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A hierarchically constrained kinetic Ising model

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A concrete model for hierarchically constrained dynamics in the sense proposed by Palmer et al. (Phys. Rev. Lett. **53**, 958 (1984)) is presented. The model is a kinetic Ising chain with an asymmetric kinetic constraint, allowing a spin to flip only if its neighbour to the right is in the up spin state. The spin autocorrelation function is obtained by numerically exact calculation for finite chain length up to $L=9$ and by Monte Carlo simulation for effectively infinite chain length. The Kohlrausch-Williams-Watts formula is found to fit the results only with limited accuracy, and within limited time intervals. We also performed an analytical calculation using an effective-medium approximation. The approximation leads to a spurious blocking transition at a critical up spin concentration $c=0.5$.

1. Introduction

It has been suggested that the stretched exponential time dependence of relaxation in supercooled liquids near the glass transition points to a characteristic kinetic pattern. Adam and Gibbs [1] described this pattern in terms of "cooperatively rearranging regions". According to Palmer et al. [2] (see also [3, 4]), relaxation proceeds in a sequence of relaxation steps successively coupled by a kinetic constraint. These authors argued that such a "hierarchy of constraints" leads to a distribution of relaxation times from which the Kohlrausch-Williams-Watts (KWW) formula of stretched exponential relaxation results. In this paper we propose a concrete one-dimensional kinetic Ising model with a kinetic constraint, which is perhaps the simplest model with "hierarchically constrained dynamics" in the sense postulated by Palmer et al. We calculate the spin autocorrelation function for this model and compare it with the KWW-formula.

The paper is organized as follows. The model is defined in Sect. 2. In Sect. 3 the equations of motion governing the time dependence of the autocorrelation function are derived, both for the infinite and finite chain. An argument for the absence of a blocking transition is given in Sect. 4. The results of numerically exact calculations of the autocorrelation function for chains of finite length and of a Monte Carlo simulation for long chains are presented in Sects. 5 and 6. They are compared with the KWW-formula in Sect. 7. Finally, an analytical calculation in the framework of the effective-medium approximation is reported in Sect. 8.

2. The model

We consider a one-dimensional kinetic Ising model with non-interacting spins in a magnetic field subject to the following kinetic constraint: spin number i can flip only if spin number $i+1$ to the right of it is in the "up" state. Otherwise spin i is blocked in its present state. By this constraint each spin is successively coupled to all spins to the right of it, and independent of all spins to the left. The model is translationally invariant, i.e. every spin relaxes identically on the average in the infinite chain. To calculate the relaxation function, which is the normalized spin autocorrelation function, for spin $i=0$, say, we need to treat only the semi-infinite chain with $i \geqq 0$.

The model can be interpreted in terms of molecular relaxation in supercooled liquids in the following way. Suppose that the flip of spin $i=0$ corresponds to a step of orientational or translational motion of a given molecule, by which relaxation occurs. Then the kinetic constraint that spin $i=1$ must be in the up state expresses a (geometric or energetic) condition to be met in the shell of nearest neighbours around the given molecule, for the relaxation step considered to be possible. A flip of spin $i=1$ into or out of the up state corresponds to transitions within the shell of first neighbours into or out of configurations in which this condition is fulfilled. The kinetic constraint requiring spin $i=2$ to be in the up state, in turn, derives from a condition on the shell of second-nearest neighbours for the transitions within the first shell to be allowed. And so on.

Our model can be regarded as an asymmetric version of the one-spin facilitated kinetic Ising model in one dimension. In the usual symmetric n-spin facilitated kinetic Ising models [5–9] a spin is allowed to flip if *any* n nearest-neighbour spins are up spins. In this case, for $n=1$, an up spin state can move around freely [8]. As a consequence, at low up spin concentration relaxation is of the defect-diffusion type [10]. In our asymmetric model,on the other hand, an up spin state can propagate freely only to the left. Motion to the right, however, requires the presence of additional up spins. The asymmetry of the kinetic constraint makes our model "cooperative". It has been shown recently [11, 12] that asymmetry of interaction rather than of kinetic constraint may also cause stretched exponential relaxation in a one-demensional kinetic Ising model.

There is a certain similarity between our model and a more general model proposed by Palmer et al. [2]. These authors considered a semi-infinite chain with a number N_n of Ising spins on site $n\,(n=0,1,2,\ldots)$. A spin on site $n+1$ can flip only if a certain number $\mu_n \leqq N_n$ of the spins on site n are all in one particular state. Contrary to our model, this kinetic constraint couples a spin to its *left* neighbours. Since the chain is bounded to the left, i.e. in the direction of decreasing n, the relaxation behaviour at different sites is different even in the semi-infinite chain. The spin autocorrelation function for this *inhomogeneous* chain is defined as the spatial average over all sites. In the special case $N_n=\mu_n=1$ for all n, which would correspond to our model, their result (7) for the spin autocorrelation function, derived in a heuristic manner, reads

$$q(t)=\frac{1}{N}\sum_{n=1}^{N}\exp(-t/2^n\tau_0)), \tag{1}$$

where N is the total number of sites. In the limit $N\to\infty$ of a semi-infinite chain $q(t)$ tends to unity for any $t\geqq 0$. It is clear then that both the model and the heuristic treatment of [2] is very different from ours.

Finally we add a remark concerning the origin of non-exponential relaxation in our model. To elucidate the nature of the model it is worth discussing an erroneous argument that would predict exponential relaxation. Calculating the relaxation function for spin $i=0$ we assume spin $i=0$ to be in the "up" state at time $t=0$, while all other spins $i>0$ are in equilibrium (see Sect. 3). Since the spins to the right of spin $i=0$ are independent of the spin at the origin, they remain in equilibrium at later times. One might - erroneously - think that this implies that the conditional probability $p(\sigma_1=\uparrow|\sigma_0)$ for finding spin $i=1$ in the up state if spin $i=0$ is in the up or down state is given by the constant equilibrium value c, independent of the value σ_0 of spin $i=0$. If this were case, a simple relaxation equation for the up spin probability of spin $i=0$, leading to exponential relaxation, would be obtained. However, the kinetic constraint coupling a spin i to its right-hand neighbour $i+1$ causes a time-dependent correlation between the directions of spin $i=1$ and the spin $i=0$ at the origin. By symmetry, not only does the conditional probability $p(\sigma_0|\sigma_1)$ depend on σ_1, but also $p(\sigma_1|\sigma_0)$ depends on σ_0. As shown in the next section, the kinetic constraint leads to an infinite hierarchy of equations of motion for the joint probabilities of larger and larger clusters of spins. As a result, the relaxation of spin $i=0$ is non-exponential.

