Models of cooperative diffusion

J Jäckle

Department of Physics, University of Konstanz, Fach M679, 78457 Konstanz, Germany

E-mail: josef.jaeckle@uni-konstanz.de

Abstract
The intuitive idea of cooperative molecular rearrangement and diffusion, which
is often invoked to rationalize experimental observations in liquids close to
their glass transition, calls for dynamical models which lead to a clearer
definition of the term 'cooperativity' and to a better understanding of its physical
implications. Work on two lattice gas models, which were designed for this
purpose, is reviewed: the hard-square-lattice gas and a cooperative triangular-
lattice gas. Possible generalizations and some unsolved problems are pointed
out.

1. Introduction

Particle diffusion in non-crystalline matter often occurs as a collective process involving many
atoms [1, 2]. For supercooled liquids near the glass transition, in particular, the slowness and
final arrest of diffusive motion is believed to reflect the coupling of a large number of particles.
According to Adam and Gibbs [3], the coordinated motion of these particles is said to occur
in 'cooperatively rearranging regions'. To support this intuitive idea with concrete meaning,
lattice gas models have been proposed in which particle hopping is subject to some kind of
kinetic constraint.

To my knowledge, it was Edwards and Vilgis [4] who proposed the first model of this
kind. It consists of hard rods moving along the axes of a simple cubic lattice. In the present
paper the hard-square-lattice gas (HSLG) [5–10] and a lattice gas on the triangular lattice with
two-vacancy-assisted hopping [11–17] are reviewed. In both models a very simple kinetic rule
leads to a highly cooperative diffusion dynamics at high particle density. Other models which
should be mentioned here are the lattice gas on the simple cubic lattice with four-vacancy-
assisted hopping [18] and the site-frustrated percolation model [19], which is related to a
spin-glass model.

The review of our two models is presented in sections 2 and 3. A short summary and
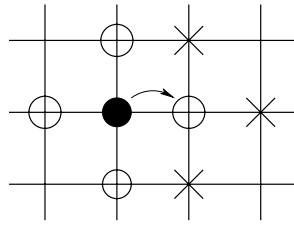outlook are given in a concluding section.

Figure 1. The jump rule for the HSLG. A particle (filled circle) can hop to an empty nearest-neighbour site (empty circles) only if three next-nearest-neighbour sites (crosses) are also empty.

2. Hard-square-lattice gas

2.1. Definition

In the HSLG [5–10] the sites of a square lattice are occupied by particles with an extended hard core, such that not only is the double occupancy of a site forbidden but so also is the simultaneous occupancy of nearest-neighbour sites. A particle thus behaves like a hard square with corners extending to the nearest-neighbour sites. The extended hard core of the particles causes a thermodynamic phase transition at $c = 0.37$ to an *ordered phase*, in which one of the two sublattices of the square lattice is preferentially occupied. At the highest possible concentration $c_{\max} = 1/2$ the particles are arranged on one sublattice in a checkerboard pattern. The particles can jump randomly to nearest-neighbour sites (Kawasaki dynamics) if no overlap with neighbouring hard squares occurs. This *jump rule* (figure 1) leads to serious kinetic restrictions at higher particle concentrations.

2.2. Cooperative processes

The study of self-diffusion of particles in the HSLG exemplifies the idea of molecular cooperativity and gives a concrete meaning to it. At higher particle concentrations, the jump rule for a particle usually requires many other particles to 'step aside' first. Because of the mutual hindrance of particles, these steps have to be performed in a certain order. The shortest sequence of steps of neighbouring particles which are necessary for making a given particle mobile may be called the *'cooperative process'* for that particle. The average radius of the region in which particles participate in such a process may be considered as the *'characteristic length of cooperativity'* (or simply the *'cooperativity length'*). Figure 2 shows an example of a cooperative process.

2.3. Dynamic size effect

An immediate consequence of the existence of a cooperativity length is the dependence of self-diffusion on system size, which is a *dynamic size effect*. The size effect occurs both for real boundaries and for periodic boundary conditions. If a system is smaller than the cooperativity length, then many particles are no longer able to complete their cooperative process. As a result, in such a small system many particles are never allowed to jump, whatever the (allowed) jumps of the other particles may be. We call these particles 'permanently blocked'. On average, this leads to a slowing down of self-diffusion with a reduced self-diffusion coefficient. On the other hand, the observation of such a dynamic size effect indicates the existence of a finite cooperativity length, the magnitude of which may be derived from it.
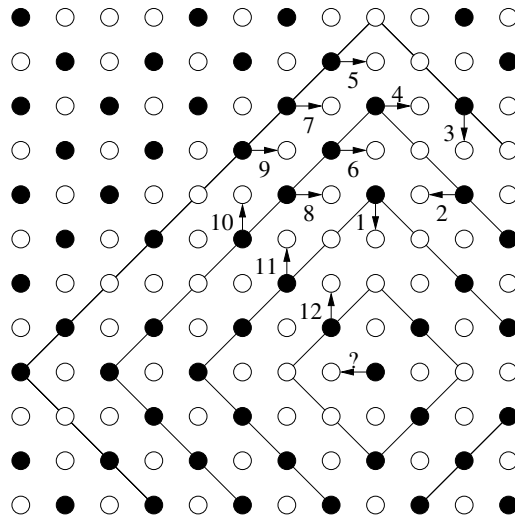
Figure 2. A numbered sequence of particle jumps after which the initially blocked particle in the centre is allowed to jump to the left (from [10]).
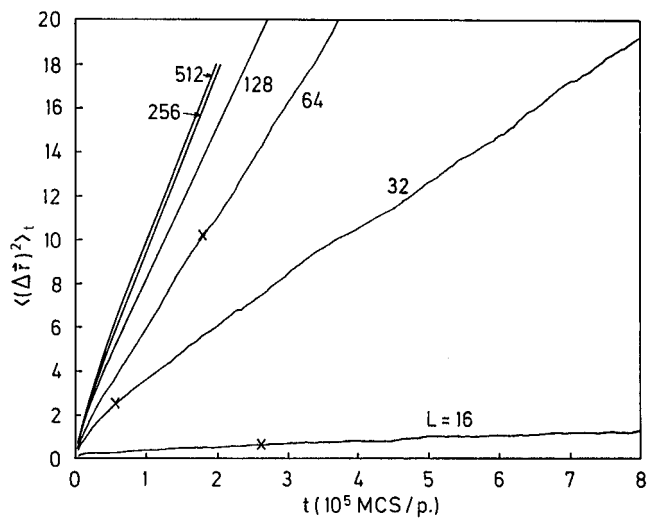

