# Diffusion in concentrated lattice gases. Self-diffusion of noninteracting particles in three-dimensional lattices

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The dynamical process of the diffusion of tagged particles in concentrated lattice gases is investigated. The lattice is fcc and the particles are noninteracting except that double occupancy is forbidden. The self-diffusion coefficient and the waiting-time distributions for two consecutive jumps of a tagged particle are calculated numerically by Monte Carlo methods. The time-dependent correlations between consecutive jumps are analyzed in detail, especially the initially increased rate for backward jumps of the tagged particle. The self-correlation function of a diffusing particle is also calculated by a correlated-jump model, which represents a generalization of the usual treatment of self-diffusion to frequency dependence and to finite concentrations. The resulting diffusion coefficient agrees well with the direct numerical calculations. Some other analytical predictions are also tested. The incoherent dynamical scattering function shows the effect of correlations at small frequencies and mean-field behavior at high frequencies.

## I. INTRODUCTION

This is the first of a series of papers on the dynamics of the diffusion in concentrated lattice gases. Regular lattices are considered whose sites are either occupied by particles or empty. In the general case several kinds of particles $A,B,\ldots$, can be present, together with vacancies $V$. The particles can hop from full to empty sites, or exchange with each other. The interactions between the particles are assumed to be known, as well as the rates of exchange $A \rightleftharpoons B$, $A \rightleftharpoons V,\ldots$, etc. The general aim is the derivation of the correlation functions for the positions of the particles. The general Markovian master equation for the description of the various possible jump processes is well known and has been used for studies of the kinetics of Ising models with conserved spins[1] and binary alloys.[2,3] Since the equation is far too complicated for an explicit solution, either numerical calculations must be performed or appropriate simplifications made.

In this paper one species of particles ($A$) at finite concentration $c=N_A/N$ is considered, where $N_A$ is the number of particles and $N$ is the number of lattice sites. It is assumed that no interactions between the particles and between particles and vacancies exist, except that double occupancy of lattice sites is prohibited. A particle can jump to a vacant site with rate $\Gamma$; exchange between different particles is excluded. The calculation of the correlation function of the position of two particles is rather simple in this model, as well as the resulting chemical diffusion coefficient.[4] The nontrivial features of the model appear in the correlations of the motion of individual, tagged particles. It is the main task of this paper to investigate these correlations and to calculate the self-diffusion coefficient and the self-correlation function.

Consecutive jumps of tagged particles of the lattice gas are correlated, because, when a particle has made a jump, there is with certainty a vacancy behind it, hence there is an increased tendency for a backward jump of the tagged particle. Bardeen and Herring[5] noted first that this effect leads to a reduction of the tracer diffusion constant in metals, which can be described by a correlation factor $f<1$. Meanwhile, the correlation factor has been thoroughly investigated for vanishingly small vacancy concentration, which is the relevant case for tracer diffusion in metals. This case can be treated exactly since it is determined by the random walk of one vacancy. For a review see Le Claire[6]; more recent work can be found, e.g., in Refs. 7 and 8. Also extensions to the case of finite but still small vacancy concentrations have been reported.[9,10]

In other physical systems such as hydrogen in metals or solid electrolytes, arbitrary concentrations of vacancies can be present and the correlation factor will depend on the concentration of the diffusing particles. Sato and Kikuchi[11] have applied the "path probability method"[12] to the diffusion in a two-dimensional honeycomb lattice and calculated $f(c)$. Owing to the use of the pair approximation the result for $f(c)$ was not satisfactory, even in the limit $c \to 1$. Murch[13] and Murch and Thorn[14,15] have made Monte Carlo calculations of the diffusion in lattice gases with variable $c$ and obtained numerical $f(c)$ for several lattices. Sankey and Fedders[16] calculated the self-correlation function of diffusing particles by diagrammatic methods and obtained approximate expressions for the correlation factor. Ross and Wilson[17] have set up a phenomeno-

 

logical random-walk model and determined numerically the pertinent quantities. Very recently Nakazato and Kitahara[18] have studied self-diffusion in the noninteracting lattice gas by a novel method of performing the statistical averaging procedures and found results in agreement with the numerical calculations in Ref. 15.

The aim of this article is the elucidation of the dynamical process of self-diffusion in three-dimensional-lattice gases of arbitrary concentration. A dynamical description of the self-diffusion is provided by the time-dependent self-correlation functions. Such self-correlation functions have been derived by several approximate methods,[16-18] however, the basic processes which determine the temporal behavior cannot be clearly recognized by these approaches. There should be a pronounced time dependence of the correlations between consecutive jumps of a tagged particle. Namely, the vacancy which is left behind a particle after its jump can be filled by other particles and thus the cause for the backward correlation disappears. In order to analyze the temporal behavior of a tagged particle in the lattice gas, so-called "waiting-time distributions" are introduced and estimated by Monte Carlo simulation. The waiting-time distribution for backward jumps exhibits the time-dependent correlations mentioned above. The numerical determination of the waiting-time distributions and their interpretation constitute the first part of this work, which is largely independent of model assumptions.

In the remainder of this article a random-walk model is introduced for the calculation of the self-correlation function which makes use of the waiting-time distributions. The model includes time-dependent correlations between two consecutive jumps of a tagged particle and thus provides a dynamical generalization, for arbitrary concentration, of the model used to calculate the correlation factor of tracer diffusion for $c \to 1$. It turns out that this model gives a very satisfactory approximation in the three-dimensional case.

The following Sec. II gives a short review of the general master equations for the diffusion of tagged particles in a lattice, and of the mean-field approximation for the self-correlation function of a tagged particle. In the third section, numerical calculations of the waiting-time distributions for the jump dynamics of a tagged particle by Monte Carlo simulation are reported. The behavior of the waiting-time distributions is analyzed and represented by physically plausible expressions. In the fourth section a correlated-jump model for the calculation of the self-correlation function of a tagged particle is presented. In the fifth section, first the results of the model for the self-diffusion coefficient are compared with results of the numerical simulations, then the resulting incoherent dynamical scattering function is discussed. In the concluding Sec. VI the results are summarized and possible extensions considered. Also the limitations of the model of correlated consecutive jumps are pointed out.

## II. MASTER EQUATIONS AND MEAN-FIELD APPROXIMATION

A very general description of the diffusion in concentrated lattice gases is provided by the following Markovian master equation:

$$\frac{d}{dt}P(\mu_1,\ldots,\mu_N,t) = -\sum_i\sum_{\vec{l}_i} W(i\to\vec{l}_i)P(\mu_1,\ldots,\mu_N,t) + \sum_i\sum_{\vec{l}_i} W(\vec{l}_i\to i) \times P_{(i,\vec{l}_i)}(\mu_1,\ldots,\mu_N,t)\,. \tag{1}$$

The $\mu$ are variables which indicate whether a particle $A$, or $B$, ... or a vacancy $V$ is present, $i$ assigns numbers to the particles and vacancies. $P(\mu_1,\ldots,\mu_N,t)$ is the probability of finding $\mu_1$ at site 1, $\mu_2$ at site 2, ..., etc. at time $t$ and for specified initial conditions. The sites of the regular Bravais lattice will be denoted by $\vec{l}$; there are $N$ sites. $P_{(i,\vec{l}_i)}$ is similarly defined as $P$, except that particle or vacancy $i$ has exchanged its position with position $\vec{l}_i$ (the particle or vacancy at that position is now at the original position of $i$). The transition probabilities $W(i\to\vec{l}_i)$ contain the effects of the interactions between the particles and they must fulfill the condition of detailed balance. An explicit form is not necessary for the case of noninteracting particles considered in this article. Also the vacancies must be treated separately in Eq. (1) if they are considered as indistinguishable; however, no complications arise in the reduced equations given below. Equation (1) has been introduced by Kawasaki[1] for the kinetics of spin exchange with conserved spins, and applied, e.g., for phase separation in binary alloys by Binder.[2] Equation (1) is the general starting point for computer simulations.

When there is only one kind of noninteracting particle present and double occupancy is forbidden the general master equation can be reduced by appropriate summations to the following equation for the self-correlation function:

$$\frac{d}{dt}P(i\vec{l},t) = \Gamma\sum_{\langle\vec{l}'\rangle}\{P(i\vec{l}',[\vec{l}],t) - P(i\vec{l},[\vec{l}'],t)\}\,, \tag{2}$$

$P(i\vec{l},t)$ is the probability of finding the particle numbered $i$ at the lattice site $\vec{l}$ at time $t$ for a specific initial condition. $P(i\vec{l}',[\vec{l}],t)$ is the joint probability of finding the particle $i$ at $\vec{l}'$, and *no* other particle at $\vec{l}$, with the same initial conditions. $\Gamma$ is the jump rate of a particle to an empty site and the sum over $\vec{l}'$ extends over all nearest-neighbor sites of $\vec{l}$.

