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The characteristic length of cooperativity derived from dynamic size effects in a lattice gas

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Abstract. Dynamic size effects in a lattice gas model with two-vacancy-assisted hopping are studied by Monte Carlo simulation. A characteristic length of cooperativity is derived from the slowing down of the relaxation of the site-occupation autocorrelation function and of the orientation autocorrelation function of non-spherical particles in confining geometries. Good agreement is found with the cooperativity length obtained previously by measuring the size dependence of the fraction of permanently blocked particles.

1. Introduction

The concept of cooperativity and of cooperatively rearranging regions has been widely used to describe molecular motion in supercooled glass-forming liquids, since the work of Adam and Gibbs [1]. Recently, a model with vacancy-assisted hopping on the triangular lattice has been proposed as a model of molecular cooperativity in supercooled liquids near the glass transition [2, 3]. It is argued [4] that the model should apply to those liquids in which diffusive motion is controlled by steric hindrance. For the model a cooperatively rearranging region can be defined as the region of minimum extent in which particles must be rearranged in order to make a blocked particle mobile. In [2] the cooperativity length, i.e. the average size of cooperatively rearranging regions, was derived from the fraction of permanently blocked particles which exist in a lattice of finite size as a result of the kinetic rule of the model. In this paper we show how the characteristic length of cooperativity can also be determined from measurement of finite-size effects on quantities which have an experimental counterpart in real physical systems. To this end we study, for a slightly modified version of the same model, the slowing down of the decay of time-dependent correlation functions in restricted geometries.

The paper is organized as follows. The model is introduced in section 2. In section 3 the definition of the cooperativity length is discussed, and the results for its concentration dependence from [2] are reviewed. In section 4 the results of simulations in restricted geometry are presented, and the characteristic lengths obtained are compared with the cooperativity length calculated in [2].

2. The model

The model is a lattice gas on a two-dimensional triangular lattice with two-vacancy-assisted hopping diffusion. In the initial configurations every lattice site is occupied with

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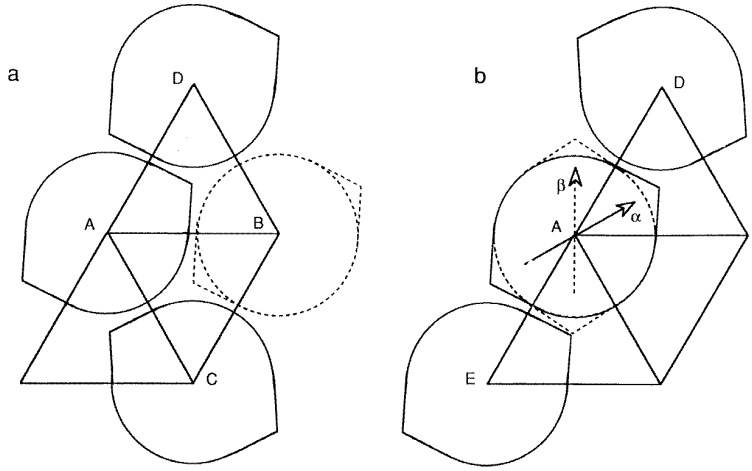

Figure 1. A geometrical interpretation of the kinetic rules of the model for translational jumps (a) and rotational jumps (b) for hard-core particles of particular shape (see the text). In the figure, both the translational jump from A to B and the rotational jump from α to β are prohibited by either of the two neighbouring particles.

a probability given by the concentration c, independently of the other sites. A particle can jump to an empty nearest-neighbour site only if the two sites on either side of the jump path are empty [2]. In addition, in the present model particles also have an orientational degree of freedom; with each particle a unit vector $\boldsymbol{p}$ is associated, which can be oriented along the bisectrices of the angles formed by the lattice bonds. In the initial configurations particles are oriented at random, independently of one another. The particles can perform rotations of $\pi/3$ between neighbouring orientations. The condition for a rotation is that the two neighbouring lattice sites located along the direction between the original orientation of $\boldsymbol{p}$ and the final one are empty. No requirement is imposed on the orientation of particles on adjacent sites, and the direction of $\boldsymbol{p}$ is conserved as the particle jumps from one site to another. The values of the attempt frequencies Γ_j and Γ_r of the translational and rotational jumps, respectively, are set equal to one. These kinetic rules are time reversible and preserve the statistical independence of the occupation of different sites and of the orientation of different particles at any given time. In other words, there are no *static* correlations.

