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Diffusion in Concentrated Lattice Gases

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The diffusion of many particles on a lattice is an example of a correlated random-walk process. Recently the waiting-time distributions for two consecutive jumps of a tagged particle have been determined numerically and the time-dependent correlations analyzed in detail. The information over these two consecutive jumps is used to determine the position and velocity autocorrelation functions, and very satisfactory results are obtained for three-dimensional lattices. However, the information of the two consecutive jumps is insufficient when the jump rate of the tagged particle is large compared to that of the other particles, and this approximation fails completely in one dimension. For the linear chain, another approximation which accounts for correlations over all jumps is compared with the numerical simulations.

KEY WORDS: Lattice-gas models; tracer diffusion; continuous-time random walk; correlated random walk.

1. INTRODUCTION

In this contribution the correlated random walk of the particles of some lattice-gas models is investigated. The models consist of regular lattices in d dimensions (for simplicity of cubic symmetry). The sites are partly occupied by particles with given concentration c ($0 < c < 1$). One or several "tracer" particles will be distinguished from the others. Double occupancy of sites is always excluded. Mainly the case will be discussed where no further interactions are present and the sites are occupied at random. Each particle can jump with rate Γ to an empty site; the tracer particles have the same rate, or a different rate Γ'. Interaction of the particles can also be considered, e.g., in form of an Ising-like short-range attraction. The occupation of the sites will then exhibit short-range and possibly long-range order. The

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jump rate of the particles must now include the energy differences between the final and initial states. The collective diffusion is simple in the noninteracting case, since it can be reduced to a single-particle problem.[1] The diffusion coefficient that appears in Fick's law is $D_{\text{coll}} = \Gamma a^2$, independent of concentration. D_{coll} is influenced by the interactions, where phenomena such as critical slowing down near a critical point occur.[2] The tracer diffusion coefficient, determined from the mean-square displacement of the tagged particles, is nontrivial already in the noninteracting case. The tagged particles perform a correlated random walk, mediated by the presence or absence of other particles which also move on the lattice. The mean-field expression for the tracer diffusion coefficient is $D_t^{\text{MF}} = (1 - c)\Gamma a^2$ (first the case $\Gamma' = \Gamma$ is considered). The factor $1 - c$ represents the mean blocking of the sites. It was pointed out by Bardeen and Herring[3] in the context of tracer diffusion in metals that this expression neglects important correlations. Namely, when the tagged atom has made a jump, there is a vacancy behind the atom immediately after the jump. The presence of this "special vacancy" leads to an inherent backward correlation of the random walk of the tracer. A correlation factor $f(c)$ is introduced by defining $D_t = D_t^{\text{MF}} f(c)$; normally $f(c) < 1$. Tracer diffusion in metals corresponds to the limit $c \to 1$.[4] The general case has been studied numerically by Murch and Thorn[5] and theoretically by several authors.[6] In this contribution the diffusion of tagged particles in the concentrated lattice gas will be discussed from the aspect of a correlated random walk. Special attention will be given to the time dependence of the correlations. In particular, the "special vacancy" mentioned above can be filled by other particles. This should lead to a strong time dependence of the backward correlations, as will be seen below.

2. WAITING-TIME DISTRIBUTIONS

The time-dependent correlations of the random walk of a tagged particle in the lattice gas will be characterized by waiting-time distributions (WTD). They have been introduced by Montroll and Weiss[7] to describe continuous-time random walk (CTRW) with general time dependence of the steps. The waiting-time distribution $\psi(t)\,dt$ of a particle, which has made its last jump at $t = 0$, is defined as the joint probability that it remains at the site until time t and jumps between t and $t + dt$. In order to include the spatial correlations it is necessary to distinguish between the WTD for backward jumps and WTD for forward or sideward jumps. The sum of the WTD for backward and forward or sideward jumps will be normalized to unity. The WTD for backward jumps is expected to be strongly time dependent, since the probability for backward jumps is increased at small times, while for large times the WTD for backward jumps should approach that for forward jumps.

The WTD have been determined by numerical simulation of diffusion on a fcc lattice with $N = 16384$ sites and various concentrations of particles.[8] Each particle is considered as tagged, and equipped with a clock. The time intervals between two consecutive jumps of the particles are determined, classified according to the relative jump directions, and collected in time histograms which represent the WTD. The time unit of the simulations is the Monte-Carlo step (MCS) per particle, defined as a total number of attempted jumps equal to the number of particles.