3. Basic equations

So far we have introduced our model as an Ising spin model, where a spin i may have values $\sigma_i=\pm 1$. As will become clear presently, it is convenient to use the occupation numbers

$$n_i=\tfrac{1}{2}(\sigma_i+1), \tag{2}$$

equal to 0 or 1 with $n_i^2=n_i$, of the equivalent lattice gas model instead of the spin variables. If site i is in the state with occupation number n_i, let

$$\bar{n}_i=1-n_i \tag{3}$$

denote the occupation number of the alternative state. We need to consider only the semi-infinite chain with $i\geqq 0$.

For Glauberian dynamics with rates $w_i(\{n\})$ of single-site transitions $n_i\to\bar{n}_i$ the Master equation for the time-dependent probability $P(\{n\};t)$ of configuration $\{n\}=(n_0,n_1,\ldots)$ reads

$$\partial_t P(\{n\},t)=\sum_{i=0}^{\infty}\{-w_i(n_0,\ldots,n_i,\ldots)P(n_0,\ldots n_i,\ldots;t) + w_i(n_0,\ldots,\bar{n}_i,\ldots)P(n_0,\ldots\bar{n}_i,\ldots;t)\}. \tag{4}$$

Instead of using the probabilities of pure configurations of the entire chain, one may work with the time-dependent expectation values of products of occupation numbers $n_{i_0},n_{i_1},\ldots n_{i_r}$, which are the joint probabilities for the selection of sites $i_0,i_1,\ldots i_r$ to be occupied:

$$\langle n_{i_0}n_{i_1}\ldots n_{i_r}\rangle_t=\sum_{\{n\}}n_{i_0}n_{i_1}\ldots n_{i_r}P(\{n\};t) = P(n_{i_0}=n_{i_1}=\ldots n_{i_r}=1). \tag{5}$$

The equations of motion for these expectation values are obtained from the Master equation in the same manner as in [13] as

$$\partial_t\langle n_{i_0}n_{i_1}\ldots n_{i_r}\rangle_t=\sum_{k=0}^{r}\langle n_{i_0}\ldots n_{i_{k-1}}(1-2n_{i_k}) \times w_k(\{n\})n_{i_{k+1}}\ldots n_{i_r}\rangle_t. \tag{6}$$

The transition rate of our model is given by

$$w_i(\{n\})=\Gamma[c+(1-2c)n_i]n_{i+1}. \tag{7}$$

Choosing the inverse of the attempt frequency Γ as the unit of time, we can drop the factor Γ in (7) further on. c is the concentration, equal to the average occupation $\langle n_i\rangle_{\mathrm{eq}}$ of any site in equilibrium. The first factor in the expression (7) for the transition rate is required by the

condition of detailed balance. The second factor in (7) derives from the kinetic constraint characteristic of our model. The fact that the constraint is expressed simply by a factor n_{i+1} is the reason for choosing the lattice gas rather than the Ising spin formulation of the model.

The kinetic constraint expressed by the transition rate (7) has the following obvious consequence. Suppose that in the initial configuration all sites to the right of a certain occupied site $i=l$ are vacant. Then the occupied site furthest to the right will always be number l. Therefore, configurations corresponding to different values of l are not dynamically accessible one from the other. The configuration space of the semi-infinite chain decomposes into irreducible sets of 2^l configurations with the same maximum site number l of the occupied sites.

Our objective is to calculate the equilibrium autocorrelation function $\langle \Delta n_0(t)\Delta n_0(0)\rangle_{\text{eq}}$ of the time-dependent occupation number fluctuation $\Delta n_0 = n_0 - c$ at site $i=0$. The normalized autocorrelation function defines the relaxation function

$$\phi(t) = \frac{\langle \Delta n_0(t)\Delta n_0(0)\rangle_{\text{eq}}}{c(1-c)} \tag{8}$$

with $\phi(t=0)=1$. According to linear response theory, $\phi(t)$ determines the expectation value $\langle \Delta n_0\rangle_t$ in non-equilibirum, which obtains for a special initial condition at time $t=0$. The initial condition prescribes a deviation $\langle \Delta n_0\rangle_{t=0}$ of the average occupation of site $i=0$ from the equilibrium value c, while leaving the rest of the chain in equilibrium. The relation of linear response theory is

$$\phi(t) = \frac{\langle \Delta n_0\rangle_t}{\langle \Delta n_0\rangle_{t=0}}. \tag{9}$$

Due to the lack of interaction between different sites, the occupation of site $i=0$ and of sites $i>0$ is uncorrelated both in equilibrium and at time $t=0$. For this reason the relation between the deviation $\langle \Delta n_0\rangle_t$ at time $t>0$ and the initial deviation $\langle \Delta n_0\rangle_{t=0}$ is linear for arbitrary values of the latter. Therefore (9) holds without restriction on the magnitude of the initial deviation. In the rest of this section we shall apply the initial condition $\langle n_0\rangle_{t=0}=1$. To calculate $\phi(t)$ by Monte Carlo simulation, however, we employ relation (9) both for $\langle n_0\rangle_{t=0}=1$ and $\langle n_0\rangle_{t=0}=0$. As mentioned already, the occupation of the sites $i\geqq 1$ to the right of site $i=0$ remains in equilibrium at later times if it is in equilibrium initially at $t=0$. This is guaranteed by the condition of detailed balance. Therefore expectation values $\langle n_{i_1} n_{i_2}\ldots n_{i_r}\rangle_t$ not involving the occupation of site $i=0$ (i.e. for $i_1, i_2, \ldots i_r \neq 0$) at all times are given by their equilibrium values:

$$\langle n_{i_1} n_{i_2}\ldots n_{i_r}\rangle_t = c^r. \tag{10}$$

We now write down the equations of motion for the hierarchy of expectation values $\langle n_0 n_{i_1}\ldots n_{i_r}\rangle_t$ (with $0<i_1<i_2<\ldots<i_r$), which derive from the initial value problem for the time-dependent average occupation $\langle n_0\rangle_t$ with given initial condition $\langle n_0\rangle_{t=0}$. The first two equations read

$$\partial_t\langle n_0\rangle_t = -\langle n_0 n_1\rangle_t + c^2 \tag{11}$$

$$\partial_t\langle n_0 n_1\rangle_t = -(\langle n_0 n_1\rangle_t + \langle n_0 n_1 n_2\rangle_t) + c\langle n_0 n_2\rangle_t + c^2. \tag{12}$$