Figure 3. Lattice-size dependence of the mean square displacement versus time (from [7]).

In figure 3 the time-dependent mean square displacement of particles on square lattices of size $L \times L$ with periodic boundary conditions is shown for different values of L. The concentration is $c = 0.415$. The dynamic size effect not only is very strong, but also occurs already at early times when the distances travelled by the particles are much shorter than the lattice diameter L. The particles 'feel' the size of the lattice through its effect on the long-range cooperative processes! This interpretation is in keeping with the value of a cooperativity length $\xi_{0.5}$, defined below, of about 35 (in units of the lattice constant of a sublattice) [6].

2.4. Cooperativity length

The question of whether the cooperativity length remains finite for all allowed particle concentrations $c < 1/2$ is of particular interest. If the cooperativity length became infinite at some *critical concentration* $c^* < 1/2$, then above c^* a fraction of particles would become permanently blocked even in an infinite system, and the lattice gas would be non-ergodic.

Before we address this question, a precise and computationally convenient definition of the cooperativity length ξ must be chosen. The most direct method of calculating ξ would require finding the cooperative processes as defined above for all particles in a large number of samples [9]. At high concentrations, where the cooperative processes are long and difficult to identify, this method would require a prohibitive amount of computer time. Rather than deriving ξ from the spatial extent of the individual cooperative processes, we choose to calculate ξ from the number of *permanently blocked particles* in systems of finite size.

Here we exploit a simple topological property of the square lattice and the jump rule for the HSLG. A square lattice of $L \times L$ sites (L even) with periodic boundary conditions can be split in two square sublattices A and B which are dual to one another. B contains the nearest neighbours of the sites of A, and vice versa. Therefore a particle changes sublattice when it jumps. Whether a particle is allowed to jump in a certain direction depends on the occupation of three sites which belong to the same sublattice. These three sites together with the site occupied by the particle form a 'plaquette', which is a unit square of the sublattice. If allowed, the particle can jump to the centre of the plaquette, thereby leaving the sublattice (see figure 1). The permanently blocked particles of a sublattice are found with the following iterative procedure on the sublattice in question, which defines a *cellular automaton* (CA) [6,8].

First, all mobile particles in the initial configuration are removed. The particles that were immobile originally and become mobile after the culling of the initially mobile particles are then removed. This process is repeated until no mobile particles are left. The remaining particles (if there are any) are the permanently blocked particles of the original configuration on the sublattice considered. It can be shown [8] that all particles may be placed on the same sublattice for the initial configuration. It is assumed that in this initial configuration the sites of the sublattice can be filled randomly.

Using the CA, a cooperativity length can be obtained in different ways. For the HSLG we derived a cooperativity length from the probability $p(c, L)$ that in a sublattice of size $L \times L$, which is occupied with particle concentration c, no permanently blocked particles exist. $p(c, L)$ is also called the percolation probability for a certain type of *bootstrap-percolation* model [20]. For a number P (with $0 < P < 1$) a cooperativity length ξ_P is defined by equating

$$p(c, \xi_P) = P. \tag{1}$$

(For the triangular-lattice gas with two-vacancy-assisted hopping described below, we used a different definition of ξ.)

In an attempt to numerically determine the asymptotic behaviour of the cooperativity length for high particle concentrations $c \to 1/2$, Fröböse [6] calculated the c-dependence of $\xi_{0.1}$ for lengths up to 20 000. Despite the large span of $\xi_{0.1}$-values, the asymptotic behaviour of the cooperativity length remained uncertain. In fact, a linear extrapolation on a $1/\log \xi_{0.1}$ versus c_h plot (figure 4), where $c_h = 1 - 2c$ is the concentration of holes, towards $\xi_{0.1} \to \infty$ would yield a critical concentration c^* of about 0.482. However, one can prove (see e.g. [7], including the erratum) that $p(c, L \to \infty) = 1$ holds for all concentrations $c < 1/2$ which, according to equation (1), excludes a divergence of ξ_P (with $P < 1$) for any $c < 1/2$. This *proof of absence of a critical concentration* for the cooperativity length below $c_{\max} = 1/2$ is based on a growth process in which a quadratic cluster of holes of size $l \times l$ on sublattice A
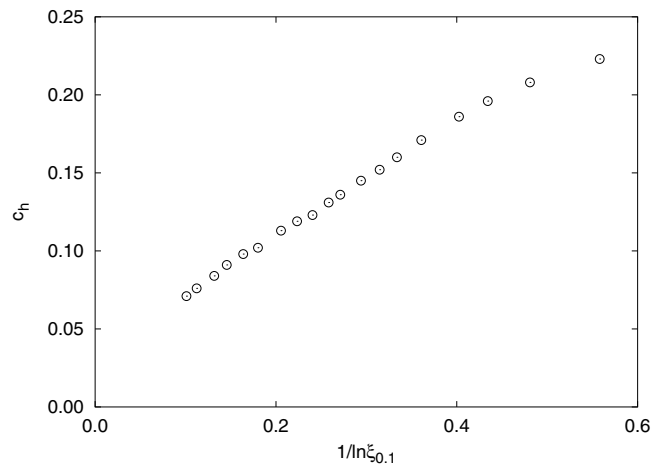
Figure 4. The dependence of the cooperativity length $\xi_{0.1}$ on the concentration of holes $c_h = 1 - 2c$ (data from [6]).