Equation (2) is not a closed expression and must be supplemented by further equations. A hierarchy of equations can be generated by considering the time derivatives of $P(i\vec{l}',[\vec{l}],t)$ and of higher-order joint probabilities. The hierarchy can be terminated by factorization methods; apart from the mean-field approximation this leads to tractable expressions for small vacancy concentrations only.[19] Another method to treat Eq. (2) consists of setting up a diagrammatic formulation and summing selected classes of diagrams[16]; results for arbitrary concentrations have been obtained in this way. In Sec. IV an alternative approach will be made; in the remainder of the present section only the lowest-order approximation to the hierarchy of equations will be considered. It is obtained by the factorization

$$P(i\vec{l}',[\vec{l}],t)\to(1-c)P(i\vec{l}',t)\,. \tag{3}$$

One then has

$$\frac{d}{dt}P(i\vec{l},t)=(1-c)\Gamma\sum_{\langle\vec{l}'\rangle}[P(i\vec{l}',t)-P(i\vec{l},t)]\,. \tag{4}$$

In this approximation the self-correlation function for the motion of particle $i$ is determined by a one-particle equation. The particle can be considered as hopping in an average background, with rate $(1-c)\Gamma$ for jumps between two sites, i.e., Eq. (3) constitutes the mean-field approximation.

For further reference some consequences of Eq. (4) will be indicated. The solution of Eq. (4) is

$$P(\vec{k},t)=P(\vec{k},0)\exp[-\Lambda(\vec{k})t]\,, \tag{5}$$

where

$$P(\vec{k},t)=\sum_{\vec{l}}\exp(-i\vec{k}\cdot\vec{R}_{\vec{l}})P(\vec{l},t)$$

and

$$\Lambda(\vec{k})=(1-c)\Gamma\sum_{\langle\vec{l}'\rangle}\{1-\exp[i\vec{k}\cdot(\vec{R}_{\vec{l}'}-\vec{R}_{\vec{l}})]\}\,.$$

$P(\vec{k},0)$ represents the initial condition, $\vec{R}_{\vec{l}}$ is a vector to lattice site $\vec{l}$, and the index $i$ has been omitted for simplicity. The diffusion coefficient of the tagged particle follows from the self-correlation function by evaluating

$$\begin{aligned}\langle R^2(t)\rangle&=-\sum_{\alpha=1}^{3}\frac{\partial^2 P}{\partial k_\alpha^2}\bigg|_{\vec{k}=0}(\vec{k},t)\,,\\ D_t&=\lim_{t\to\infty}[\langle R^2(t)\rangle/6t]\,.\end{aligned} \tag{6}$$

From Eq. (5) in mean-field (MF) approximation and for cubic symmetry,

$$D_t^{\mathrm{MF}}=(1-c)\Gamma a^2\,, \tag{7}$$

where $a$ is the lattice constant. Compared to the chemical diffusion coefficient[4] $D=\Gamma a^2$ which describes the decay of a density gradient in the lattice gas, the tracer diffusion coefficient is reduced in mean-field approximation, in the simple hopping model considered, by the "blocking factor" $1-c$. The incoherent dynamical scattering function follows directly from the self-correlation function, cf. Eq. (36). In mean-field approximation[17,20]

$$S_{\mathrm{inc}}^{\mathrm{MF}}(\vec{k},\omega)=\frac{\Lambda(\vec{k})/\pi}{\omega^2+\Lambda^2(\vec{k})}\,. \tag{8}$$

In mean-field approximation and for Bravais lattices, the incoherent dynamical scattering function is a simple Lorentzian whose width is proportional to $(1-c)\Gamma$.

## III. WAITING-TIME DISTRIBUTIONS

### A. Definition

The diffusion of tagged particles of the concentrated lattice gas is more complicated than is suggested by the mean-field approximation. This approximation is equivalent to an uncorrelated random walk. As already pointed out in the introduction, correlations between consecutive jumps of a tagged atom exist. When the atom has made a jump there is an increased probability for a backward jump due to the vacancy left behind the atom. The correlations are time dependent since the vacancy can also be filled by other atoms. Hence the probability of a backward jump of the tagged atom decreases with time and approaches, for large times, the probability for forward jumps.

In order to describe the dynamics of this process, "waiting-time distributions" will be used. Waiting-time distributions have been introduced by Montroll and Weiss[21] in their treatment of the continuous-time random walk. Let $\psi(t)$ be the waiting-time distribution of a particle which has made a jump at $t=0$. $\psi(t)dt$ is the joint probability that the particle has made no jump until time $t$ and performs a jump between $t$ and $t+dt$. An obvious example is provided by the Poisson process where $\psi(t)dt=\exp(-t/\bar{t})dt/\bar{t}$, with $\bar{t}$ the mean time of stay of the particle. The mean-field approximation corresponds to a Poisson process

with $\bar{t}^{-1} = z(1-c)\Gamma$, where $z$ is the number of nearest-neighbor sites. In general $\psi(t)$ represents more complicated processes. For the problem of tracer diffusion, the waiting-time distributions $\psi_b(t)$ for backward jumps, and $\psi_f(t)$ for forward jumps will be considered separately. $\psi_b(t)$ is expected to exhibit the correlation effects discussed above. Also, the waiting-time distributions for forward jumps can be different for different orientations of the jumps with respect to the previous jump. In the three-dimensional fcc lattice every site has $z = 12$ nearest neighbors; the forward jumps can be classified into 4 classes as is described in Fig. 1. Implicit in the introduction of the waiting-time distributions $\psi_{(1)}(t)$, ..., $\psi_{(4)}(t)$, $\psi_b(t)$ for the jumps of a tracer particle is the assumption that only the memory to the previous step of the particle is important, not to more distant steps. Otherwise, knowledge of these distributions alone does not provide a complete description of the diffusion process.

### B. Numerical procedure

The diffusion process of the particles is simulated on the computer by extension of standard Monte Carlo procedures.[22] We typically work with a finite lattice of $N = 4\times16^3 = 16\,384$ sites and periodic boundary conditions [this size is sufficient even for the study of phase transitions produced by interactions between particles (see Ref. 23)]. Then an initial configuration of the system is generated. For the noninteracting case considered in the present paper, the probability that a given site is occupied is independent of the occupation of all other sites. Hence a "typical" configuration of a system at concentration $c$ could be generated by choosing a random number $\xi$ for each site, with $0 \leq \xi < 1$, and taking the site occupied ($c_\uparrow = 1$) if $\xi < c$, and empty otherwise ($c_\uparrow = 0$). In the presence of interactions, however, correlations between the local occupation variables $c_\uparrow$ occur, and the relaxation process from the completely random configuration (which then is a configuration far from equilibrium), towards configurations close to thermal equilibrium, is known to be often very slow.[23] Hence we follow a different procedure for preparing an initial configuration for the simulation of the diffusion process, exploiting the standard analogy between lattice gases and Ising ferromagnets.[24] We start considering a system of $N$ spins in a magnetic field $H$ (in the present noninteracting case these spins are independent, but the generalization to an interacting case is straightforward). With the usual procedure[22] one lets the system relax towards equilibrium characterized by the Boltzmann factor $\exp[-\mathcal{H}(s_\uparrow)/k_BT]$, where in our case the Hamiltonian is $\mathcal{H}(s_\uparrow) = -H\sum_\uparrow s_\uparrow$, $s_\uparrow = \pm 1$. An equilibrium configuration thus generated is then stored and reinterpreted in terms of the lattice-gas model, using $c_\uparrow = (1 - s_\uparrow)/2$. The average concentration of the system is then given by the average magnetization, $c = (1 - \langle s_\uparrow \rangle)/2$. The particles thus generated are then labeled. (Even for small $c$ the size of the lattice is large enough to allow for a total number of particles much larger than one, and hence one can obtain reasonable statistics. Similarly, for $c$ close to unity one can still have a sufficiently large number of vacancies. For this reason, $N$ should not be chosen much smaller than done here.) Then the simulation of the diffusion process starts by randomly selecting a particle and (also randomly) selecting one of the twelve possible nearest-neighbor sites. If this site is already occupied, the old configuration is counted once more for the averaging. If this site is empty, the chosen particle is moved to that site, and the resulting new configuration is counted. The time in which each particle has had, *on the average*, one chance to jump to a neighboring site is called a Monte Carlo step/particle (MCS), and is the natural time unit to measure the time lapse for the diffusion process. Note that due to the random selection of particles, the time a particle has to wait before it can attempt the next jump is not fixed at $t = 1$ MCS but rather distributed according to a Poisson process. Since in the computer program all particles are individually labeled, one obtains the self-diffusion coefficient most efficiently by computing the mean-square displacement of all particles. For this purpose, we keep track of which of the "images"