The general equation of motion can be written as

$$\begin{aligned}\partial_t\langle n_0 n_{i_1}\ldots n_{i_r}\rangle_t &= -\langle n_0 n_1 n_{i_1}\ldots n_{i_r}\rangle_t + c^{r'} \\ &+ \sum_{k=1}^{r}(-\langle n_0 n_{i_1}\ldots n_{i_k} n_{i_k+1}\ldots n_{i_r}\rangle_t \\ &+ c\langle n_0 n_{i_1}\ldots \not{n}_{i_k} n_{i_k+1}\ldots n_{i_r}\rangle_t)\end{aligned} \tag{13}$$

with

$$r' = r+1+\delta_{i_1,1}. \tag{14}$$

The constant inhomogeneous term $c^{r'}$ obtains from the term

$$c\langle n_1 n_{i_1}\ldots n_{i_r}\rangle \tag{15}$$

using Eq. (10). Consider the set of the 2^{l-1} different expectation values $\langle n_0 n_{i_1}\ldots n_{i_r}\rangle_t$ with $0<i_1<\ldots<i_r$ for fixed $i_r=l$. Since for each of these expectation values the equation of motion (13) contains a term proportional to $\langle n_0 n_{i_1}\ldots n_l n_{l+1}\rangle_t$ and to $\langle n_0 n_{i_1}\ldots \not{n}_l n_{l+1}\rangle_t$, in all the 2^{l-1} equations of motion all 2^l different expectation values $\langle n_0, n_{i_1}\ldots n_{i'_r}\rangle_t$ with fixed $i'_r = l+1$ occur. For $l=1$ (12) couples $\langle n_0 n_1\rangle_t$ to $\langle n_0 n_2\rangle_t$ and $\langle n_0 n_1 n_2\rangle_t$. This proves that the quantity of interest $\langle n_0\rangle_t$ couples to the complete hierarchy of expectation values $\langle n_0 n_{i_1}\ldots n_{i_r}\rangle_t$.

Chains of finite length

Until now we dealt with the semi-infinite chain. It is of interest also to treat chains of finite length L with sites $i=0,1,\ldots L$. In Sect. 5 we present exact calculations for chain lengths up to $L=9$. Monte Carlo calculations (Sect. 6) naturally are done for finite chains. We distinguish two different boundary conditions for finite chains:

i) Blocking boundary condition, by which the occupation of the last site to the right is blocked and remains in the initial state. This corresponds to chopping off the rest of the chain, so that the last site is permanently blocked by the kinetic constraint.

ii) Free boundary conditions, by which the kinetic constraint on the last site $i=L$ is lifted.

Either of the two types of boundary condition may be obtained by keeping a fictive site $i=L+1$ permanently empty or occupied.

All 2^{L+1} configurations of a chain of length L with free boundary condition are kinetically accessible one from the other and correspond to the irreducible partition of the configurations of the infinite chain in which the occupied site furthest to the right is site number $L+1$.

A finite chain of length $L > 0$ with free boundary condition is ergodic. To indicate the chain length L and the type of boundary condition chosen, we shall use a superscript (L, b) or (L, f), respectively.

A useful relation exists between the solutions $\langle n_0 \rangle_t$ for finite chains with different boundary conditions. It derives from the following consideration. In a chain of length L with blocking boundary condition the last site $i = L$ is permanently occupied with probability c and permanently vacant with probability $1 - c$. If it is occupied, the rest of chain behaves like a chain of length $L - 1$ with free boundary condition. If it is vacant, the neighbouring site $i = L - 1$ is also permanently blocked, so that the rest of the chain of length $L - 1$ has a blocking boundary condition. In terms of the solution $\langle n_0 \rangle_t$ this is expressed by the relation

$$\langle n_0 \rangle_t^{L,b} = c \langle n_0 \rangle_t^{L-1,f} + (1-c) \langle n_0 \rangle_t^{L-1,b}, \tag{16}$$

valid for any $L \geqq 1$. Solving for the solution with free boundary condition we find

$$\langle n_0 \rangle_t^{L,f} = \frac{1}{c} \langle n_0 \rangle_t^{L+1,b} - \frac{1-c}{c} \langle n_0 \rangle_t^{L,b}. \tag{17}$$

Iteration of relation (16) yields the solution with blocking boundary condition in terms of solutions with free boundary condition for different lengths:

$$\langle n_0 \rangle_t^{L,b} = (1-c)^L + \frac{c}{1-c} \sum_{L'=0}^{L-1} (1-c)^{L-L'} \langle n_0 \rangle_t^{L',f}. \tag{18}$$

An identical relation holds for the corresponding relaxation functions $\phi(t)$, related to $\langle n_0 \rangle_t$ by (see (9))

$$\phi(t) = \frac{\langle n_0 \rangle_t - c}{1-c}. \tag{19}$$

Formula (18) reflects the decomposition of the configuration space of a chain of length L with blocking boundary condition into the irreducible partitions. Since the relaxation functions for the chains with free boundary condition decay to zero for $t \to \infty$ (Sect. 4), the limiting value for blocking boundary condition is given by

$$\lim_{t \to \infty} \phi^{L,b}(t) = (1-c)^L. \tag{20}$$

This is just the probability of the configuration with all sites $1 \leqq i \leqq L$ vacant. This last formula enables us to estimate how long a chain must be if the decay of the relaxation function for the infinite chain $\phi^{(\infty)}$ from 1 to a given value ε is to be calculated. Equating $(1-c)^L$ with ε yields the condition

$$L > \frac{\ln \varepsilon}{\ln (1-c)}. \tag{21}$$

For $c = 0.5$ and $\varepsilon = 10^{-2}$, e.g., L must be at least 7. The r.h.s. of (21) estimates the maximum distance over which neighbouring sites influence the decay of the perturbation $\langle \Delta n_0 \rangle$ from its initial value $\langle \Delta n_0 \rangle_{t=0}$ to $\varepsilon \langle \Delta n_0 \rangle_{t=0}$.