The constraints imposed in the present model both on translation and rotation of particles follow geometrically if the particles are hard discs with small 'noses' in the direction of $\boldsymbol{p}$ and $-\boldsymbol{p}$, and the disc diameter is between a and $a\sqrt{3}/2$, where a is the lattice constant. The constraint on translational jumps is obtained under the assumption that the particle has to follow a straight line in a jump. Figure 1(a) illustrates that under this condition a particle cannot jump to a nearest-neighbour vacancy unless the two adjacent nearest-neighbour sites are vacant, too. Figure 1(b) shows that a rotation of a particle of this shape requires two specific nearest-neighbour sites to be vacant.

3. The cooperativity length and size effects

The kinetic rules of the model induce *dynamic* correlations between particles on different sites of the lattice. At high concentrations, at a given time, the vast majority of particles

are blocked by neighbouring particles. The mobile particles, which are allowed to jump in at least one of the six nearest-neighbour directions, tend to occupy regions of relatively low concentration. Making a blocked particle mobile, at high concentration, requires the coordinated motion of many surrounding particles. A cooperatively rearranging region can be defined as the region of minimum extent within which particles must be reshuffled in order to make a given particle mobile. The size of this region varies from particle to particle and depends on the total configuration. The average value of the size of the cooperatively rearranging regions defined in this way is the characteristic length of cooperativity [5]. Since the average number of particles which are blocked at a given time increases with increasing concentration, the cooperativity length must also be an increasing function of concentration.

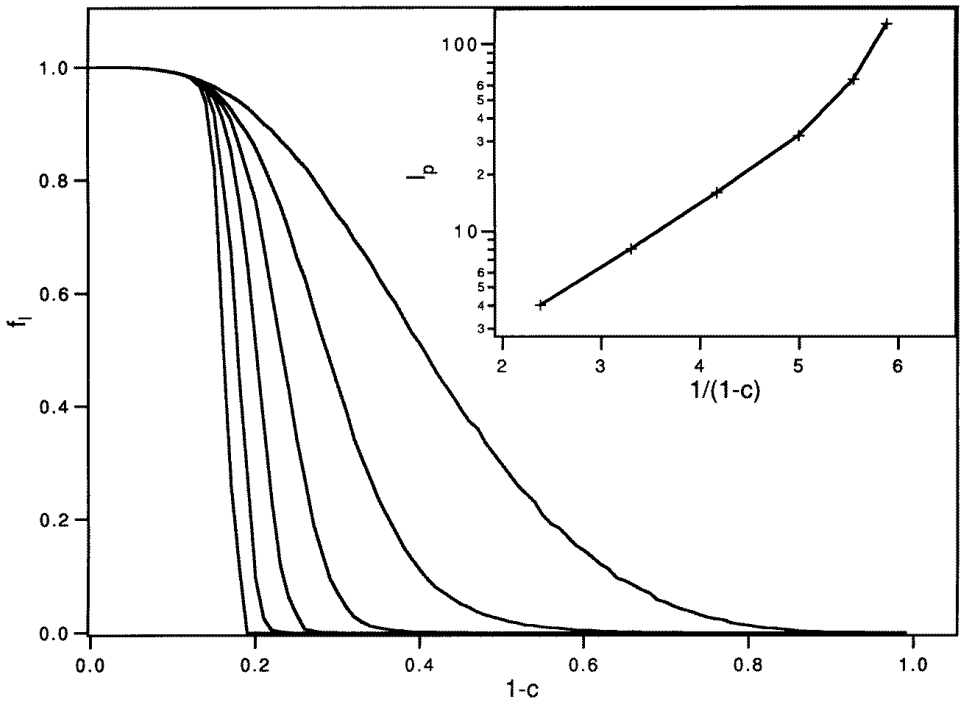

Figure 2. The fraction f_l of permanently blocked particles as derived by the cellular automaton for $l \times l$ lattices with periodic boundary conditions. From left to right: $l = 128, 64, 32, 16, 8, 4$. Inset: characteristic length l_p (see equation (1) and the text).