grows to size $(l + 2) \times (l + 2)$. The $l \times l$ cluster grows if on each of its four edges at least one additional vacancy occurs, which becomes increasingly probable with increasing l.

2.5. Extension to three dimensions

The HSLG is a two-dimensional model. The *extension to three dimensions* is expected to have qualitatively similar properties. On a three-dimensional simple cubic lattice, particles with an extended hard core behave like hard octahedra. Similarly to in the two-dimensional case, a CA can be used for finding the permanently blocked particles in lattices of finite size. In [8] a detailed argument is given that the cooperativity length remains finite for all concentrations below $c_{\max} = 1/2$ even in three dimensions. Since five instead of three vacancies on the same sublattice are now required for a particle to jump, the kinetic constraints on self-diffusion are even more serious than in two dimensions. Also in [8], it is speculated that the cooperativity length of this *hard-octahedron-lattice gas* for $c \to 1/2$ might increase in doubly exponential form as the hole concentration c_h decreases to zero:

$$\xi \sim \exp(A \exp(B/c_h)) \tag{2}$$

with positive A and B. This form of divergence was shown to occur for the characteristic length in the related $m = 4$ bootstrap-percolation problem on the simple cubic lattice by van Enter *et al* [21]. For this type of divergence, close to $c = 1/2$ the cooperativity length would be infinite by all physical standards, although still finite mathematically.

2.6. Self-diffusion coefficient

The results for the self-diffusion coefficient $D_s(c)$ of the HSLG obtained from Monte Carlo simulation have given no indication of a critical concentration below $c_{\max} = 1/2$ either. D_s-values, derived in the usual way from the linear long-time behaviour of the mean square displacement, can be fitted by the formula

$$D_s(c) \propto \exp(1.03/(0.5 - c)) \tag{3}$$

in the concentration range from $c = 0.35$ to 0.415, which was the highest concentration in the simulations [7]. Formula (3) is analogous to an Arrhenius formula with the hole concentration

$c_h = 1 - 2c$ replacing the temperature. Of course, it is by no means clear whether formula (3) holds all the way up to $c = 1/2$. In principle, one cannot even exclude the possibility that $D_s(c)$ goes to zero at some critical concentration below $c_{max} = 1/2$, despite the proven absence of a critical concentration for the cooperativity length. For example, a transition from normal diffusion (with linear time dependence of the mean square displacement and $D_s > 0$) to anomalous diffusion (with sublinear time dependence of the mean square displacement and $D_s = 0$) at some $c^* < 1/2$ would be compatible with a finite cooperativity length. The theorem about the cooperativity length is a statement about the *existence* of kinetically allowed processes. The self-diffusion coefficient depends on the *statistical weight* of these processes in stochastic particle motion.

With the available data, a direct functional relation between $D_s(c)$ and a cooperativity length $\xi_P(c)$ could not be established.

2.7. Analytical approximations

A satisfactory *analytical treatment* of self-diffusion in the HSLG has so far been obtained only for the concentration range $c < 0.37$ of the disordered phase, where the cooperative processes are of short range (see e.g. [22] and also [23]; for the 3D case see [24]). In the analytical theory static correlations, which exist between the simultaneous occupation of different sites for this model, need to be taken into account. Such static correlations are absent in the lattice gas model for the triangular lattice which is reviewed in the following.

3. Cooperative triangular-lattice gas [11–18]

3.1. Definition

The lattice gas model on the triangular lattice, which resembles the HSLG as far as the cooperativity of diffusion is concerned, but lacks any static correlations, is defined as follows: the sites of the triangular lattice can be occupied by single particles with no restriction. In equilibrium at concentration c, all lattice sites are independently occupied with probability c. The maximum concentration of particles on the lattice is $c = 1$. The following kinetic constraint for the hopping of particles is built into the model: a particle can jump to an empty nearest-neighbour site only if the two sites which are nearest neighbours of both the initial and the final site of the jumping particle are empty, too (figure 5). This *jump rule* defines a *two-vacancy-assisted hopping* mechanism. No interaction potential between particles on lattice positions exists. However, the kinetic constraint expressed by the jump rule may be visualized as the result of a hard-core repulsion which operates only while a particle is transferred from one site to the other. If it is assumed that during transfer to a nearest-neighbour site a particle moves on a straight line, and that the hard-core diameter d of the particles is in the range

$$(\sqrt{3}/2)a < d < a \tag{4}$$

where a is the lattice constant of the triangular lattice, the transition is only possible if the above jump rule is fulfilled. (The diameter of the circles drawn in figure 5 fulfils this condition.)