In the fcc lattice there are five different orientations of a jump of a particle with respect to its preceding jump: backward jumps $b(1)$, and jumps to neighbors of the order 1(4), 2(2), 3(4), and 4(1), relative to the starting site of the preceding jump. The numbers n_i of sites of each type have been indicated in parentheses. Figure 1 gives the results of the

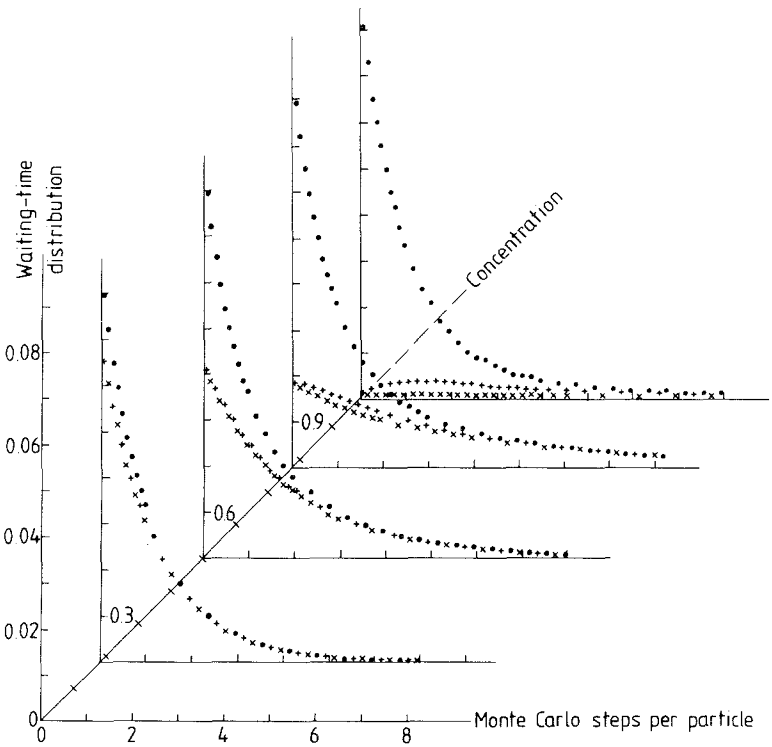

Fig. 1. Waiting-time distribution for backward jumps (●), and forward jumps to sites of type 1 (+) and type 4 (×), for $c = 0.182$, 0.498, 0.777, and 0.988.

simulations for $\psi_b(t)$, $\psi_1(t)$, and $\psi_4(t)$, at 4 concentrations. Not shown are $\psi_2(t)$ and $\psi_3(t)$; they are practically identical to $\psi_4(t)$. One recognizes the following features: For $t \to 0$ the WTD for backward jumps approaches the jump rate Γ in the empty lattice ($12\Gamma = 1$ when the time is measured in MCS/particle). For $t \to 0$ the WTD for forward jumps approach the value $(1-c)\Gamma$. There is an intermediate increase of $\psi_1(t)$ at the two larger concentrations, compared to $\psi_4(t)$. This feature is peculiar to the fcc lattice: the special vacancy can move to a neighbor site of type 1 and thus enable the jump of the tagged atom to it.

In order to further analyze the WTD, time-dependent conditional jump rates will be introduced, the condition being that no jump of a tagged particle has occurred between 0 and t. They are related to the WTD through ($i = b, 1, \ldots, 4$)

$$\psi_i(t) = \Gamma_i(t) \exp\left[- \sum_{j=b,1\ldots 4} n_j \int_0^t dt' \, \Gamma_j(t') \right] \tag{1}$$

The rapid decay of the backward correlations can now be analyzed quantitatively. It is given, apart from a small correction term, by

$$\Gamma_b(t) - \Gamma_4(t) \approx c\Gamma \exp[-11\Gamma t] \tag{2}$$

This expression can be deduced from the stochastic process of the filling of a vacancy in the lattice gas by the other particles.[8] One notes that the concentration of the lattice gas does not appear in the decay rate. Further, one finds that for large times the jump rates approach smaller values than predicted by mean-field theory, $\Gamma_i(t \to \infty) \to (1 - c^*)\Gamma$, where $c^* = c + \alpha$ and $\alpha(c)$ is a phenomenological parameter. For example, at $c = 0.498$ the value of α is 0.048. The reduction of the jump rate at large times is probably caused by clusters of higher than average concentration which retain the tracer particle immobile. The reduction is also necessary for proper normalization of the sum of the WTD. The rate $\Gamma_1(t)$ for sideward jumps of type 1 can be quantitatively deduced by taking the jump process of the special vacancy to these sites into account.[8] In summary, one can say that the overall behavior of the WTD for consecutive jumps of tagged particles in three-dimensional lattice gases is understood.

