions for finite systems, we arrived at a sum formula for the normalized autocorrelation function of the infinite system, which contains the probabilities p_L of cooperativity lengths L and the associated relaxation rates γ_L as parameters. The relaxation rate γ_L is chosen to be the smallest relaxation rate of a system of size L with blocking boundary. This choice of the relaxation rate is not unique since the autocorrelation function for spins with a particular value of the cooperativity length is also of stretched exponential form. However, for our choice the sum formula was found to yield good overall agreement with the Monte Carlo data for the autocorrelation function of the NE model for up-spin concentration $c = 0.5$. In particular, the effective fractional exponent $\beta_m = 0.36$ for the intermediate time region is well reproduced. It would be of interest to test the validity of our sum formula for other models and concentrations as well.

Acknowledgments

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