For convenience, I refer to this model as the 'cooperative triangular-lattice gas' (CTLG) in the following.

3.2. Cooperativity length

As in the HSLG, in the CTLG a *cooperative process* can be identified as the shortest sequence of jumps of neighbouring particles by which a jump of a given particle is made possible (for an
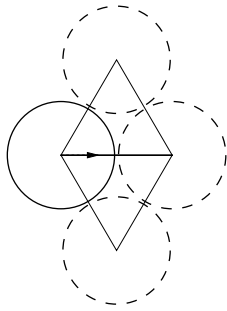
Figure 5. The jump rule for the cooperative triangular-lattice gas. Dashed circles represent vacancies.

example, see figure 2 of [15] or figure 1 of [16]). Again a *cooperativity length* can be defined as the largest distance from the reference particle of all particles participating in this process, but another definition, which is related to the number of permanently blocked particles in finite lattices, is computationally more convenient. Here the different topology of the triangular lattice compared with the square lattice causes a slight complication. As described above, for the HSLG the problem of finding the permanently blocked particles in finite lattices can be solved rigorously by the application of a certain CA. This rigour is lost for the CTLG, because the triangular lattice cannot be split into two sublattices such that the sites of one sublattice are the nearest neighbours of the sites of the other. As a consequence, it is possible that particles on a finite triangular lattice are permanently blocked by other particles which are not permanently blocked themselves (see figure 10 of [11] for an example). Such permanently blocked particles are lost if a CA is used for the CTLG, which at every step culls all mobile particles as for the HSLG. The number of permanently blocked particles obtained with this CA for the CTLG therefore represents a lower bound. We have checked the accuracy of the lower bound for the concentration $c = 0.7$ by comparing with the number of particles which have not moved in a MC run of long duration (3×10^4 MC steps per particle). The difference was negligibly small [13]. We assume that this holds generally, so the lower bound is a good approximation to the total number of permanently blocked particles for all concentrations examined.

Compared with the procedure used for the HSLG, we defined the characteristic length of cooperativity for the CTLG in a slightly different way. First the fraction f_l of permanently blocked particles on finite lattices of size $l \times l$ with periodic boundary conditions is determined as a function of concentration c. With increasing c, f_l rises from 0 to 1. The gradual transition of f_l from 0 to 1 sharpens and shifts to higher concentrations with increasing l. An l-dependent transition concentration $c_p(l)$ can be defined by [25]

$$c_p(l) = -\int_0^1 c \frac{\mathrm{d} f_l}{\mathrm{d} c} \, \mathrm{d} c. \tag{5}$$

$c_p(l)$ increases monotonically with increasing l. The characteristic length $\xi(c)$ for the CTLG is obtained as the function inverse to $c_p(l)$.

The results for the cooperativity length are shown in figure 6 in an Arrhenius plot of $\log \xi$ versus the inverse of the hole concentration $c_h = 1 - c$. For the highest particle concentrations $0.85 \leqslant c \leqslant 0.88$ the data follow the Arrhenius formula

$$\xi(c) = 0.0128 \exp(1.46/c_h). \tag{6}$$

The extrapolation of the numerical data using formula (6) to higher concentrations suggests that the divergence of ξ occurs at $c = 1$, implying the absence of a critical concentration $c^* < 1$ for the cooperativity length.

Independently of the numerical data shown in figure 6, an argument for the absence of such a critical concentration can be given, based on the idea of the 'large-void instability' [26].
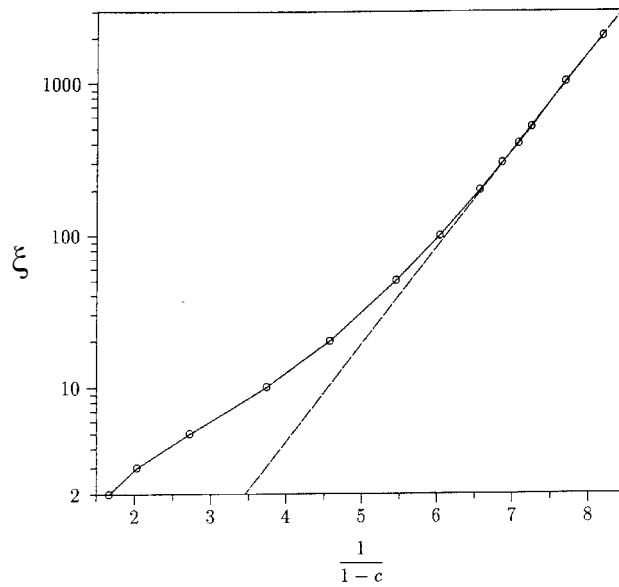
Figure 6. The cooperativity length of the CTLG derived from the fraction of permanently blocked particles f_l via equation (5) as a function of particle concentration. The dashed curve is fit by equation (6) (from [11]).

As indicated in figure 7, a hexagonal ring of vacancies on the triangular lattice of edge length l, which may have been generated by successive shifting of mobile particles to the inner hexagon (shaded region in figure 7), grows to edge length $l + 1$ if every edge of the wider ring contains at least one vacancy. Repeating this growth process, one concludes that it continues to infinity with non-zero probability. The existence of a non-zero probability for the growth of a hexagonal ring of vacancies to infinite size implies that the growth process continues to infinity almost with certainty once an edge length $l \gg 1/c_h$ has been reached ('large-void instability'). An infinite system with certainty contains a region where such a large ring of vacancies can be generated. From there, the growth is very likely to continue to infinity. This completes the argument. So far the argument has not been made rigorous, as it has been in the case of the HSLG (see the erratum in [7]).