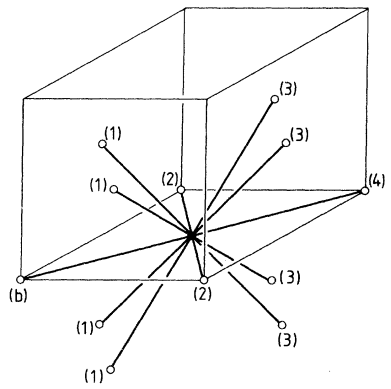


FIG. 1. Classification of jumps of a tracer atom. The tracer has made a jump from ($b$) to the site represented by a full black dot, hence ($b$) represents a possible site for a backward jump. The other nearest-neighbor sites are designated according to the order of neighborhood with respect to ($b$), e.g., (2) is a second neighbor of ($b$).

of the finite system (which are generated by the periodic boundary condition), each particle is situated in at any instant of time. Thus, by storing two positions for each particle (the position in the basic box of $N$ spins and the appropriate image position) it is possible to follow the particles up to arbitrarily large displacements, which hence are not limited by the size of the box.

Storing in this way the positions $\vec{R}_i(t)$ of the $N_A$ particles present one obtains the generalized time-dependent tracer diffusion coefficient as follows

$$D_t(t) = \frac{1}{6N} \sum_{i=1}^{N_A} \langle [\vec{R}_i(t+t_0) - \vec{R}_i(t_0)]^2/t \rangle_{av}, \qquad (9)$$

where the angular brackets denote an average over the time $t_0$. For large time $t$ this expression becomes independent of $t$ (in practice a few MCS were sufficient) and reduces to the standard tracer diffusion coefficient. It turns out that for having good statistics the time average in the above equation is indispensable. It would not be reasonable to use a simple observation for $t \to \infty$, since also the fluctuation of the mean-square displacement diverges so strongly as $t \to \infty$ that the error in $[\vec{R}_i(t + t_0) - \vec{R}_i(t)]^2$ becomes independent of $t$ for large $t$.

The jump rate per particle is trivially found from averaging the number of successful jumps per MCS. The waiting-time distributions are obtained approximately by considering a total time interval up to $t_{max}$ and dividing each MCS/particle into $n$ subintervals. For each jumping particle one records the subinterval to which the time belongs, which it has spent on a specific site, and thus approximates the distribution by a histogram. (In practice $t_0$ as small as 1 MCS and $n = 10$–$50$ turned out to give sufficient accuracy; larger values of $t_0$ have also been used but gave identical results. By suitably increasing these numbers any desired accuracy can be reached, at least in principle.) By keeping track of the site each particle had taken before the considered attempt to jump, it is straightforward to sample separately the different waiting-time distributions defined above.

### C. Results

Figure 2 reproduces the results for the waiting-time distributions $\psi_b(t)$, $\psi_{(1)}(t)$, and $\psi_{(4)}(t)$ for four different concentrations. The waiting-time distributions $\psi_{(2)}(t)$ and $\psi_{(3)}(t)$ are not shown in this figure. They are practically identical to $\psi_{(4)}(t)$ although there are small systematic deviations [$\psi_{(2)}(t)$ tends to be larger than $\psi_{(3)}(t)$ and $\psi_{(4)}(t)$]. One sees that the waiting-time distribution for backward jumps is similar for all concentrations.

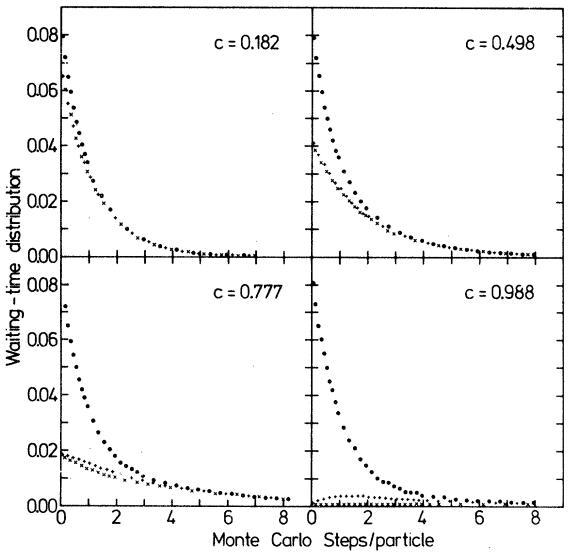


FIG. 2. Waiting-time distributions for backward jumps (●) and forward jumps to sites (1) (+) and (4) (×), respectively, for four different concentrations. Only a part of the calculated points is shown.

For small time it approaches the jump rate $\Gamma$ without any blocking effect. The natural time unit is 1 MCS/particle; it corresponds to setting $12\Gamma = 1$, hence $\psi_b(t=0) = \frac{1}{12}$. For increasing time, $\psi_b(t)$ decays rapidly towards the waiting-time distributions for forward jumps. The waiting-time distributions for forward jumps are reduced for larger concentrations and for small times they approach the mean-field value $\psi_{(1)\ldots(4)}(0) = (1-c)\Gamma$. For large concentration, $\psi_{(1)}(t)$ shows a marked deviation from $\psi_{(4)}(t)$, and even an increase for small times at $c = 0.988$. The physical process responsible for this behavior is the possibility that the vacancy existing at site ($b$) can jump to one of the nearest-neighbor sites and thus increase the probability of jumps of the tagged particle to these sites. An explicit analysis will be given below.

### D. Analysis of the results

In this subsection the waiting-time distributions are further analyzed in order to understand the physical processes which contribute to their behavior, and to obtain analytic expressions which can be used in subsequent calculations. The waiting-time distributions have to fulfill several requirements. First, the sum of the waiting-time distributions has to be normalized to unity:

$$\int_0^\infty dt \sum_{i=1}^{12} \psi_i(t) = 1. \qquad (10)$$

Here and in the following the sum runs over all

nearest-neighbor sites, i.e., the sites of type (1) and (3) appear four times and sites of type (2) twice. Second, as already mentioned,

$$\psi_b(t=0)=\Gamma,$$
$$\psi_{(1)\cdots(4)}(t=0)=(1-c)\Gamma. \tag{11}$$

Third, the first moment of the sum of the waiting-time distributions must be

$$\int_0^\infty dt\, t \sum_{i=1}^{12} \psi_i(t)=\bar{t}, \tag{12}$$

$$\bar{t}=[12(1-c)\Gamma]^{-1}, \tag{13}$$

where $\bar{t}$ is the mean residence time of a particle. In the noninteracting lattice gas the mean time of stay of any particle is just given by the expression (13); apart from $12\Gamma$ only the mean vacancy availability factor $1-c$ enters.

In order to analyze $\psi_i(t)$ further the following procedure is adopted. First the "sojourn probability" $\Psi(t)$ of a tracer particle is introduced,

$$\Psi(t)=1-\int_0^t dt' \sum_{i=1}^{12} \psi_i(t').$$

This is the probability that a tagged particle, which arrived at a site at $t=0$, has made no jump until time $t$. From (10) and (12) we have

$$\Psi(\infty)=0, \tag{14}$$

$$\int_0^\infty dt\,\Psi(t)=\bar{t}. \tag{15}$$

We introduce

$$\psi_i(t)=\Gamma_i(t)\Psi(t).$$

The sojourn probability can be represented as

$$\Psi(t)=\exp\left(-\int_0^t dt' \sum_{i=1}^{12} \Gamma_i(t')\right). \tag{16}$$

The $\Gamma_i(t)$ are time-dependent jump rates for jumps in specified directions which are defined under the condition that no jump of the tracer atom has occurred from $t=0$ until time $t$. $\Gamma_i(t)$ are *defined* by the relations given above; it would not make sense to use them in other contexts, e.g., in master equations.