The determination of the characteristic length of cooperativity as the average size of such cooperatively rearranging regions presents heavy computational problems. A simpler and computationally more efficient way to proceed is by studying dynamic size effects. The first effect to study is the existence of permanently blocked particles in lattices of finite size l. In an infinite lattice permanently blocked particles would not exist [2]. The permanent blocking of particles in a finite lattice is determined by the initial configuration. Averaging over an equilibrium ensemble of initial configurations presents no problem because of the statistical independence of site occupation and particle orientation. In [2] the number of permanently blocked particles is computed using a cellular automaton. The automaton at each step removes all mobile particles from the lattice. The particles left in the final state are permanently blocked in the starting configuration. The fraction of permanently blocked

particles increases with increasing concentration c and decreasing lattice size l. For any size l, as a function of concentration, a transition occurs from a situation where almost all particles are mobile to a situation where all particles are permanently blocked. This is shown in figure 2 for $l \times l$ lattices with periodic boundary conditions in both directions. An l-dependent transition concentration $c_p(l)$ can be defined by [6]

$$c_p(l) = \int_0^1 c \frac{\partial f_l}{\partial c} \, \mathrm{d}c. \tag{1}$$

By inverting this function we obtain a concentration-dependent characteristic length $l_p(c)$, shown in the inset in figure 2. The unsatisfactory aspect of this method is that in real physical systems no quantity corresponding to the number of permanently blocked particles can be measured.

The second method, which is used in this paper, can in principle also be applied to real systems. It consists in studying the size dependence of the relaxation of time-dependent correlation functions of dynamical quantities. When the size of a system in one or more directions is smaller than the cooperativity length, the dynamics of the system is slowed down by the cutting off of cooperative processes. Therefore the correlation function will decay more slowly in a system of small size. It is also possible that the asymptotic long-time limit for the infinite system is never reached for the finite system, because of the existence of permanently blocked particles.

4. Restricted geometries

In this section we study a system confined to a strip of width B and infinite length. The outer walls of the strip influence the mobility of particles located at the strip boundaries as if they were lines of completely filled sites. Therefore, particles at the strip boundaries cannot jump in a direction parallel to the walls. Due to the presence of rigid walls, permanently blocked particles can occur. The probability of finding permanently blocked particles increases with decreasing strip width. Due to the kinetic constraints, particles arranged in a line block each other, and any completely filled line crossing the strip is permanently blocked. Such filled lines form a rigid structure which divides the strip into separate regions, between which particles cannot be exchanged.

4.1. Density fluctuations

We present the results obtained by Monte Carlo simulation for the normalized site-occupation autocorrelation function defined by

$$\phi_0(t) = \frac{\langle \Delta n_0(t) \Delta n_0(0) \rangle}{c(1-c)} \tag{2}$$

where c is the concentration of particles and $\Delta n_0(t)$ is the fluctuation of the site-occupation number $n_0(t)$ of site 0 at time t given by

$$\Delta n_0(t) = n_0(t) - \langle n_0 \rangle = n_0(t) - c. \tag{3}$$

The brackets $\langle \cdots \rangle$ indicate an ensemble average. It is obtained by averaging over a sufficient number of initial configurations, which depends on the size of the system. The denominator in equation (2) is the mean square fluctuation of the site-occupation number