3.3. Dynamic size effects

Again the existence of a cooperativity length causes *dynamic size effects*, of which the reduction of the time-dependent mean square displacement is the easiest to study by means of MC simulation. As in the case of the HSLG, the reduction occurs when the linear dimension L of the lattice is comparable to or smaller than the cooperativity length. I note that for the CTLG the opposite effect—an *increase* of the mean square displacement!—has also been observed [11]. This puzzling result was found when the total particle number N was allowed to fluctuate, which is the case if the concentration c is the independent probability of site occupation rather than the fixed fraction $N/(L^2)$ of occupied sites. The effect was attributed to the relatively large particle number fluctuations in small lattices, which in the case of low lattice occupation lead to accelerated particle diffusion and large displacements.

As a different class of dynamic size effects, in [14] the *size-dependent slowing down of the decay of time-dependent correlation functions* for the CTLG was investigated. The cases
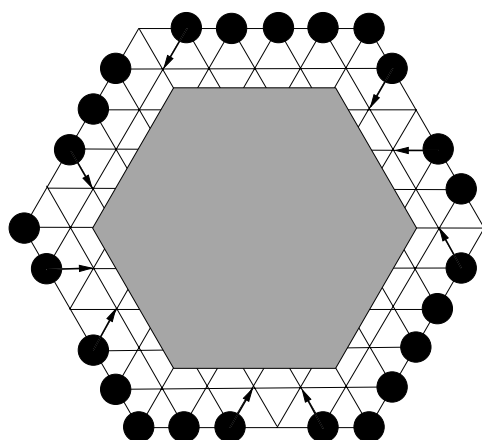
Figure 7. Growth of a hexagonal ring of vacancies. The arrows indicate the first of a sequence of particle jumps by which the outer ring is vacated (see text).

studied were the autocorrelation function for site occupation and, for a modified model with an orientational degree of freedom of the particles, the autocorrelation function for particle orientation. It was shown that, up to a constant factor of proportionality, the cooperativity length ξ can indeed be derived from the observed size dependence of the correlation function decay.

These simulations of dynamic size effects for our model raise the question of whether similar effects can be found in real experiments with confined glass-forming liquids [27]. Here it is important to realize that a dynamic size effect depends crucially on the type of boundary conditions imposed. In real systems boundary conditions can be of very different type (free surface, or rigid wall with slip or non-slip boundary conditions), and the resulting dynamic size effects are qualitatively different. The dynamic size effects found in our simulations, all of which were performed with periodic boundary conditions, may be expected to qualitatively resemble those found in real confined liquids with non-slip boundary conditions at rigid walls.

3.4. Extension to three dimensions

The interpretation of the jump rule of the CTLG in terms of hard-core repulsion (see equation (4)) is possible because on the triangular lattice the sites before and after a jump share two other sites as nearest neighbours (see figure 5). The square lattice does not possess this property. To obtain a model in three dimensions that can be interpreted similarly, one has to use the *face-centred cubic* rather than the simple cubic lattice.

A model of cooperative dynamics on the *simple cubic* lattice has been studied in [18]. Here, in addition to the vacancy on the final site, four more vacancies are required on the shell of ten sites which are either nearest neighbours of the initial or of the final site of the jumping particle. For this model the authors concluded that a critical concentration $c^* = 0.881$ exists above which the self-diffusion coefficient is zero. On the FCC lattice, however, only the four sites which are common nearest neighbours of the sites occupied by the particle before and after the jump need to be involved in the jump rule. These four sites lie symmetrically in the plane perpendicular to the jump path and halfway across it (see figure 8 in [11]). Either two, three or four of these sites may be required to be empty. The degree of cooperativity of the model increases with the necessary number of vacancies. To my knowledge, this model of cooperative diffusion on the FCC lattice has not been studied so far.
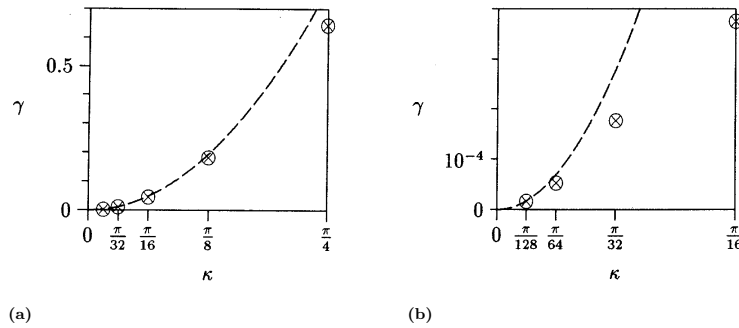
Figure 8. The rate $\gamma(k)$ of exponential decay of $F(\vec{k}, t)$ (equation (11)) at longer times for $c = 0.2$ (a) and $c = 0.7$ (b). Dashed curves: equation (12).

3.5. Simulations of self-diffusion

Despite the random statistical distribution of particles in equilibrium configurations of the CTLG, the distribution of the mobile particles is correlated and shows a certain cluster structure (for figures see [15] or [16]), which changes with time. The hopping of particles is naturally limited to these clusters. Therefore self-diffusion at higher concentrations is a spatially inhomogeneous process *(dynamic heterogeneity)*.