The conditional jump rates $\Gamma_i(t)$ have been obtained by numerically calculating $\Psi(t)$ and using the definition given above. $\Gamma_{(4)}(t)$, $\Gamma_{(1)}(t)$, and $\Gamma_b(t)$ are represented in Fig. 3 for four different concentrations. One recognizes that the jump rates approach the values $\Gamma$ for the backward jump, and $(1-c)\Gamma$ for forward jumps, respectively, in accordance with (11). The qualitative behavior of $\Gamma_i(t)$, especially of $\Gamma_b(t)$ is as expected. However, the asymptotic value for larger times is not the mean-field value $(1-c)\Gamma$, instead, a reduced value is found which is the same for the different $\Gamma_i(t)$ at fixed concentration. Hence $\Gamma_i(t)$ will be represented for larger times as

$$\Gamma_i(t)\xrightarrow[t\ \text{large}]{}(1-c-\alpha)\Gamma, \tag{17}$$

where a reduction parameter $\alpha(c)$ appears. The decay to this asymptotic behavior is assumed to be exponential. It is assumed that $\Gamma_{(4)}(t)$ is essentially determined by the two limiting cases described above, i.e., the ansatz is made

$$\Gamma_{(4)}(t)=(1-c-\alpha)\Gamma+\alpha\Gamma\exp(-z\gamma\Gamma t), \tag{18}$$

where a second parameter $\gamma(c)$ appears. With $\alpha$,

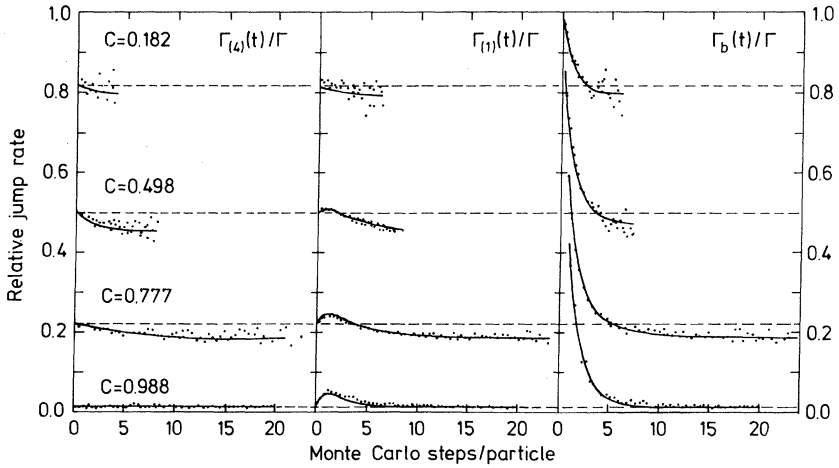


FIG. 3. Jump rates $\Gamma_i(t)$/as defined in Eq. (16) and divided by $\Gamma$ for four different concentrations. The points give the result of the numerical simulations, the full lines represent the fit by the expressions given in the text, and the dashed lines indicate the mean-field values.

$\gamma$ as fit parameters a good description of the computed jump rate $\Gamma_{(4)}(t)$ is obtained (see Fig. 3). The jump rates to (2) and (3) are assumed to be equal to $\Gamma_{(4)}$,

$$\Gamma_{(2)}(t) = \Gamma_{(3)}(t) = \Gamma_{(4)}(t). \tag{19}$$

It is shown in Fig. 4 that this assumption is reasonable at $c = 0.777$; the same is true at other concentrations.

The following ansatz will be made for $\Gamma_{(1)}(t)$:

$$\Gamma_{(1)}(t) = \Gamma_{(4)}(t) + c\Gamma^2 t \exp[-(z-1)c\Gamma t]. \tag{20}$$

The second term on the right-hand side (rhs) represents the Poisson process of the vacancy at $(b)$ which jumps from its original site $(b)$ to one of the neighboring sites and thus enables a jump of type (1) of the tracer atom. This process is peculiar to lattices with "triangular" relations such as fcc. Figure 3 demonstrates the good description of the numerical results for $\Gamma_{(1)}(t)$ by (20). One could think of also considering the Poisson process of the vacancy jumping to second-neighbor sites. This would lead to a contribution to $\Gamma_{(2)}(t)$ of

$$c^2\Gamma^3 t^2 \exp[-(z-1)c\Gamma t]. \tag{21}$$

This is a correction which improves somewhat the fit of the numerical $\Gamma_{(2)}(t)$, however, it is so small that its validity cannot be established.

Finally, the rate for backward jumps will be represented by

$$\Gamma_b(t) = \Gamma_{(4)}(t) + c\Gamma \exp[-(z-1)\Gamma t] + \tfrac{1}{2}(z-1)c^2\Gamma^3 t^2 \exp[-(z-1)c\Gamma t]. \tag{22}$$

The quality of this representation can also be seen in Fig. 3. The second term on the rhs describes how the vacancy left behind the tracer atom disappears in the average background. It is remarkable that the decay rate of this process is independent of the concentration $c$. It will be shown in the Appendix that the decay of an additional hole in the lattice gas to the average background is governed by the rate $z\Gamma$. Here the jump rates are considered with the condition of no jump of the tracer atom until time $t$, hence $z\Gamma$ is replaced by $(z-1)\Gamma$. The third term on the rhs describes the second-order Poisson process of the vacancy jumping to a neighboring site and returning to site $(b)$. Compared to the two-step process (21) for $\Gamma_{(2)}$ a factor $(z-1)$ appears. Hence this term is visible for larger $c$ although it is still small. For small $c$ this term has been omitted. The contributions of the second and third term on the rhs of (22) are explicitly displayed in Fig. 5 for $c = 0.777$.

It appears that a good description of the rates $\Gamma_i(t)$ and hence of the waiting-time distributions $\psi_i(t)$ has been found; however, there remain two unknown parameters $\alpha(c)$ and $\gamma(c)$. One can first ask whether the asymptotic behavior given in (17) has been satisfactorily established. For this purpose the sojourn probability $\Psi(t)$ has been calculated directly since, when no subdivision into the different types of jumps is made, better statistics can be achieved. $\Psi(t)$ has been calculated up to 64 Monte Carlo steps per particle and agreement with (17) has been found. Figure 6 compares the computed $\Psi(t)$ with the mean-field form at $c = 0.777$. The values of $\alpha$ and $\gamma$ obtained from the fits of $\psi_i(t)$, $\Psi(t)$ at different concentrations are given in Table I. At present no quantitative explanation for $\alpha$ and $\gamma$ has been found. A qualitative explanation for the average reduction of the jump rates at large times can be given as follows. $\Gamma_i(t)$ represents a conditional jump

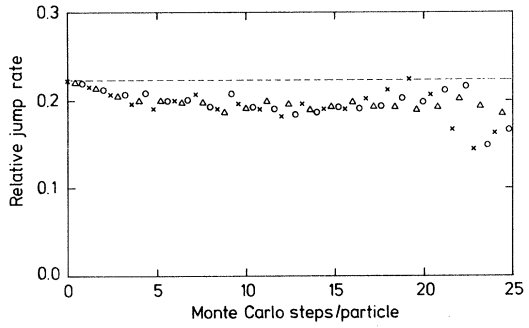


FIG. 4. Jump rates $\Gamma_{(2)}(\bigcirc)$, $\Gamma_{(3)}(\triangle)$, and $\Gamma_{(4)}(\times)$ divided by $\Gamma$ for $c = 0.777$.

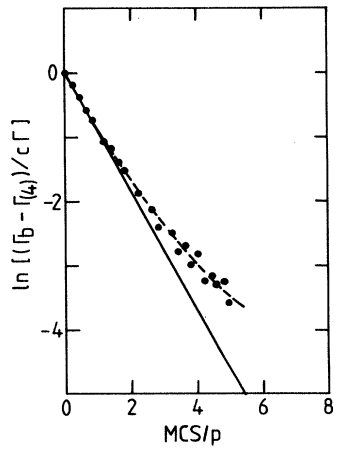


FIG. 5. Behavior of $\ln[(\Gamma_b - \Gamma_{(4)})/c\Gamma]$ as a function of time. The points represent the numerical results. The full line corresponds to the exponent $-(z-1)\Gamma t$ in the second term on the rhs of Eq. (22), the dashed line represents the effect of adding the third term on the rhs of (22).