3. APPROXIMATION OF CORRELATED CONSECUTIVE JUMPS

This section indicates the derivation of the autocorrelation function of the tagged particle. Its random walk has been characterized by general WTD, hence a CTRW description must be employed. In addition, the WTD depend on the direction of a jump relative to the preceding jump, hence a correlated random walk must be considered. Both characteristics are incorporated by the approximation of correlated consecutive jumps, sometimes also called "backward jump model." Correlated random walk has been introduced by Taylor[9] and Goldstein.[10] The extension to CTRW has been made by Haus, Zwerger, and the author,[11] and Landman and Shlesinger.[12] Correlated random walk can be considered as a special case of random walk with internal states. Formally, the derivations are extensions of the classic CTRW theory of Montroll and Weiss.[7]

The derivation of the position autocorrelation function for the backward jump model on a fcc lattice requires the solution of 12 coupled linear equations, which reduce to 5 or 3 equations in the main symmetry directions. The results are given in Ref. 8. The frequency-dependent diffusion coefficient, identical with the Fourier transform of the velocity autocorrelation funtion, is

$$D_t(\omega) = D_t^{\mathrm{MF}} f(\omega) \tag{3}$$

with the frequency-dependent correlation factor

$$f(\omega) = \mathrm{Re}\,\frac{1 + \Delta(\omega)}{1 - \Delta(\omega)} \tag{4}$$

and

$$\Delta(\omega) = \int_0^\infty dt \exp(-i\omega t)\left[\psi_4(t) + 2\psi_3(t) - 2\psi_1(t) - \psi_b(t)\right] \tag{5}$$

In the static case the correlation factor is given by

$$f(0) = \frac{1 + \Delta(0)}{1 - \Delta(0)} \tag{6}$$

This form is typical for the correlated random walk, and $\Delta(0) = \langle \cos\theta \rangle$ is the average of the angle between consecutive jumps,

$$\langle \cos\theta \rangle = \sum_{i=b,1\ldots4} n_i \cos\theta_i \int_0^\infty dt\, \psi_i(t) \tag{7}$$

Hence the dynamical information on the jump process enters $\langle \cos\theta \rangle$ via the integrals of the WTD.

The integrals over the WTD have been estimated in the course of the numerical simulations. The correlation factor according to Eqs. (6) and (7) has been compared in Ref. 8 to the correlation factor determined directly in the simulation. One representative value appears in Table I and Fig. 2, for

Table I. Theoretical and Simulated Correlation Factor for $c_A = 0.876$

Γ'/Γ	0.1	1	10	100
$\langle \cos\theta \rangle$	-0.0146	-0.0983	-0.3596	-0.5448
f_{theor}	0.971	0.821	0.471	0.295
f_{sim}	0.99	0.83	0.37	0.095

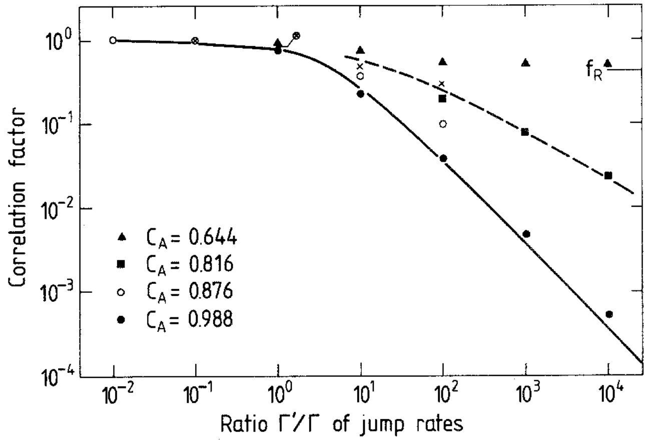

Fig. 2. Correlation factor for tracer with different jump rate. The full line represents Eq. (9) and the dashed line is a fit with an asymptotic power law according to Eq. (11). The crosses ($\times$) indicate the theoretical correlation factor of Table I.