The dynamical matrix

To write the system of differential equations (13) in vector form, we need to number the expectation values $\langle n_0 n_{i_1} \ldots n_{i_r} \rangle$ as the components of a vector $\mathbf{x}$. We number such an expectation value by the binary number $j(i_1, i_2 \ldots i_r)$ which is defined by the site numbers $i_1, i_2, \ldots i_r$ with $0 < i_1 < i_2 \ldots < i_r$. The i_k-th binary digit (for $k = 1, 2, \ldots r$) of this number is one, the other digits are zero. The value of the binary number is given by

$$j(i_i, i_2 \ldots i_r) = \sum_{k=1}^{r} 2^{i_k - 1}. \tag{22}$$

For $r = 0$ we have $j(\emptyset) = 0$. We note that for fixed maximum site number $i_r = l \geqq 1$ the binary numbers $j(i_1, i_2, \ldots i_r)$ range from 2^{l-1} to $2^l - 1$. All expectation values occurring in a finite portion of the chain from site 0 to site l are contained in the first 2^l components of the vector $\mathbf{x}$. The first components of $\mathbf{x}$ read

$$\mathbf{x} = \begin{pmatrix} x_0 \\ x_1 \\ x_2 \\ x_3 \\ x_4 \\ \vdots \end{pmatrix} = \begin{pmatrix} \langle n_0 \rangle \\ \langle n_0 n_1 \rangle \\ \langle n_0 n_2 \rangle \\ \langle n_0 n_1 n_2 \rangle \\ \langle n_0 n_3 \rangle \\ \vdots \end{pmatrix}. \tag{23}$$

We get rid of the constant inhomogeneous terms in the differential equations (13) by introducing the deviations from equilibrium

$$\Delta x_j = x_j - x_{j,\mathrm{eq}}. \tag{24}$$

For $j = 0$: $\Delta x_0 = \langle \Delta n_0 \rangle$. The equilibrium value of x_j is given by

$$x_{j,\mathrm{eq}} = c^{r+1}, \tag{25}$$

where $r + 1$ is the number of factors in the equation value. The initial value of Δx_j is

$$\Delta x_j (t = 0) = (1-c) c^r. \tag{26}$$

The system of homogeneous differential equations can then be written as

$$(\partial_t \delta_{j,j'} + M_{jj'}) \Delta x_{j'} = 0 \quad (j = 0, 1, 2, \ldots). \tag{27}$$

We turn to the block structure of the dynamical matrix M. In the system of differential equations (13) an expectation value with maximum site number l is only coupled to expectation values with maximum site number equal to l or $l+1$. Therefore, for $l \geqq 1$ and j ranging from 2^{l-1} to $2^l - 1$, non-zero matrix elements $M_{jj'}$ exist only in the range $2^{l-1} \leqq j' \leqq 2^{l+1} - 1$. The matrix M is composed of rectangular $2^{l-1} \times (3 \cdot 2^{l-1})$ matrices for $l = 1, 2, \ldots$. The first row M contains only one single non-zero matrix element:

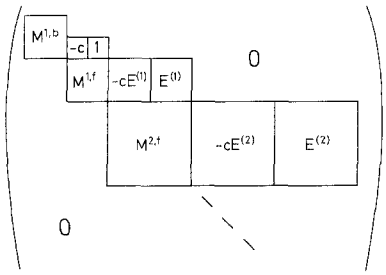

Fig. 1. The block matrix form of the dynamical matrix M. Submatrices are explained in the text

$$M_{0,j'} = \delta_{j',1}. \tag{28}$$

The matrix M is built by adding the rectangular $2^{l-1} \times (3 \cdot 2^{l-1})$ blocks underneath the first row for $l = 1, 2, \ldots$ successively. The blocks are shifted horizontally in such a way that their left-hand quadratic $2^{l-1} \times 2^{l-1}$ parts are along the diagonal of M. The structure of the matrix obtained is that of Fig. 1 (see below). Apparently, the block structure of M is self-similar.

Let us denote the rectangular $2^l \times 2^{l+1}$ matrix ($l \geqq 1$) formed by the non-zero matrix elements in the first 2^l rows of M by $M^{(l)}$. The left-hand quadratic $2^l \times 2^l$ part of $M^{(l)}$ is the dynamical matrix $M^{l,b}$ for the finite chain of length l with blocking boundary condition. Let us denote the dynamical matrix for a chain of length l with free boundary condition by $M^{l,f}$. We give without proof the rules for building $M^{(l)}$, $M^{l,f}$ and $M^{l+1,b}$ from $M^{l,b}$. The rules are explained in terms of the block structures of the different matrices as follows:

$$M^{(l)} = \begin{pmatrix} M^{l,b} & 0 \\ & \begin{matrix} -cE^{(l-1)} & E^{(l-1)} \end{matrix} \end{pmatrix}, \tag{29}$$

$$M^{l,f} = \begin{pmatrix} M^{l,b} & 0 \\ & \begin{matrix} -cE^{(l-1)} & E^{(l-1)} \end{matrix} \end{pmatrix} + \begin{pmatrix} 0 & \\ & \begin{matrix} -cE^{(l-1)} & E^{(l-1)} \end{matrix} \end{pmatrix}, \tag{30}$$

$$M^{l+1,b} = \begin{pmatrix} M^{(l)} & \\ 0 & M^{l,f} \end{pmatrix}. \tag{31}$$

Here $E^{(l)}$ denotes the $2^l \times 2^l$ unit matrix. Using these rules, the matrices $M^{(l)}$, $M^{l,f}$, $M^{l+1,b}$ for $l = 1, 2, \ldots$ can be written down successively starting from

$$M^{1,b} = \begin{pmatrix} 0 & 1 \\ 0 & 1 \end{pmatrix}. \tag{32}$$

Combining (29) and (31) and iterating, one can express M by the sequence of matrices $M^{l,f}$ for $l = \geqq 1$, together with $M^{1,b}$ and the unit matrices $E^{(l)}$. This is shown in Fig. 1. The matrices $M^{l,f}$ for $l \geqq 1$ are the block diagonal parts of M.