$$\langle (\Delta n_0(0))^2 \rangle = c(1-c). \tag{4}$$

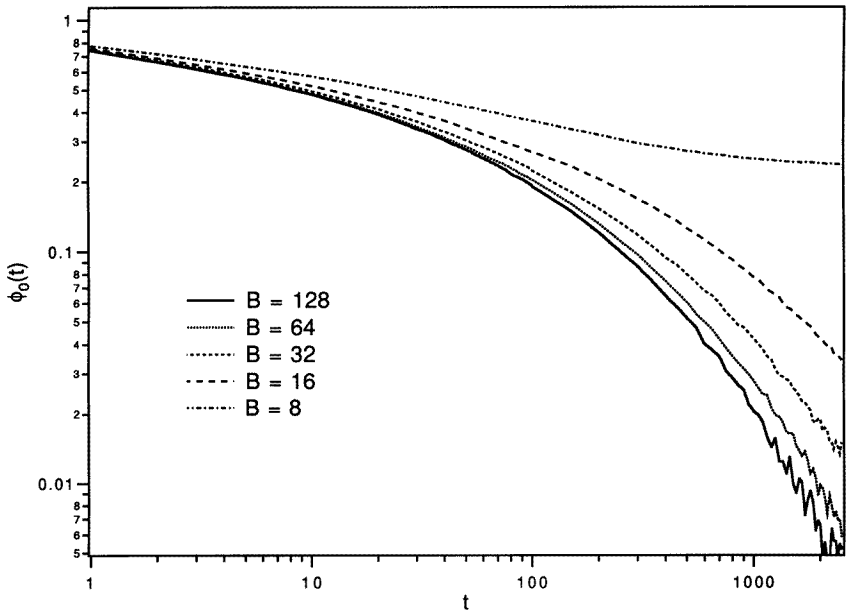

Figure 3. The site-occupation autocorrelation function $\phi_0(t)$ for concentration $c = 0.65$ for systems confined in strips of different widths B.

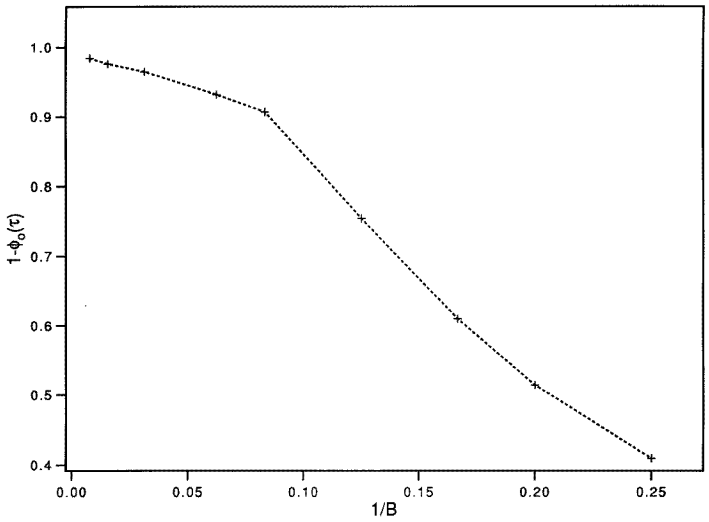

Figure 4. The size dependence of the value of $\phi_0(t)$ at time $t = \tau$ for $c = 0.65$. τ is defined as the time when $\phi_0(t)$ has decayed to 0.01 in the infinite system.

Note that $\phi_0(t)$ is the integral of the coherent intermediate scattering function (or density–density correlation function) $F(\boldsymbol{k}, t)$ over all wave vectors of the first Brillouin zone. In figure 3 the results for $\phi_0(t)$ are shown for the concentration $c = 0.65$ for different values of the width B of the strip. Similar families of curves are obtained at other concentrations.

It is apparent that, as the width of the strip is decreased, the relaxation of $\phi_0(t)$ becomes slower. The slowing down occurs since rearrangement processes that would extend beyond the width of the strip are cut off by the walls. For the smaller widths, $\phi_0(t)$ decays to a non-zero value in the long-time limit, signalling that a fraction of particles (and vacancies) are permanently blocked. It is then possible to measure the extension of the cooperatively rearranging regions by studying the slowing down of the decay of $\phi_0(t)$ with decreasing strip width. We proceed in the following way: we define a relaxation time τ as the time at which the correlation function $\phi_0(t)$ in the 'infinite system' has decayed to 1% of its value at $t = 0$, which is unity. By 'infinite system' we mean a large system with fully periodic boundary conditions. We then plot the value of the correlation function at $t = \tau$ in strips of width B as a function of $1/B$. In figure 4 we show the values of $1 - \phi_0(\tau)$ as a function of $1/B$ for concentration $c = 0.65$. The function decreases monotonically from the value of 0.99 at $B = \infty$. A characteristic width B_ϕ can be defined as the width at which the correlation function ϕ_0 at $t = \tau$ assumes the value ϕ, which can be chosen arbitrarily within certain limits. B_ϕ is obtained from curves like that of figure 4 by interpolation.