The self-diffusion coefficient D_s was calculated from the linear portion of the mean square displacement curves for concentrations up to $c = 0.77$ [11]. At concentrations $c \geqslant 0.8$ the linear portion was not reached within the length of the MC runs of 10^6 MC steps/particle. The $D_s(c)$ data could again be fitted by an Arrhenius formula

$$D_s(c) = 6.05 \exp(-2.44/c_h) \tag{7}$$

but the power-law formula

$$D_s(c) = 2.26 \times (0.835 - c)^{3.54} \tag{8}$$

fits as well, if not slightly better. Extrapolation of the data using the second formula (8) implies a critical concentration $c^* = 0.835$, at which normal self-diffusion would cease to occur. Whether a critical concentration $c^* < 1$ for the self-diffusion coefficient really exists remains an open question. Even if the cooperativity length ξ remains finite for all concentrations $c < 1$, as suggested by our data and argument, the existence of such a critical concentration D_s cannot be excluded.

Again, a functional relation between the cooperativity length $\xi(c)$ and the self-diffusion coefficient $D_s(c)$ cannot be established. Comparing expressions (6) and (7) one would obtain a power-law relation, but the regions of validity of these expressions do not overlap.

The self-intermediate-scattering function defined as

$$F_s(\vec{k}, t) = \langle \exp[i\vec{k} \times (\vec{r}(t) - \vec{r}(0))] \rangle \tag{9}$$

was calculated for concentrations up to $c = 0.75$ at different wavevectors $\vec{k}$ [11]. The decay of $F_s(\vec{k}, t)$ is exponential for low concentrations and increasingly stretched-exponential at higher concentrations. A more detailed analysis of these results was not undertaken.

3.6. Simulation of collective diffusion [12]

The intermediate-scattering function $F(\vec{k}, t)$, defined as the density–density correlation function

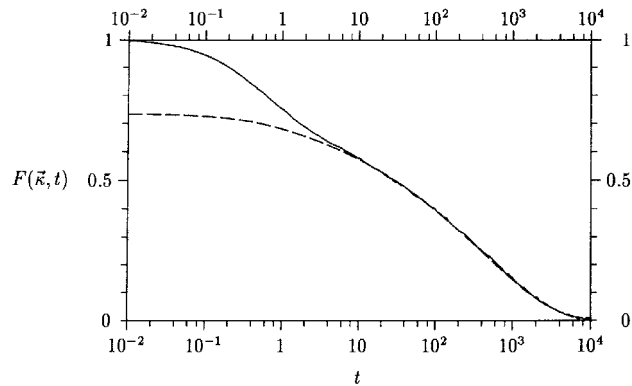$$F(\vec{k}, t) = \langle n_{\vec{k}}(t) n_{-\vec{k}}(0) \rangle \tag{10}$$

Figure 9. Two-stage decay of $F(\vec{k}, t)$ for $\vec{\kappa} = (\pi, 0)$. Dashed curve: $0.83 f_{bl}(t)$ (see the text).

for wavevector $\vec{k}$, was simulated for concentrations up to $c = 0.7$. Most interesting is the behaviour of this function at long times. *For smaller wavevectors* up to a certain limiting value k_c, the long-time decay is exponential:

$$F(\vec{k}, t) \propto \exp(-\gamma(k)t) \tag{11}$$

with a decay rate

$$\gamma(k) = D_c(c)k^2 \tag{12}$$

corresponding to collective diffusion. $D_c(c)$ is the collective diffusion coefficient (see below). Figures 8(a), (b) show that κ_c, which measures the range of validity of the diffusion equation, is about $\pi/16$ for $c = 0.2$, but only about $\pi/128$ at $c = 0.7$. (Here the wavevectors $\vec{k}$ are expressed in terms of the wavevectors $\vec{\kappa}$ obtained for the square lattice, onto which the triangular lattice is mapped; see section 5.1 of [11].) For the chosen directions of $\vec{\kappa}$, the relation between $\vec{\kappa}$ and $\vec{k}$ is $\vec{k} = 2\vec{\kappa}/\sqrt{3}$. The small range of validity of the diffusion equation for high c must be due to long-range dynamic heterogeneity. However, a quantitative explanation of k_c in terms of a properly defined characteristic length of dynamic heterogeneity has not yet been given.

For large wavevectors $\vec{k}$ and high concentrations, $F(\vec{k}, t)$ decays with time in two stages, which resembles the behaviour of $F(\vec{k}, t)$ for supercooled liquids near the glass transition. For $k = 2\pi/\sqrt{3}$ (figure 9) the slow decay of $F(\vec{k}, t)$ in the second stage is, up to a 'fudge factor' of order one, given by $f_{bl}(t)$, which is the fraction of particles that between time zero and t have always been immobile. This coincidence is due to the fact that for such a large wavevector an initially prepared density modulation is destroyed by any particle jump in the direction of the wavevector of the modulation.

3.7. Analytical approximations for self-diffusion [11]

Due to the long range of the cooperative processes the analytical calculation of dynamic properties of the CTLG at high lattice filling is a formidable and as yet unsolved problem. It is nevertheless of interest to apply established approximation schemes, which are successful for other problems but fail here. Compared with the HSLG, the CTLG offers the considerable advantage that there are no static correlations that need to be taken into account.