We now take the Laplace transform with respect to the time of the vector equation of motion (27), which yields for $j = 0, 1, 2, \ldots$

$$(s\delta_{j,j'} + M_{jj'})\, \widetilde{\Delta x}_{j'}(s) = \Delta x_j(t=0) \tag{33}$$

with

$$\widetilde{\Delta x}_j(s) = \int_0^\infty \mathrm{d}t\, \mathrm{e}^{-st} \Delta x_j(t) \tag{34}$$

and the initial values $\Delta x_j(t=0)$ given by (26). According to Kramer's rule, the solution for the component $\widetilde{\Delta x}_0$ can be written as

$$\widetilde{\Delta x}_0(s) = \frac{\det B}{\det A}, \tag{35}$$

where

$$A_{ij} = s\delta_{j,j'} + M_{jj'} \quad (j, j' \geqq 0), \tag{36}$$

and B is the matrix obtained from A by substituting the vector of initial values $\Delta x_j(t=0)$ for the zeroth column of A. The zeros of the denominator of expression (35) determine the relaxation rates occurring in the time-dependent solution $\Delta x_0(t)$. It follows from the block structure of the matrix M (Fig. 1) that only the block diagonal part of matrix A contributes to its determinant. The result for the denominator in (35) therefore has the form of an infinite product:

$$\det A = s(s+1) \prod_{l=1}^{\infty} \det(sE^{(l)} + M^{l,f}). \tag{37}$$

For a finite chain of length L with blocking boundary the product extends only to a maximum value $l_{\max} = L - 1$. By comparison, for a chain of length L with free boundary, the denominator of (35) is given by

$$\det(sE^{(L)} + M^{L,f}). \tag{38}$$

The factorization (37) of the denominator of (35) for the semi-infinite chain or for a finite chain with blocking boundary is due to the fact that each irreducible partition of 2^{l+1} configurations independently determines 2^l relaxation frequencies. These are also the relaxation frequencies occurring in the finite chain of length l with free boundary.

For illustration of these general formulae, we give the results for $\widetilde{\Delta x}_0^{L,b}$ for $L=1$ and $L=2$:

$$\widetilde{\Delta x}_0^{1,b}(s)=\frac{(1-c)^2}{s}+\frac{c(1-c)}{s+1}, \tag{39}$$

$$\widetilde{\Delta x}_0^{2,b}(s)=\frac{(1-c)^3}{s}+\frac{c(1-c)^2}{s+1}+\frac{c(1-c)}{2}\sum_{\pm}\frac{1\pm\sqrt{1-c}}{s+1\mp\sqrt{1-c}}. \tag{40}$$

Using relation (17) the solution $\widetilde{\Delta x}_0^{1,f}$ for $L=1$ and free boundary is obtained from these results as

$$\widetilde{\Delta x}^{1,f}=\frac{1-c}{2}\sum_{\pm}\frac{1\pm\sqrt{1-c}}{s+1\mp\sqrt{1-c}}. \tag{41}$$

The relaxation frequencies

$$s_{1,2}=-1\pm\sqrt{1-c} \tag{42}$$

arise from the irreducible partition of the four configurations

0, 0, 1, 0,... 0, 1, 1, 0,... 1, 0, 1, 0,... 1, 1, 1, 0,...

corresponding to the free chain of length $L=1$.

4. Absence of a blocking transition

The first question to be asked regarding the relaxation behaviour of our model is whether the semi-infinite chain with relaxation function $\phi^{(\infty)}(t)$ relaxes to equilibrium at all concentrations $c>0$, in which case $\phi^{(\infty)}(t)$ decays to zero asymptotically for long times. In the opposite case a blocking transition would exist at some critical concentration $c^*>0$, below which $\phi^{(\infty)}(t)$ would tend to a finite limit for $t\to\infty$. We give an argument for the absence of such a transition. The argument combines three statements which seem evident, although we so far have no mathematical proofs for them. The statements, which are also confirmed by the numerical results presented below, are:

a) Since shifting the *blocking* boundary of a finite chain from L to $L+1$ facilitates the relaxation at site $i=0$, the inequality

$$\phi^{L+1,b}(t)\leqq\phi^{L,b}(t) \tag{43}$$

holds for the L-dependence of $\phi^{L,b}$ at any t.

b) Similarly, the reverse inequality

$$\phi^{L+1,f}(t)\geqq\phi^{L,f}(t) \tag{44}$$

holds for $\phi^{L,f}$ as a function of L, since shifting the *free* boundary of a finite chain to the right has the opposite effect of slowing down the relaxation at the origin.

c) The third statement concerns the ergodicity of a finite chain with free boundary, which implies that

$$\lim_{t\to\infty}\phi^{L,f}(t)=0 \tag{45}$$

holds. Using relation (18), we then obtain

$$\lim_{t\to\infty}\phi^{L,b}(t)=(1-c)^L. \tag{46}$$

The relaxation function $\phi^{(\infty)}$ of the semi-infinite chain is given by the limits

$$\phi^{(\infty)}(t)=\lim_{L\to\infty}\phi^{L,b}(t)=\lim_{L\to\infty}\phi^{L,f}(t). \tag{47}$$

Note that the desired results

$$\lim_{t\to\infty}\phi^{(\infty)}(t)=0 \tag{48}$$

does not follow from (45) or (46) alone, since the limits with respect to L and t may not be interchangeable. However, iterating (43) and (44) we deduce that for any $L>0$ and $t>0$ the relaxation function $\phi^{L,b}(t)$ and $\phi^{L,f}(t)$ represent an upper and lower bound to $\phi^{(\infty)}(t)$:

$$\phi^{L,f}(t)\leqq\phi^{(\infty)}(t)\leqq\phi^{L,b}(t). \tag{49}$$

Taking the limit $t\to\infty$ and letting L go to infinity we arrive at the result (48).

5. Numerical solution for finite chains

Using the formulas developed in the last section, we calculate the relaxation function numerically for chains of finite size with either blocking or free boundary condition.

The elements of the matrix $M^{L,b}$ or $M^{L,f}$ are obtained recursively with the use of rules (29–31), starting from $M^{1,b}$. The equation

$$(M+sE)\,\widetilde{\Delta x}=\Delta x(t=0) \tag{50}$$

for the 2^L-component vector $\widetilde{\Delta x}$ is solved for $\widetilde{\Delta x}_0$ by standard numerical methods. The result is transformed back into the time domain numerically using the Stehfest algorithm [14] for inverse Laplace transformation. This algorithm works with good accuracy for monotonic and continuous functions like our relaxation function. It has the advantage of performing the Laplace-inversion on the real s-axis.

Since the dimension of the vector $\widetilde{\Delta x}$ increases with L as 2^L, the storage capacity of the computer limits the numerically manageable chain length to $L\lesssim 10$. In Eq. (21) we have given a condition for the relaxation function of a finite chain to be a good approximation to the relaxation function $\phi^{(\infty)}$ of the infinite chain. It follows from this condition that, for $L\leqq 10$, the decay of $\phi^{(\infty)}(t)$ from 1 to a chosen value $\varepsilon=10^{-2}$ can be obtained with good accuracy only for concentrations $c\gtrsim 0.5$.