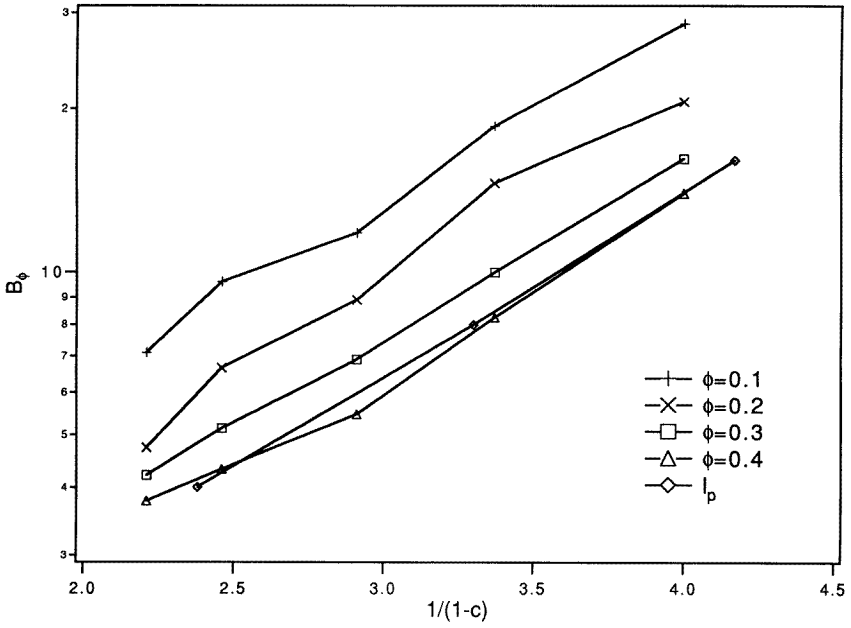

Figure 5. The characteristic width B_ϕ derived from the site-occupation autocorrelation function $\phi_0(t)$ for different values of ϕ (see the text). The characteristic length of cooperativity l_p (the inset in figure 2) is included for comparison (diamonds). Lines are guides to the eye only.

In figure 5 we show the results obtained for different choices of ϕ. The data are plotted on a logarithmic scale, and the curves are roughly parallel to each other. This means that our characteristic length is a function of ϕ and c of the form of a product of a term depending only on ϕ multiplied by a term depending only on c:

$$B_\phi(c, \phi) = \alpha(\phi)\beta(c). \tag{5}$$

In figure 5 the data are compared to the cooperativity length l_p obtained by inverting equation (1). The data show a good agreement between the concentration dependence of B_ϕ and that of l_p.

4.2. Orientational relaxation

In this section we study the orientational autocorrelation function $\phi_p(t)$ defined as

$$\phi_p(t) = \langle \boldsymbol{p}(t) \cdot \boldsymbol{p}(0) \rangle \tag{6}$$

where $\boldsymbol{p}(t)$ is a unit vector which describes the orientation of a particle. The kinetic rule for the rotation of a particle couples its rotational motion to the occupation of the sites in its first-neighbour shell. If in a given configuration a particle is not allowed to rotate, the unblocking of rotation requires the jumping of one or two particles out of the nearest-neighbour shell around that particle. In this way the rotational motion is coupled to the cooperative processes of the translational motions.

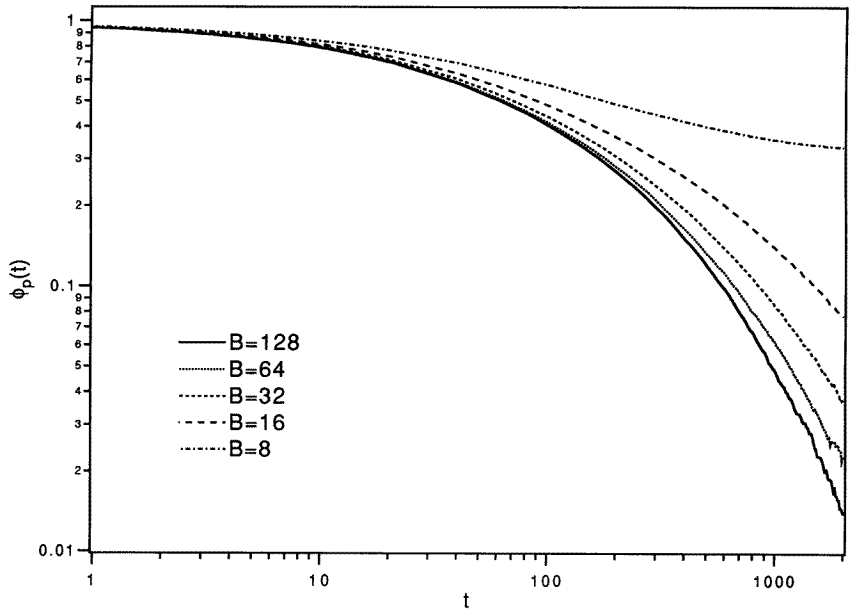

Figure 6. The orientation autocorrelation function $\phi_p(t)$ for concentration $c = 0.65$ for systems confined in strips of different widths B.