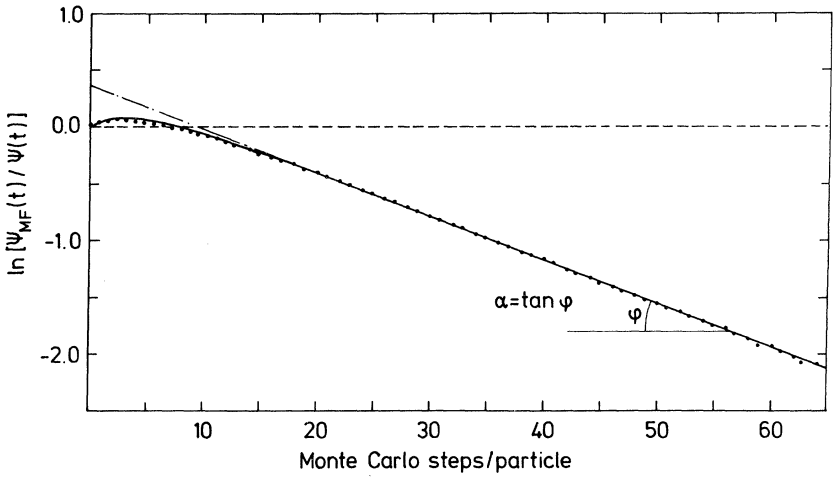


FIG. 6. Quotient of the mean-field result for the sojourn probability to the numerical (points) and fitted (line) sojourn probability for $c=0.777$. The deviation from the horizontal dashed line indicates the presence of an additional factor $\exp(-\alpha\Gamma t)$ in the sojourn probability for larger times.

rate, the condition being that no jump has occurred until time $t$. When the tagged particle has made no jump for a longer time $t$ then it is very likely that it is in a cluster of increased concentration, resulting in a reduction of the jump rate.

The necessity of a reduced conditional jump rate $\Gamma_i(t)$ at larger times can also be seen from the requirement that $\Psi(t)$ is normalized to $\bar{t}$ [cf. (15)]. Due to the possibility of backward jumps, $\Psi(t)$ decays more rapidly for small times than the corresponding mean-field expression $\Psi_{\mathrm{MF}}(t)$. This faster decay has to be compensated at larger time. We have checked numerically that the sojourn probability $\Psi(t)$ resulting from our forms for $\Gamma_i(t)$ is properly normalized.

It would be convenient if one could represent the waiting-time distributions, e.g., $\psi_b(t)$, as a sum of two (or a few) Poisson processes. We found it impossible to approximate the $\psi_i(t)$ in such a simple way and, at the same time, to fulfill the requirements pointed out at the beginning of the section. A representation of the $\psi_i(t)$ in terms of a sum of two Poisson processes would correspond to simplifying assumptions on the time dependence of the different correlated jump processes which are not in accordance with the actual behavior.

TABLE I. Values of the parameters $\alpha(c)$ and $\gamma(c)$ determined by the fit of the jump rates $\Gamma_i(t)$ and sojourn probability $\Psi(t)$.

| $c$ | $\alpha$ | $\gamma$ |
|---|---|---|
| 0.1823 | 0.0246 | 0.4408 |
| 0.4977 | 0.0482 | 0.5354 |
| 0.7773 | 0.0390 | 0.1515 |
| 0.9526 | 0.0058 | 0.0335 |
| 0.9879 | 0.0023 | 0.0218 |

## IV. CORRELATED-JUMP MODEL

### A. Introduction

It will be shown in this section how the self-correlation function of diffusing tagged particles can be derived from the waiting-time distributions which have been determined in the last section. We will introduce a model which incorporates the correlations which have been studied. By specifying the sites where a tracer particle will jump to, relative to the previous jump, the tracer has a memory where it came from, i.e., to one step before. The corresponding model is a special class of models with correlated jumps, namely, a model where a correlation between the actual and the preceding jump is taken into account.

Models with correlations between consecutive jumps have been investigated in the form of "backward-jump models" with constant jump rates for forward and backward jumps by Haus and Kehr,[25] and for a special choice of waiting-time distributions by Landman and Shlesinger.[26,27] A one-dimensional model with general waiting-time distributions has been studied by Zwerger and Kehr.[28] The general approach consists of setting up recursion relations for appropriate generating functions. For simple examples of the general procedure the reader is referred to the papers mentioned above.

### B. Derivation of the self-correlation function

The basic quantity of the correlated-jump model is the probaility distribution $Q_n(\vec{l},\vec{l}_1,t)$. It is defined as the probability density that the tracer atom performs its $n$th jump at time $t$, jumps to site $\vec{l}$ and comes from site $\vec{l}_1$. The initial condition will be specified below. This probability density obeys the recursion relation

$$Q_n(\vec{l},\vec{l}_1,t)=\sum_{\langle\vec{l}\,'_1\rangle}\int_0^t dt'\,Q_{n-1}(\vec{l}_1,\vec{l}\,'_1,t')\times\psi_{(\vec{l},\vec{l}_1,\vec{l}\,'_1)}(t-t'),\quad n\geq 2\,. \tag{23}$$

$\vec{l}\,'_1$ are nearest-neighbor sites of $\vec{l}_1$. The case $n=1$ will be treated separately. The waiting-time distribution depends on the relative orientation of $\vec{l}$, $\vec{l}_1$, and $\vec{l}\,'_1$. For example, one term on the rhs is that where $\vec{l}\,'_1=\vec{l}$: the particle comes from $\vec{l}$ in the $(n-1)$th step and the $n$th jump is a backward jump, hence $\psi_b(t-t')$ must be used in this term.

The following procedures and simplifications will be performed on Eq. (23).

(i) Laplace tranformation:

$$\tilde{f}(s)=\int_0^\infty dt\exp(-st)f(t)\,.$$

(ii) Fourier transformation with respect to the first lattice index:

$$Q_n(\vec{k},\vec{l}_1,t)=\sum_{\vec{l}}\exp(-i\vec{k}\cdot\vec{R}_{\vec{l}})\,Q_n(\vec{l},\vec{l}_1,t)\,.$$

(iii) Introduction of a relative notation, e.g., $Q_n(\vec{l},\vec{l}_1,t)$ depends on $\vec{l}$ and $\Delta\vec{l}_1=\vec{l}-\vec{l}_1$ only. There are 12 different $\Delta\vec{l}_1$ in the fcc lattice, $\Delta\vec{l}_1=(a/2,a/2,0)$ will be denoted by $xy$, and so on.

(iv) Summation of the recursion relation (23). The summary probability density is introduced,

$$Q(\vec{l},\Delta\vec{l}_1,t)=\sum_{n=1}^{\infty}Q_n(\vec{l},\Delta\vec{l}_1,t)\,.$$

When the recursion relation is summed over $n$, the initial condition has to be added. The tracer atom is assumed to be at $\vec{l}=0$ at $t=0$, and jumps with probability $1/z=1/12$ to a neighboring site, The waiting-time distribution $h(t)$ for the *first* jump is given by (cf. Refs. 29 and 30)

$$h(t)=\frac{\int_0^\infty dt'\sum_{i=1}^{12}\psi_i(t'+t)}{\int_0^\infty dt\int_0^\infty dt'\sum_{i=1}^{12}\psi_i(t'+t)}=\frac{\Psi(t)}{t}\,. \tag{24}$$

Hence

$$Q_1(\vec{l},\Delta\vec{l}_1,t)=\begin{cases}\dfrac{h(t)}{12} & \text{if } \vec{l} \text{ is nearest neighbor to } \vec{l}=0\\ 0 & \text{otherwise.}\end{cases}$$

Performing the procedures described above one obtains a system of 12 linear equations,

$$\tilde{Q}(\vec{k},\Delta\vec{l}_1,s)-f_{\Delta\vec{l}_1}(\vec{k})\sum_{\Delta\vec{l}\,'_1}M(\Delta\vec{l}_1,\Delta\vec{l}\,'_1)\,\tilde{Q}(\vec{k},\Delta\vec{l}\,'_1,s)=\tfrac{1}{12}f_{\Delta\vec{l}_1}(\vec{k})\,\tilde{h}(s)\,, \tag{25}$$

where

$$f_{\Delta\vec{l}_1}(\vec{k})=\exp(i\vec{k}\cdot\Delta\vec{l}_1)\,.$$

The matrix $M(\Delta\vec{l}_1,\Delta\vec{l}\,'_1)$ contains the different waiting-time distributions, and is given explicitly in Table II.