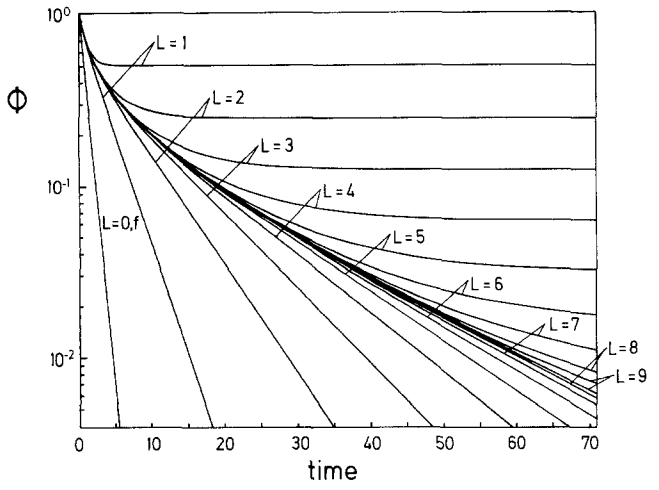

Fig. 2. Semi-log plot of relaxation functions for chains of length L with blocking (upper curve) and free boundary (lower curve) for $c=0.5$

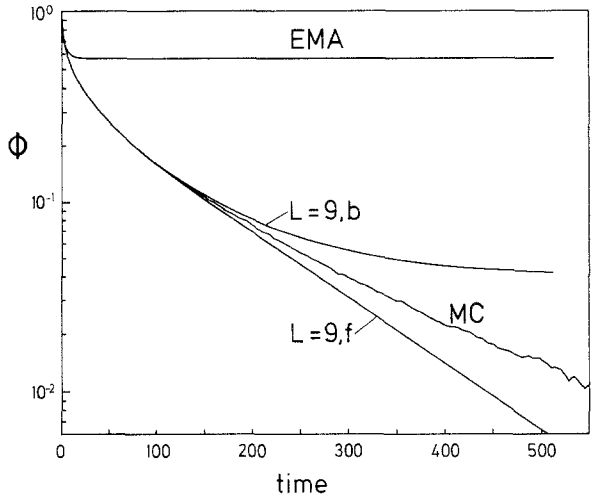

Fig. 3. Semi-log plot of relaxation functions for $L=9$ with blocking and free boundary conditions, and Monte Carlo data for semi-infinite chain. Concentration is $c=0.3$. Upper curve: result of effective-medium approximation (Sect. 8)

The results of the numerical calculation of the relaxation function for $c=0.5$ and chain lengths L from 1 to 9 are shown in Fig. 2. For each value of L, the upper curve represents the relaxation function $\phi^{L,b}$ for blocking boundary condition, the lower curve describes the relaxation function $\phi^{L,f}$ for free boundary condition. Asymptotically for long times, $\phi^{L,b}$ approaches the constant value $(1-c)^L$, while $\phi^{L,f}$ decays exponentially. The inequalities (43) and (44) and equations (45) and (46) are fulfilled. For $L=9$ the two curves for $\phi^{L,b}(t)$ and $\phi^{L,f}(t)$ start to deviate from one another at $\phi \approx 10^{-2}$. Therefore they both are good approximations to $\phi^{(\infty)}(t)$ for ϕ-values larger than this, in agreement with our criterion.

6. Monte Carlo simulation

In the preceding section $\phi^{(\infty)}(t)$ could be obtained by calculations for finite chains of length $L \leqq 10$, provided that the concentration was not lower than $c \approx 0.5$. Using Monte Carlo simulation, which can be performed for much longer chains, we can extend this range of concentration. The main limitation of the Monte Carlo simulations is due to the enormous slowing down of relaxation, which occurs at low concentrations. Using an elementary algorithm, we followed the Monte Carlo process for times $t \leqq 550$ in chains of length $L \lesssim 25$. This is sufficient to calculate the decay of $\phi^{(\infty)}(t)$ from 1 to $\varepsilon = 10^{-2}$ for concentrations $c \geqq 0.3$. Results obtained with a refined Monte Carlo program, designed to eliminate some of the effects of the slowing down at low concentrations, will be reported in a subsequent publication.

We estimate the number of runs required for obtaining the relaxation function $\phi(t)$ with a certain relative accuracy. If of $\phi(t)$ is the average of $n_0(t)$ over N independent runs, the relative error is given by

$$\frac{(\Delta\phi(t))_N}{\phi(t)}$$

$$= \frac{1}{\sqrt{N}} \frac{1}{\phi(t)} \sqrt{\left\langle \left(\frac{n_0 - c}{1-c}\right)^2 \right\rangle_t - \left\langle \frac{n_0 - c}{1-c} \right\rangle_t^2}$$

$$= \frac{1}{\sqrt{N}} \frac{1}{\phi(t)} \sqrt{\left(\frac{c}{1-c} + \phi(t)\right)(1-\phi(t))} \tag{51}$$

The last result is obtained using $n_0^2 = n_0$ and the definition of $\phi(t)$. To follow the decay of $\phi(t)$ down to a value of $\varepsilon = 10^{-2}$ with an accuracy of 1 percent, the minimum number of runs required is

$$N_{\min} = 10^8 \left(\frac{c}{1-c} + 10^{-2}\right). \tag{52}$$

For $c=0.5$ a hundred million runs are needed. For $c \to 1$ $N_{\min}$ diverges due to the normalization factor $1-c$ in the definition of ϕ.