In figure 6 we show the result for $\phi_p(t)$ for concentration $c = 0.65$ for different values of the strip width B. The results at different concentrations are qualitatively similar. The same qualitative behaviour as for the site-occupation autocorrelation function is found, i.e. a slowing down is observed as the width of the strip is decreased. This means that the orientational relaxation is strongly influenced by the cooperative processes dominating the density fluctuations at high concentrations. To determine a concentration-dependent characteristic width B_ϕ we can repeat the procedure used in the previous section for the case of density fluctuations. We define a time τ as the time at which the correlation function $\phi_p(t)$ in the infinite system has decayed to 1% of its value at $t = 0$. B_ϕ is that strip width for which $\phi_p(t)$ at time $t = \tau$ has decayed only to a value ϕ, which can be chosen arbitrarily within certain limits.

In figure 7 the results for B_ϕ are shown and compared with the cooperativity length $l_p(c)$. Again good qualitative agreement is found.

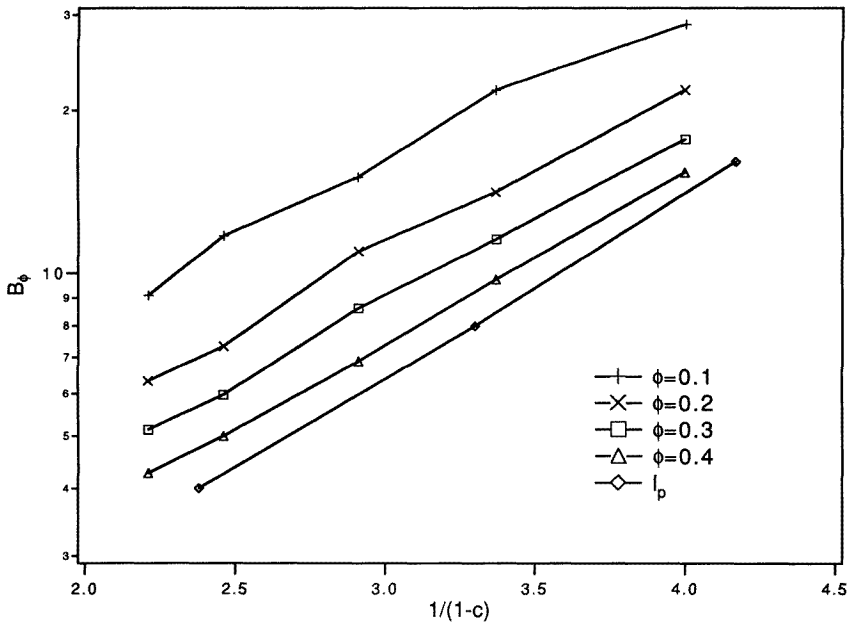

Figure 7. The characteristic width B_ϕ derived from the orientation autocorrelation function $\phi_p(t)$ for different values of ϕ (see the text). The characteristic length of cooperativity l_p is included for comparison (diamonds). Lines are guides to the eye only.

5. Summary

We have studied, by Monte Carlo simulation, the size dependence of the decay of the correlation functions for site occupation and for the orientation of non-spherical molecules in a two-dimensional lattice gas with two-vacancy-assisted hopping dynamics. Moving a particle in this model requires the coordinated motion of particles within a certain region, whose average size is the characteristic length of cooperativity. The most direct evidence of the existence of this natural length scale is given by size effects. We have studied the consequences of confinement of the system in strips of width B, showing that the decay of both correlation functions is slowed down appreciably when the characteristic length of cooperativity becomes comparable with B. The concentration dependence of this length has been determined, showing good agreement with the result obtained previously from the size dependence of the number of permanently blocked particles.

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