Equation (25) can be solved with respect to $\tilde{Q}(\vec{k},\Delta\vec{l}_1,s)$ either by numerical means or directly. This is most easily done for special symmetric directions of $\vec{k}$, for example in [100] direction, $\vec{k}=(k,0,0)$. Because of the symmetry

TABLE II. Matrix of waiting-time distributions used in Eq. (25). Only the indices of the $\psi$'s are given.

| $\Delta\vec{l}_1$ \ $\Delta\vec{l}\,'_1$ | $xy$ | $-xy$ | $-x-y$ | $x-y$ | $yz$ | $-yz$ | $-y-z$ | $y-z$ | $zx$ | $-zx$ | $-z-x$ | $z-x$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $xy$ | (4) | (2) | $b$ | (2) | (3) | (1) | (1) | (3) | (3) | (3) | (1) | (1) |
| $-xy$ | (2) | (4) | (2) | $b$ | (3) | (1) | (1) | (3) | (1) | (1) | (3) | (3) |
| $-x-y$ | $b$ | (2) | (4) | (2) | (1) | (3) | (3) | (1) | (1) | (1) | (3) | (3) |
| $x-y$ | (2) | $b$ | (2) | (4) | (1) | (3) | (3) | (1) | (3) | (3) | (1) | (1) |
| $yz$ | (3) | (3) | (1) | (1) | (4) | (2) | $b$ | (2) | (3) | (1) | (1) | (3) |
| $-yz$ | (1) | (1) | (3) | (3) | (2) | (4) | (2) | $b$ | (3) | (1) | (1) | (3) |
| $-y-z$ | (1) | (1) | (3) | (3) | $b$ | (2) | (4) | (2) | (1) | (3) | (3) | (1) |
| $y-z$ | (3) | (3) | (1) | (1) | (2) | $b$ | (2) | (4) | (1) | (3) | (3) | (1) |
| $zx$ | (3) | (1) | (1) | (3) | (3) | (3) | (1) | (1) | (4) | (2) | $b$ | (2) |
| $-zx$ | (3) | (1) | (1) | (3) | (1) | (1) | (3) | (3) | (2) | (4) | (2) | $b$ |
| $-z-x$ | (1) | (3) | (3) | (1) | (1) | (1) | (3) | (3) | $b$ | (2) | (4) | (2) |
| $z-x$ | (1) | (3) | (3) | (1) | (3) | (3) | (1) | (1) | (2) | $b$ | (2) | (4) |

$$\begin{aligned}\tilde{Q}(\vec{k};\Delta\vec{l}_1) &= xy, x-y, xz, x-z; s)\\ &= A(k,s)\,,\\ \tilde{Q}(\vec{k};\Delta\vec{l}_1) &= -xy, -x-y, -xz, -x-z; s)\\ &= A^*(k,s)\,,\\ \tilde{Q}(\vec{k},\Delta\vec{l}_1) &= yz, -yz, y-z, -y-z; s)\\ &= B(k,s)(\text{real})\,.\end{aligned} \tag{26}$$

One is interested in the summary probability density $Q(\vec{l},t)$ where all possibilities of the previous jump are added:

$$Q(\vec{l},t)=\sum_{\Delta\vec{l}_1} Q(\vec{l},\Delta\vec{l}_1,t)\,.$$

In [100] direction

$$\tilde{Q}(\vec{k},s)=4A(k,s)+4A^*(k,s)+4B(k,s)\,. \tag{27}$$

One finds

$$A+A^*=\frac{\tilde{h}}{6D}\left(\cos\frac{ka}{2}+\tilde{\delta}(s)\right)[2\tilde{\psi}_{(1)}(s)-2\tilde{\psi}_{(2)}(s)+2\tilde{\psi}_{(3)}(s)-\tilde{\psi}_{(4)}(s)-\tilde{\psi}_b(s)+1]\,, \tag{28}$$

$$B=A+A^*+\frac{\tilde{h}}{12D}\left(1+\tilde{\delta}(s)\cos\frac{ka}{2}-2\cos\frac{ka}{2}-2\tilde{\delta}(s)\right), \tag{29}$$

where

$$\begin{aligned}D(k,s)=&\left(1+\tilde{\delta}(s)\cos\frac{ka}{2}\right)[1-2\tilde{\psi}_{(2)}(s)-\tilde{\psi}_{(4)}(s)-\tilde{\psi}_b(s)]\\ &-\left(\cos\frac{ka}{2}+\tilde{\delta}(s)\right)\{[1-2\tilde{\psi}_{(2)}(s)-\tilde{\psi}_{(4)}(s)-\tilde{\psi}_b(s)]\\ &\times[2\tilde{\psi}_{(1)}(s)+2\tilde{\psi}_{(2)}(s)+2\tilde{\psi}_{(3)}(s)+\tilde{\psi}_b(s)+\tilde{\psi}_{(4)}(s)]+8[\tilde{\psi}_{(1)}(s)+\tilde{\psi}_{(3)}(s)]^2\}\end{aligned} \tag{30}$$

and

$$\tilde{\delta}(s)=\tilde{\psi}_b(s)+2\tilde{\psi}_{(1)}(s)-2\tilde{\psi}_{(3)}(s)-\tilde{\psi}_{(4)}(s)\,. \tag{31}$$

A similar solution can be derived for the [111] direction. In [110] direction already five independent quantities appear and a system of five equations has to be solved. In this case we found it more convenient to solve (25) numerically.

Finally $\tilde{Q}(\vec{k},s)$ has to be related to the self-correlation function. $Q(\vec{l},t')$ is the probability density that site $\vec{l}$ is occupied by the tagged atom at time $t'$ after an arbitrary number of steps. The self-correlation function $P(\vec{l},t)$ follows from $Q(\vec{l},t')$ by requiring that no further jump occurs between $t'$ and $t$ and by adding the possibility that the tagged atom has made no jump at all until time $t$. In Fourier-Laplace domain

$$\tilde{P}(\vec{k},s)=\tilde{Q}(\vec{k},s)\tilde{\Psi}(s)+\frac{1-\tilde{h}(s)}{s}\,. \tag{32}$$

This expression completes the derivation of the self-correlation function.

### C. Tracer diffusion coefficient

The diffusion coefficient of tagged particles of the lattice gas is derived by calculating the mean-square displacement from the self-correlation function, i.e., by evaluating Eq. (6). It is most convenient to employ the explicit form for $\tilde{P}(\vec{k},s)$ in [100] direction; one can also start from Eq. (25). One has in the Laplace domain

$$\langle\tilde{R}^2\rangle(s)=\frac{a^2}{2fs^2}\,\frac{1-\tilde{\delta}(s)}{1+\tilde{\delta}(s)}\,, \tag{33}$$

where $\tilde{\delta}(s)$ has been defined in Eqs. (31). With $s=i\omega$, Eq. (33) represents a frequency-dependent mean-square displacement. A generalized frequency-dependent diffusion coefficient is obtained by multiplication with $-\omega^2/6$; the static diffusion coefficient follows by letting $\omega\to 0$. We find

$$D_t=D_t^{\mathrm{MF}}f,\quad f=\frac{1-\tilde{\delta}(0)}{1+\tilde{\delta}(0)}, \tag{34}$$

where $D_t^{\mathrm{MF}}$ is given by Eq. (7). The result (34) corresponds to the usual expression for the correlation factor for tracer diffusion,

$$f=\frac{1+\langle\cos\theta\rangle}{1-\langle\cos\theta\rangle}, \tag{35}$$

where $\langle\cos\theta\rangle$ is the average of the angle between two consecutive jumps. In fact the approximation used in deriving (35) is identical to our approximation, i.e., a memory between two steps of a tagged particle has been taken into account. $\tilde{\delta}(s)$, Eq. (31), is a weighted sum of the individual waiting-time distributions, with weights given by the product of the number of jumps of a given type and the cosine of the angle between the consecutive jumps of the particle, hence in our model $\langle\cos\theta\rangle=-\tilde{\delta}(0)$. In summary, a generalization of the usual result has been achieved; i.e., it has been shown how the correlation factor is expressed by the waiting-time distribution of the

correlated jump process. In addition, the formulation is valid for arbitrary concentration and also gives the frequency-dependent diffusion coefficient.