We note that the simulation of a finite chain of length L includes the simulation of all shorter lengths $L' < L$. There are two reasons for that. First, the relaxation at a site i depends only on the part of the chain to the right of this site. The occupation of site number i of a chain of length L on the average relaxes like the occupation at the origin of a chain of length $L-i$. Secondly, the relaxation function can be obtained by sampling both the initially occupied and empty sites, using formula (9) with the respective initial value $\langle n_0 \rangle_{t=0} = 0$ or 1. The method of using all the data of a Monte Carlo run with a long chain is particularly suitable for calculating $\phi^{(\infty)}(t)$. Let us denote the r.h.s. of condition (21) by $L_{\min}(\varepsilon, c)$. For chains with length $L \geqq 2L_{\min}(\varepsilon, c)$, say, the condition for obtaining $\phi^{(\infty)}(t)$ in the range $\varepsilon \leqq \phi^{(\infty)} \leqq 1$ is safely met. Performing a single Monte Carlo run for a very long chain of length $L \gg L_{\min}$ yields a contribution to $\phi^{(\infty)}$ from every site i with $0 \leqq i \leqq L - 2L_{\min}$. The $L - 2L_{\min}$ contributions obtained from a single run are, of course, not

statistically independent. One may expect that the contributions of sites separated by a distance of at least $L_{\min}$ are statistically independent. This expectation is confirmed by the simulation. In Fig. 3 the Monte Carlo result for $\phi^{(\infty)}(t)$ for a concentration $c=0.3$ is shown. The curve is obtained by averaging over four independent runs for chains of length $L=1.5\cdot 10^6$. From the roughness of the curve a relative accuracy $\Delta\phi/\phi=5.4$ percent is deduced for $t=500$, where $\phi^{(\infty)}(t)=0.014$. These values of c and $\phi^{(\infty)}$ correspond to a value $L_{\min}=12$. With an effective number of statistically independent runs calculated as

$$N_{\text{eff}}=4\,\frac{L-2l_{\min}}{L_{\min}} \tag{53}$$

formula (51) yields $\Delta\phi/\phi=6.6$ percent, in reasonable agreement withthe result deduced from the Monte Carlo curve.

7. Comparison with the Kohlrausch-Williams-Watts formula

It is clear form the concave shape of the curves in Figs. 2 and 3 that $\phi^{(\infty)}(t)$ is of stretched exponential form, in the sense that the effective relaxation rate given by

$$-\mathrm{d}(\ln\phi(t))/\mathrm{d}t \tag{54}$$

is a monotonically decreasing function of the time. The assumption [15] that the effective relaxation rate (54) decreases with increasing time according to a power law, viz.

$$-\mathrm{d}(\ln\phi(t))/\mathrm{d}t=At^{-\alpha} \tag{55}$$

with positive constants A and α, leads to the Kohlrausch-Williams-Watts (KWW)-formula

$$\phi(t)=\exp(-[t/\tau]^{\beta}) \tag{56}$$

with positive constants τ and $\beta=1-\alpha$. Here the initial condition $\phi(t=0)=1$ is used. If (55) does not apply from the beginning at $t=0$, but only in a limited time interval at later times, the constant of integration is no longer determined by the initial condition at $t=0$. In this case formula (56) may be multiplied by a constant factor C as a free parameter. We examine now how accurately $\phi^{(\infty)}(t)$ is described by (56) or (55).

In Fig. 4, for concentration $c=0.3$, the decay of $\phi^{(\infty)}(t)$ from a value of 0.97 to a value of 0.01, which occurs in the time range $0.1\leqq t\leqq 500$, is shown on a logarithmic time scale (full line). We note that for times $t\leqq 100$ there is no difference between the Monte Carlo data for long chains and the exact numerical calculation for chain length $L=9$ with free boundary. The dashed line in the figure represents a fit of the KWW-formula with parameters $\tau=19$, $\beta=0.403$ and amplitude $C=1.1$. The maximum deviation of the fit is 0.01. There is a very slight identation in the $\phi^{(\infty)}(t)$-curve around $t=2$, which is not reproduced by the fit. With the KWW-formula (56) with fixed amplitude factor $C=1$ the fit is less satisfactory (dotted line). Here a best fit with maximum deviation 0.035 is obtained for $\tau=26$ and $\beta=0.50$. It appears that

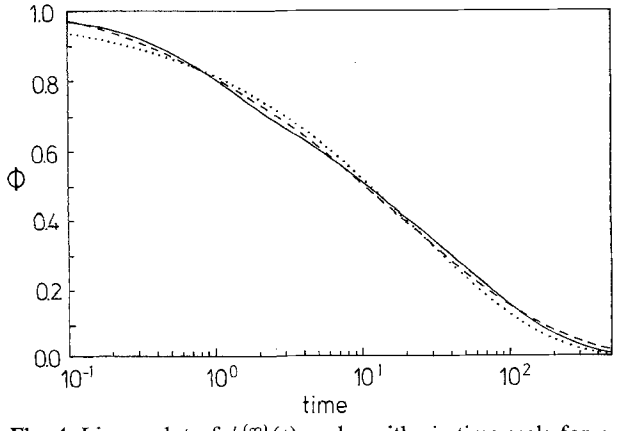

Fig. 4. Linear plot of $\phi^{(\infty)}(t)$ on logarithmic time scale for $c=0.3$ (full line). Dashed and dotted line: best fits with formula (55) and (56), respectively (see text)

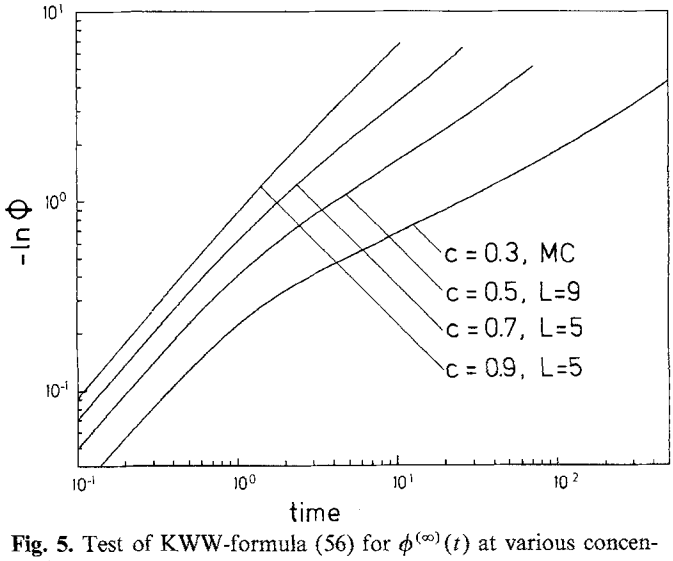

Fig. 5. Test of KWW-formula (56) for $\phi^{(\infty)}(t)$ at various concentrations

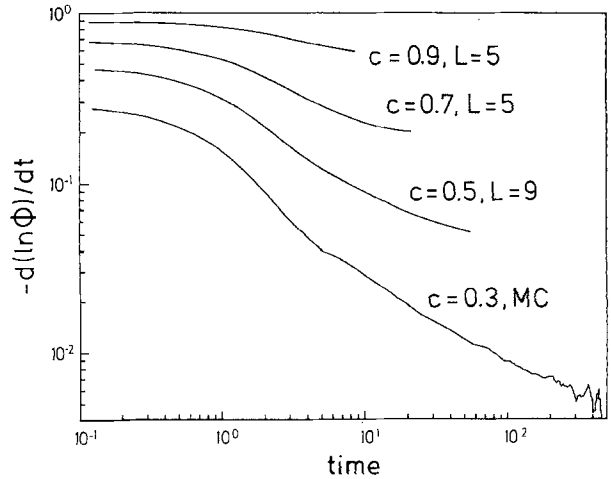

Fig. 6. Test of validity of formula (55) for $\phi^{(\infty)}(t)$ at various concentrations

the relaxation function $\phi^{(\infty)}(t)$ of our model is less well fitted by either (56) or (55) than the function derived heuristically by Palmer et al. (see the figure in [4]).