For the simple triangular-lattice gas, where the hopping of a particle need not be assisted by additional vacancies, *self-diffusion* occurs through the motion of independent particles for $c \to 0$ and of independent holes for $c \to 1$. An approximation scheme which is exact in both these limits and reasonably accurate at intermediate concentrations is the so-called *pair*
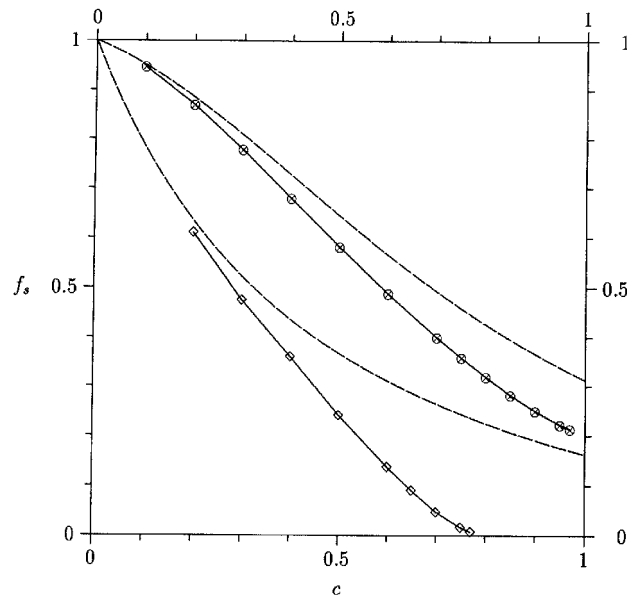
Figure 10. Comparison of MC data (full curves) with the result of the pair approximation (dashed curve) for the tracer correlation factor. The upper pair of curves is obtained for the model with one-vacancy-assisted hopping.

approximation [28, 29]. It describes the coupled motion of the tagged particle and a vacancy. We applied this approximation scheme not only to the CTLG, but also to a hybrid model where only one instead of two additional vacancies is required for hopping. It is easy to see that in the model with one-vacancy-assisted hopping a nearest-neighbour pair of vacancies can explore the entire lattice in a tumbling motion, independent of assistance from other vacancies. In figure 10 the results of the calculations for the *tracer correlation factor* f_s are shown for both models together with the results obtained from MC simulation. f_s is defined as $D_s/((3/2)\Gamma)$, where the average jump frequency Γ is given by $(1 - c)^3$ for two-vacancy-assisted hopping and $(1 - c)(1 - c^2)$ for one-vacancy-assisted hopping. The approximate analytical calculation in both cases yields a non-zero limit of f_s for $c \to 1$, which is qualitatively correct for one, but completely wrong for the other model. In general, the pair approximation is qualitatively correct if a finite cluster of vacancies can propagate freely through an otherwise full lattice. In the CTLG, however, any finite cluster of vacancies in an otherwise full lattice is locked in the smallest hexagon which encloses all vacancies. Therefore the pair approximation qualitatively fails to describe particle diffusion over long distances for this model.

3.8. Analytical approximations for collective diffusion [12]

We calculated the intermediate-scattering function $F(\vec{k}, t)$ in the so-called *'two-variable approximation'*. This approximation is obtained by calculating the memory function in the Mori–Zwanzig projection operator formalism in the subspace spanned by the two functions $n_{\vec{k}}$ and $\dot{n}_{\vec{k}}$. In terms of the correlation factor f_c for collective diffusion, which is defined as the collective diffusion coefficient divided by its mean-field value, namely

$$f_c = D_c/((3/2)(1 - c)^2) \tag{13}$$

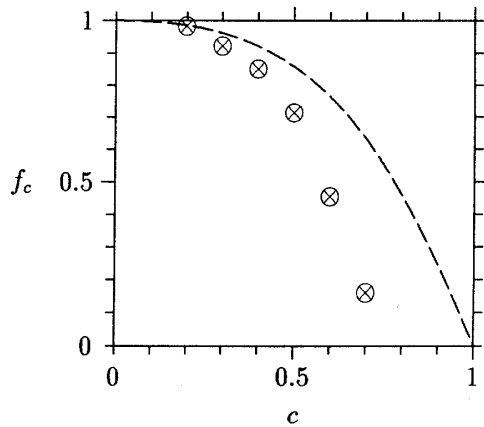the result of the two-variable approximation reads

Figure 11. Comparison of the result of the two-variable approximation for the correlation factor f_c for collective diffusion (dashed curve) with the result from MC simulation.

$$f_c^{(2)} = \frac{7 - 2c}{7 - 9c + 4c^2}(1 - c). \tag{14}$$

This result is shown in figure 11 together with the results derived from the MC data for $F(\vec{k}, t)$ for small $\vec{k}$ and long times (see equations (11), (12)). Although $f_c^{(2)}$ goes to zero for $c \to 1$, the agreement with the MC data at higher concentrations is very poor. The two-variable approximation for collective diffusion at high concentrations is as inadequate as the pair approximation is for self-diffusion.

$F(\vec{k}, t)$ was also calculated in a *mode-coupling approximation* following the standard recipe. Except for low concentrations, the approximation fails completely, as $F(\vec{k}, t)$ diverges with time. Probably this serious defect of the mode-coupling approximation can be corrected by introducing an irreducible memory kernel as in the case of kinetically constrained Ising spin models [30–33]. However, it seems very unlikely that such a modified mode-coupling approximation would be accurate at high concentrations.