## V. RESULTS FOR THE TRACER DIFFUSION COEFFICIENT AND THE INCOHERENT DYNAMICAL SCATTERING FUNCTION

### A. Tracer diffusion coefficient

In this section direct calculations of the tracer diffusion coefficient are compared with results obtained from the model of correlated jumps and with other predictions.[16] The mean-square displacement of the individual particles of the lattice gas has been calculated directly as explained in Sec. II B. The resulting diffusion coefficient has been divided by the mean-field result and the correlation factor displayed in Fig. 7 for various concentrations. Murch[13] has given similar numerical results for $f(c)$ on the fcc lattice, with surprisingly small scatter of the data points. The tracer diffusion coefficient has also been determined by applying Eq. (34). It is necessary to know the waiting-time distributions at $s=0$ or the zero moments in the time domain, since $\tilde{\psi}_i(s=0) = \int_0^\infty dt\, \psi_i(t)$. The integration has been done numerically on the computed waiting-time distributions and also on the waiting-time distributions which result from the expressions for the jump rates $\Gamma_i(t)$ given in Eqs. (18)–(22). The resulting $\tilde{\psi}_i(s=0)$ will be called "numerical" and "analytical," respectively; they agree within 1–2%. The correlation factor resulting from both evaluations is also shown in Fig. 7. First one sees a very good agreement of the correlation factor resulting from the numerical $\tilde{\psi}_i(0)$ with the directly determined correlation factor. Hence the model of correlations between consecutive jumps seems to be a very good approximation in three dimensions and the fcc lattice studied. Second, one sees a good agreement of $f$ resulting from the analytical $\tilde{\psi}_i(0)$ with the directly determined $f$. However, there is a tendency for larger values of $f$, especially at $c=0.988$. This fact is due to the simplifying assumptions in the representation of the jump rates by Eqs. (18)–(22), especially to the assumption $\Gamma_{(2)}(t) = \Gamma_{(3)}(t) = \Gamma_{(4)}(t)$. One should note that this representation includes *additional* assumptions in comparison to the model of correlated jumps alone. In Fig. 7 also, the result of Sankey and Fedders[16] is included. It represents a good overall fit, although it lies somewhat below the numerical results between $c=0.7$ and $c=0.9$. Also, Kitahara and Nakazato[31] have obtained similar results for the fcc lattice. The results for the diffusion coefficient show a smooth crossover, as a function of concentration, between the regime where diffusion is carried by many vacancies ($c$ small and intermediate) and the regime where tracer diffusion is carried by few vacancies ($c \to 1$).

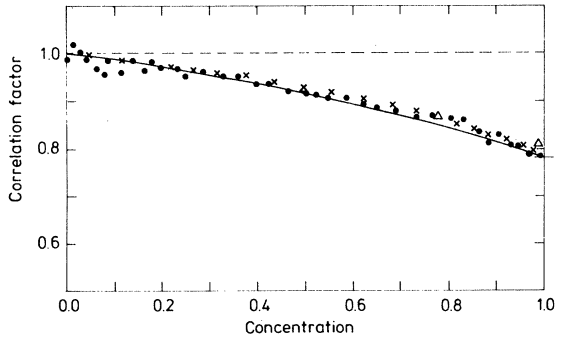


FIG. 7. Correlation factor as a function of concentration, obtained from the numerical simulation (points) and from the correlated-jump model, where numerically (crosses) and analytically determined (open triangles) waiting-time distributions have been used (the triangle at $c=0.182$ coincides with the corresponding cross). The dashed line corresponds to the mean-field theory, the full line to the theory of Sankey and Fedders (Ref. 17). The limiting value (Ref. 6) for $c \to 1$ is indicated by a bar.

### B. Incoherent dynamical scattering function

In principle the incoherent dynamical scattering function is known once the self-correlation function $P(\vec{l}, t)$ is given. They are related by

$$S_{\text{inc}}(\vec{k}, \omega) = \frac{1}{\pi} \text{Re}[\tilde{P}(\vec{k}, s=i\omega)] . \tag{36}$$

In practice, the Fourier-Laplace transforms of the waiting-time distributions $\psi_i(t)$ are needed when (36) is evaluated, e.g., using the explicit form of $\tilde{P}(\vec{k}, s)$ given by Eqs. (27)–(32). The numerical waiting-time distributions $\psi_i(t)$ can be Fourier transformed directly by numerical methods. However, one would like to use the forms for $\psi_i(t)$ given in Sec. III D. Here the practical problem appears of Fourier-transforming expressions such as $\exp[-\exp(-\lambda t)]$. Since the detailed procedures for the various waiting-time distributions are very tedious, only the principle of our approach will be indicated here. The double exponential functions are expanded,

$$\exp[-\exp(-\lambda t)] = \sum_{n=0}^{\infty} \frac{1}{n!} \exp(-n\lambda t) , \tag{37}$$

and the terms of the series are Fourier transformed. The parameter $\lambda$ is of such a nature that the resulting series converges rapidly. Also it is

no problem to sufficiently take many terms of the series into account to achieve a prescribed precision, for example, usually $n=4$ terms have been used. After the $\tilde{\psi}_i(i\omega)$ have been determined, $S_{\rm inc}(\vec{k},\omega)$ has been derived from Eqs. (27)–(32) for the [100] direction, or from Eq. (25) for general directions. All results will be compared with the mean-field result Eq. (8).

The results for $S_{\rm inc}(\vec{k},\omega)$ of the model of correlated jumps are given in Fig. 8 for $c=0.988$ and two values of $\vec{k}$ in [100] direction. For small $\vec{k}$ and in the frequency range shown, the result can be represented as a diffusion-broadened Lorentzian with width $D_t k^2$, where $D_t = f(c) D_t^{\rm MF}$, as expected. Also for large $\vec{k}$, e.g., $\vec{k}$ at the zone boundary and in the frequency range shown, the result is in good approximation given by a single Lorentzian with width $f_{\rm eff}(\vec{k},c)\Lambda(\vec{k})$. In Fig. 9 the quotient of the scattering function of the model to a single Lorentzian of width $f_{\rm eff}\Lambda$ is shown; there is only a small deviation from unity below $\omega=0.1$. Similar results are found for other concentrations and other directions: The scattering function is always well represented, for smaller $\omega$, by a single Lorentzian of width $f_{\rm eff}(\vec{k},c)\Lambda(\vec{k})$. In Fig. 10, $f_{\rm eff}(\vec{k},c)$ has been plotted for three concentrations. For $c=0.498$ practically no $\vec{k}$ dependence is observed; for $c=0.777$ and for $c=0.988$ a small dependence on $\vec{k}$ is found. [Owing to the use of the analytical $\tilde{\psi}_i(0)$ in the determination of the effective correlation factor, $f_{\rm eff}(\vec{k},c=0.988)$ approaches a somewhat too-large value for $\vec{k}\to 0$; cf. the corresponding triangle for this concentration in Fig. 7.]

A qualitative behavior of $S_{\rm inc}(\vec{k},\omega)$ similar to our results has been found by Ross and Wilson.[17] It is also instructive to compare the results with the "encounter model"[32] where a small concentration $c_v \ll 1$, $c_v = 1-c$ of vacancies is assumed. Then a separation can be made into the encounter of one vacancy with a tracer atom, resulting in a net effective transition of the tracer atom, and into the time span between different encounters. In the encounter model the scattering function is purely Lorentzian and its width is derived from net effective transition probabilities.[32] We have included in Fig. 10 $f_{\rm eff}(\vec{k})$ resulting from the encounter model. A similar, but more pronounced dependence on $\vec{k}$ than in our results is seen.

The qualitative description given above applies to frequencies of the order of $12(1-c)\Gamma$. When $\omega$ is of the order of $12\Gamma$, the effects of the increased backward jumps should become visible. In fact, it is found that the scattering function obtained from our model approaches the mean-field scattering function, when $\omega$ becomes larger than $12\Gamma$. This is shown in Fig. 9 for one concentration and $\vec{k}$ at the zone boundary; the quotient $S_{\rm inc}/S_{\rm inc}^{\rm MF}$ approaches unity. If the scattering function could be represented by a single Lorentzian of width $f_{\rm eff}(\vec{k},c)$ in the whole frequency region, the quotient would approach $f_{\rm eff}$. It can be shown generally that in our model $S_{\rm inc}(\vec{k},\omega)$ approaches the mean-field behavior for $\omega \gg 12\Gamma$,

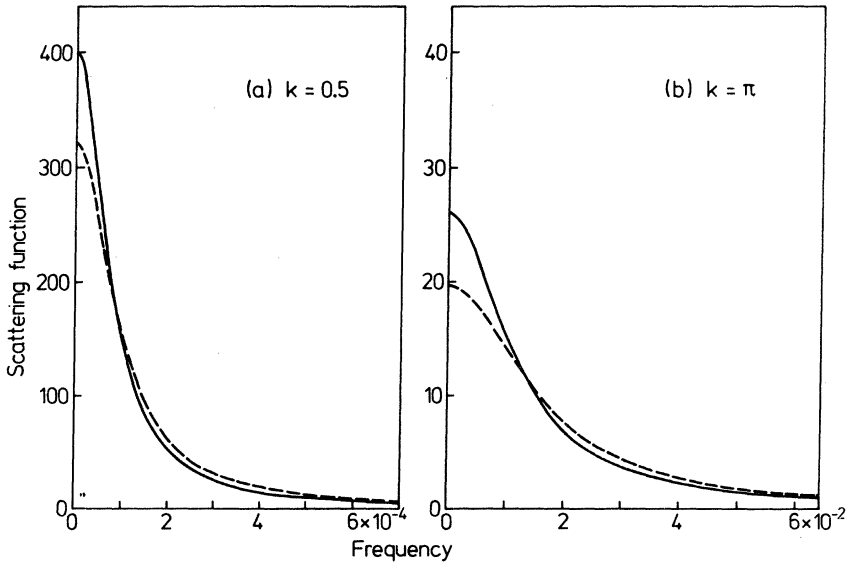


FIG. 8. Incoherent dynamical scattering function for two different values of $\vec{k}$ in [100] direction, as a function of frequency, for $c=0.988$. Full line: result of correlated-jump model, dashed line: mean-field result. Note the different scales in part (a) and (b) of this figure. The lattice constant has been chosen $a=2$. The frequency is given in units of $12\Gamma$.