A more sensitive test of the validity of the formulae (56) and (55) is shown in Figs. 5 and 6. In Fig. 5 $[-\ln\phi^{(\infty)}]$ as function of t is plotted in doubly logarithmic form. In such a plot formula (56) yields a straight line with a slope given by the exponent β. For concentrations $c \geqq 0.5$ $\phi^{(\infty)}(t)$ was obtained from calculations for finite chains of sufficient length (Sect. 5). Similarly, in Fig. 6 the effective relaxation rate (54) as function of time is plotted on a doubly logarithmic scale. A straight line here indicates that Eq. (55) is valid. It is obvious from these figures that formulae (56) and (55) only hold approximately within limited time intervals. For short times the decay of the relaxation function is exponential, corresponding to an exponent $\beta = 1$. This is consistent with the equation of motion (11), from which we derive

$$\phi(t) \sim \exp(-ct) \tag{57}$$

for $t \to 0$. For long times, the bending of the curves shown in Figs. 5 and 6 indicates that there also $\phi^{(\infty)}(t)$ follows (56) or (55) only approximately. E.g. for concentration $c = 0.3$, in the time range $5 \leqq t \leqq 500$ $\phi^{(\infty)}(t)$ is approximated by the KWW-formula (56) with $\tau = 34.5$ and $\beta = 0.54$ with a relative error of at most 17%. It remains open whether the asymptotic time dependence of $\phi^{(\infty)}(t)$ for $t \to \infty$ is of exponential ($\beta = 1$) or of KWW-form ($\beta < 1$).

8. Effective-medium approximation

As a first attempt towards an analytical treatment of the semi-infinite chain, we present an effective-medium approximation. The approximation leads to an integro-differential equation first proposed by Jacobs [16] to describe the slow relaxation in supercooled liquids near the glass transition. The kinetic constraint on the transitions at site 1, described by the occupation number of site 2 in the expression (7) for the transition rate w_1, is replaced by coupling site 1 to an effective medium, giving rise to a frequency-dependent attempt frequency $\Gamma_1(s)$. The function $\Gamma_1(s)$ is determined by the requirement that for the two-site cluster coupled to the effective medium the same relaxation function is obtained for site 0 and site 1.

Calculating the relaxation functions ϕ_0 and ϕ_1 from the averages $\langle n_i \rangle_t$ with initial value $\langle n_i \rangle_{t=0} = 1$ for site $i = 0$ and site $i = 1$, respectively, we find

$$\tilde{\phi}_0(s) = \frac{s + 1 + \Gamma_1(s) - c}{s(s + 1 + \Gamma_1(s)) + c\Gamma_1(s)} \tag{58}$$

and

$$\tilde{\phi}_1(s) = \frac{1}{s + \Gamma_1(s)} . \tag{59}$$

Equating both expressions and substituting $(\tilde{\phi})^{-1} - s$ for Γ_1 yields the following equation for $\tilde{\phi}(s)$

$$(s + 2c - 1)\tilde{\phi}(s) + (1 - c)s(\tilde{\phi}(s))^2 = 1 . \tag{60}$$

This equation is the Laplace transform of the integro-differential equation

$$\dot{\phi}(t) + c\phi(t) + (1 - c)\int_0^t \phi(t - t')\dot{\phi}(t')\,\mathrm{d}t' = 0 \tag{61}$$

for the time-dependent relaxation function $\phi(t)$. Apart from a missing acceleration term prop. $\ddot{\phi}(t)$, Eq. (61) is identical to the equation proposed by Jacobs to describe the slowing down of relaxation in glass-forming liquids. Jacobs arrived at his equation by intuitive physical reasoning. His equation is also a limiting case of an equation put forward by Götze and Sjögren [17] in the framework of mode-coupling theory. According to Jacobs, the acceleration term missing in our Eq. (61) is not relevant for the case of slow relaxation. Therefore we may regard our result as essentially equivalent to Jacobs' equation. As shown by Jacobs, there is a critical point which marks a blocking transition. In our notation, the critical point is at $c = 1/2$. The relaxation function $\phi(t)$ decays to zero only for $c > 1/2$, while for $c < 1/2$ the decay is incomplete:

$$\phi(t \to \infty) = \begin{cases} 0 & \text{for } c > 1/2 \\ \dfrac{1 - 2c}{1 - c} & \text{for } c < 1/2 . \end{cases} \tag{62}$$

This follows from the behaviour of $\Gamma_1(s)$ for $s \to 0$ which is given by

$$\Gamma_1(s) = \begin{cases} 2c - 1 + 0(s) & \text{for } c > 1/2 \\ \dfrac{c}{1 - 2c}\, s + 0(s^2) & \text{for } c < 1/2 . \end{cases} \tag{63}$$

For $c = 1/2$ one obtains $\Gamma_1(s) \sim (s/2)^{1/2}$, leading to an asymptotic decay $\phi(t) \sim t^{-1/2}$. For completeness, we give the result for $\Gamma_1(s)$ which reads

$$\Gamma_1(s) = -\tfrac{1}{2}(s + 1 - 2c) \pm \tfrac{1}{2}\sqrt{s^2 + 2s + (1 - 2c)^2} . \tag{64}$$

The upper (+) sign has to be taken for the initial condition $\phi(t = 0) = 1$ to hold. $\Gamma_1(s)$ has a branch cut on the negative real s-axis in the interval

$$-1 - 2\sqrt{c(1 - c)} \leqq s \leqq -1 + 2\sqrt{c(1 - c)} . \tag{65}$$

It follows from our results in Sects. 5 and 6 that for our model the appearance of a blocking transition at $c = 1/2$ is an artefact of the effective-medium approximation. As regards the behaviour of real glass-forming liquids, we refer to the discussion given in [18].

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