4. Summary and outlook

The above review deals with two kinetically constrained lattice gas models which illustrate and give concrete meaning to the idea of cooperative particle diffusion. By analysing the kinetics of the models, cooperative processes could be identified and a characteristic length of these processes could be defined. In lattices of finite size, dynamic size effects are the signature of such cooperativity. These properties have been amply demonstrated by MC simulation for both models. For the HSLG it has been proved that the cooperativity length remains finite for all concentrations c below $c_{\max} = 1/2$. Among the many unsolved problems, let me mention the most urgent ones:

- Can the argument for the absence of a critical concentration for the cooperativity length of the CTLG (section 3.2 and figure 7) be made rigorous?
- What is the asymptotic form of the cooperativity lengths ξ at high c for both models?
- Does a dynamic phase transition with a critical concentration $c < c_{\max}$ exist, above which the self-diffusion coefficient vanishes?
- How is the range of wavevectors for which the diffusion equation holds (section 3.6 and figures 8(a), (b)) related to dynamic heterogeneity?

These problems can be tackled by improved MC simulation, but ultimately a breakthrough in the analytical treatment of the models is needed.

Let me finally address the question of how cooperative diffusion in these models compares with the diffusion in *simple models of real glass-forming liquids*, such as a binary mixture of hard spheres. In real liquids, cooperative rearrangements of particles are difficult to pin down, and it has not been possible to directly relate the cooperative processes in the models to diffusive motion in these liquids. However, a dependence of the self-diffusion coefficient on system size has also been found in real liquids, and becomes more pronounced with increasing density [34]. This dynamic size effect is therefore similar to that found in the lattice models and, if the calculations are extended to higher densities, a characteristic length of cooperativity can be derived for the model liquids.

References

[1] Heesemann A, Rätzke K, Faupel F, Hoffmann J and Heinemann K 1995 *Europhys. Lett.* **29** 221
[2] Ohligschleger C and Schober H R 1999 *Phys. Rev.* B **59** 811
[3] Adam G and Gibbs J H 1965 *J. Chem. Phys.* **43** 139
[4] Edwards S F and Vilgis T 1985 *Physics of Disordered Materials* ed D Adler, H Fritzsche and S R Ovshinsky (New York: Plenum) p 63
    Edwards S F and Vilgis T 1986 *Phys. Scr.* T **13** 7
[5] Ertel W, Froböse K and Jäckle J 1988 *J. Chem. Phys.* **88** 5027
[6] Froböse K 1989 *J. Stat. Phys.* **55** 1285
[7] Jäckle J, Froböse K and Knödler D 1991 *J. Stat. Phys.* **63** 249
    Jäckle J, Froböse K and Knödler D 1991 *J. Stat. Phys.* **65** 415 (erratum)
[8] Jäckle J 1991 *Materials Research Society Symp. Proc.* vol 215 (Pittsburgh, PA: Materials Research Society) p 151
[9] Sappelt D and Jäckle J 1993 *J. Phys. A: Math. Gen.* **26** 7325
    Sappelt D and Jäckle J 1997 *J. Phys. A: Math. Gen.* **30** 3739 (corrigendum)
[10] Jäckle J 1994 *Disorder Effects on Relaxational Processes* ed R Richert and A Blumen (Berlin: Springer) p 233
[11] Jäckle J and Krönig A 1994 *J. Phys.: Condens. Matter* **6** 7633
[12] Krönig A and Jäckle J 1994 *J. Phys.: Condens. Matter* **6** 7655
[13] Krönig A 1993 *Diploma Thesis* University of Konstanz
[14] Donati C and Jäckle J 1996 *J. Phys.: Condens. Matter* **8** 2733
[15] Jäckle J 1996 *Non-Equilibrium Phenomena in Supercooled Fluids, Glasses and Amorphous Materials* ed M Giordano, D Leporini and M P Tosi (Singapore: World Scientific) p 41
[16] Jäckle J 1996 *Phys. Bl.* **52** 351
[17] Jäckle J 1999 *Anomalous Diffusion. From Basics to Applications* ed A Pekalski and K Sznajd-Weron (Berlin: Springer) p 235
[18] Kob W and Andersen H C 1993 *Phys. Rev.* E **48** 4364
[19] Scarpetta S, De Candia A and Coniglio A 1997 *Phys. Rev.* E **55** 4943
[20] Adler J 1991 *Physica* A **171** 453
[21] van Enter A C D, Adler J and Duarte J A M S 1990 *J. Stat. Phys.* **60** 323
[22] Pitis R 1990 *Phys. Rev.* B **41** 7156
[23] Chaturvedi D K 1986 *Phys. Rev.* B **34** 8080
[24] Pitis R 1990 *Phys. Rev.* B **42** 8375
[25] Nakanishi H and Takano H 1986 *Phys. Lett.* A **115** 117
[26] Straley J P 1979 unpublished
    as quoted by
    Kogut P M and Leath P L 1981 *J. Phys. C: Solid State Phys.* **14** 3187
[27] Frick B, Zorn R and Büttner H (ed) 2000 *Proc. Int. Workshop on Dynamics in Confinement; J. Physique* IV **10** Pr7
[28] Tahir-Kheli R A and Elliott R J 1983 *Phys. Rev.* B **27** 844
[29] Tahir-Kheli R A 1983 *Phys. Rev.* B **27** 6072
[30] Kawasaki K 1995 *Physica* A **215** 61
[31] Pitts S J and Andersen H C 2000 *J. Chem. Phys.* **113** 3945
[32] Pitts S J and Andersen H C 2001 *J. Chem. Phys.* **114** 1101
[33] Pitts S J, Young T and Andersen H C 2000 *J. Chem. Phys.* **113** 8671
[34] Jäckle J and Kawai H 2001 *Physica* A **291** 184