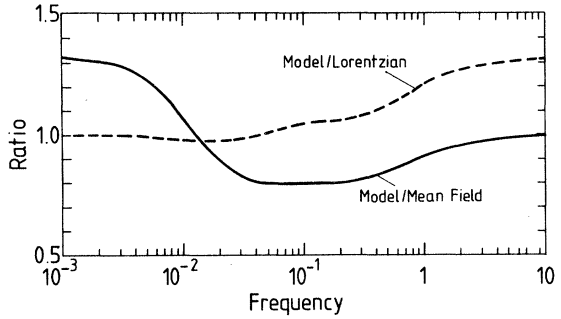


FIG. 9. Quotients of the scattering function of the correlated-jump model to a single Lorentzian fitted near $\omega = 0$ (full line) and to the mean-field result (dashed line). The quotients are shown as a function of $\omega$, for fixed $\vec{k}$ in [100] direction at the zone boundary, and for $c = 0.988$. The frequency is given in units of $12\Gamma$.

$$S_{\text{inc}}(\vec{k}, \omega) \underset{\omega \to \infty}{\longrightarrow} \frac{\Delta(\vec{k})}{\pi \omega^2} . \tag{38}$$

This formula can be shown by taking the limit $s \to \infty$ of Eq. (25) and observing that

$$\tilde{\psi}_i(s) \underset{s \to \infty}{\longrightarrow} \Gamma_i / s , \quad \tilde{\Psi}(s) \underset{s \to \infty}{\longrightarrow} 1/s ,$$

and

$$\tilde{h}(s) \underset{s \to \infty}{\longrightarrow} 1/\bar{t}s . \tag{39}$$

Equation (38) expresses the fact that the high frequency or average short-time behavior is determined by the average jump rate of a particle. While the encounter model[32] does not give the correct high-frequency behavior, the model of Ref. 17 is in accordance with Eq. (38). Since the changeover from a Lorentzian with reduced width $f\Lambda(\vec{k})$ to a Lorentzian with width $\Lambda(\vec{k})$ occurs at frequencies where the scattering function is already small, it is doubtful whether this effect can be seen by neutron scattering. It should be noted, however, that the fcc lattice is the least

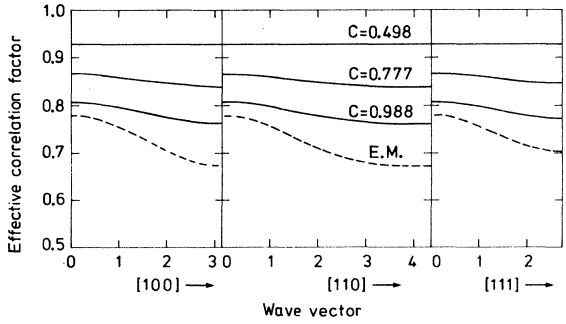


FIG. 10. Effective correlation factor $f_{\text{eff}}(\vec{k}, c)$ for three different concentrations (full line) and for the encounter model (dashed line) as a function of $\vec{k}$. The lattice constant has been chosen $a = 2$.

favorable lattice for these effects since its correlation factor is close to unity due to the large number of nearest neighbors.

## VI. CONCLUSION

In this article the self-diffusion in concentrated lattice gases has been studied where double occupancy of sites is forbidden but no other interactions are taken into account. The dynamical process of the diffusion of tagged particles has been analyzed in detail. The new feature of our approach is the description of the time dependence of the self-diffusion process by appropriate waiting-time distributions. The main new results of our work are the following:

(1) Waiting-time distributions for two consecutive jumps of a tagged particle, where different orientations of the two jumps have been distinguished, have been obtained numerically for a variety of concentrations.

(2) The time dependencies of the basic physical processes which determine the waiting-time distributions have been accounted for. Especially the strong time dependence of the backward jump probability of a tagged particle has been quantitatively explained by the filling of the vacancy which is present after the initial jump.

(3) It has been shown that a correlated-jump model with general waiting-time distributions is applicable to describe the self-diffusion in concentrated lattice gases. By comparison with the numerical results it is seen that the model of correlated jumps provides a very satisfactory description of the self-diffusion in the three-dimensional fcc lattice. Moreover, the time-dependent self-correlation function and thus the incoherent scattering function have been given in terms of this model.

While results (1) and (2) of the first part of this article are rather independent of model assumptions, result (3) refers to a specific model of correlations over two consecutive jumps of a tagged particle. This model represents a generalization of the usual static treatment of self-diffusion (Ref. 6) to frequency dependence and to arbitrary concentration of the lattice gas.

The present investigations have been restricted to the fcc lattice. We believe that analogous results can be established for all other three-dimensional lattices. Less trivial is the inclusion of interaction between the particles, where also the the collective diffusion becomes nontrivial. Also in this case we expect a generalization of the present approach to be possible. Another extension with nontrivial aspects is the case of differing jump rates of the tagged particle and the particles

of the lattice gas, or more generally, the extension to a lattice gas with three constituents $A, B, V$, where $A, B$ denote two species of particles and $V$ the vacancies. These more complicated cases will form the subject of separate studies.

The limitations of the present approach appear in low-dimensional systems. A model with correlations between two or a finite number of consecutive jumps completely fails for self-diffusion in one dimension. Richards[33] has studied numerically the self-diffusion in a linear chain and observed a $t^{1/2}$ behavior of the mean-square displacement of tagged particles. We have confirmed his result.[34] It is known that a model with correlations over a finite number of steps always leads to a mean-square displacement $\propto t$. This result can be inferred from the attempts of describing the end-to-end distance of polymer chains in ideal solvents by analogous models, where the corresponding result has been found.[35] In one dimension the correlations imposed on a given particle by the presence of the neighboring particles are so persistent that they cannot be approximated by correlations over a finite number of steps. However, our results show that for three-dimensional systems a model with correlations over just two consecutive jumps is quite satisfactory.

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## APPENDIX: CORRELATION FUNCTION FOR PRESENCE OF VACANCY

In the Appendix the correlation function $p_{00}(t)$ is calculated which is defined as the probability of finding a vacancy at a given site at time $t$ when there was one at this site at $t=0$. It obeys the equation

$$\frac{d}{dt}p_{00}(t) = -\frac{1}{\tau_0}p_{00}(t) + \frac{1}{\tau_1}p_{10}(t) . \tag{A1}$$

$p_{10}(t) = 1 - p_{00}(t)$ is the probability of finding a particle at time $t$ at the site considered. The solution of (A1) is

$$p_{00}(t) = \frac{\tau_0}{\tau_0+\tau_1} + \frac{\tau_1}{\tau_0+\tau_1}\exp\left[-\left(\frac{1}{\tau_0}+\frac{1}{\tau_1}\right)t\right] . \tag{A2}$$

The mean time $\tau_1$ of the occupation of the site by a particle is identical to the mean residence time $\bar{t}$ given in Eq. (13),

$$\tau_1 \equiv \bar{t} = [z(1-c)\Gamma]^{-1} .$$

The mean time of the presence of a vacancy at the site $\tau_0$ is given by

$$\tau_0 = (zc\Gamma)^{-1} . \tag{A3}$$

This follows from the requirement that the mean occupation is $c = \tau_1/(\tau_0+\tau_1)$. Hence $p_{00}(t)$ is given by

$$p_{00}(t) = (1-c) + c\exp(-z\Gamma t) . \tag{A4}$$

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