$\Gamma = \Gamma'$. One notes very good agreement between the directly and indirectly determined values, hence the approximation of correlated consecutive jumps seems to be very satisfactory in three-dimensional lattice gases. The frequency dependence of $D_t(\omega)$ has not yet been tested by the simulations. It should be pointed out, however, that the zero-frequency value $D_t(0)$ is most sensitive to the proper inclusion of correlations. For very high frequencies, $\omega \gg 12\Gamma$, the diffusion coefficient $D_t(\infty)$ approaches the mean-field result D_t^{MF}, according to Eqs. (3)–(5), as it should be.

4. DIFFERING JUMP RATE OF THE TRACER PARTICLE

Now the jump rate Γ' of the tracer particle is chosen different from that of the other particles (called A). In order to achieve sufficiently accurate results in the numerical simulations, a finite concentration of tracer particles (called B) must be taken. A typical set of numbers is $N = 4000$ lattice sites on a fcc lattice, 2576 A particles and 26 B particles. It was checked that the results were practically independent of the concentration c_B of the B particles. A correlation factor for the tracer diffusion of B particles in the limit $c_B \ll c_A$ will be defined through

$$D_t^B = (1 - c_A)\Gamma' a^2 f(c_A, \Gamma'/\Gamma) \tag{8}$$

Variation of both parameters c_A and Γ'/Γ allows one to cover quite different physical situations, as is seen in Fig. 2.

(i) For $\Gamma' \ll \Gamma$ the correlation factor approaches 1. This is the case of motion of the tracer particles in a rapidly fluctuating background where correlation effects quickly disappear. Hence the mean-field description applies.

(ii) When $c_A \to 1$ a formula given by Manning[13] can be applied,

$$f(c_A \to 1, \Gamma'/\Gamma) = \frac{f}{f + (1-f)\Gamma'/\Gamma} \tag{9}$$

where f is the usual correlation factor $f(c)$ for equal jump rates. For $\Gamma'/\Gamma \to \infty$

$$D_t^B \to (1 - c_A)\frac{f}{1-f}\Gamma a^2 \tag{10}$$

In this limit the diffusion coefficient of the B particles is determined by the jump rate Γ of the A particles. When $c_A \to 1$ the concentration of vacancies c_V is clearly less than their percolation concentration c_{pV} (≈ 0.199 in the fcc lattice); hence diffusion must cease when the A particles become immobile.

(iii) For $1 - c_A \approx c_{pV}$ and $\Gamma'/\Gamma \to \infty$ a power-law behavior is observed,

$$f(c_A \approx 1 - c_{pV}, \Gamma'/\Gamma \to \infty) \to \text{const} \times (\Gamma/\Gamma')^{0.56} \tag{11}$$

This behavior is in agreement with scaling laws near the percolation threshold.[14]

(iv) When $1 - c_A > c_{pV}$ diffusion of tracer particles is possible even when the A particles are immobile. Hence the correlation factor will approach a finite value,

$$f(c_A < 1 - c_{pV}, \Gamma'/\Gamma \to \infty) \to f_R(c_A) \tag{12}$$

The residual value f_R should follow from the theory of diffusion of a particle in an incomplete lattice.

Also the waiting-time distributions between consecutive jumps of tagged B particles have been determined by numerical simulation, for larger c_A. In order to achieve sufficiently good statistics somewhat larger particle numbers are necessary, for example $N = 13500$, $N_A = 11832$, and $N_B = 623$. Some deviations from the limit $c_B \ll 1$ are now visible. The results for the WTD will be discussed in detail in a subsequent publication.[15] Here only some features will be indicated. For $t \to 0$ the WTD for backward jumps approaches Γ' for small times, whereas the WTD for forward jumps approach approximately $(1 - c_A)\Gamma'$. There is a rapid decay of the WTD of backward jumps towards the WTD of forward jumps, governed by the jump rate Γ of the background (A) particles.

It is evident that the approximation of correlated consecutive jumps must fail in the limit $\Gamma' \gg \Gamma$, since especially the backward correlation will persist over many steps of a tracer particle. The failure of the backward jump model for $\Gamma' \gg \Gamma$ becomes evident by comparing the ensuing correlation factor with the directly determined one; see Table I and Fig. 2.

It is an open question whether the long-time behavior of the autocorrelation functions and thus the correct diffusion coefficient can be determined in this situation from the knowledge of the detailed short-time behavior, provided by the WTD between consecutive jumps.

5. TRACER DIFFUSION ON THE LINEAR CHAIN

Finally diffusion of tagged particles on the linear chain will be considered, in the case $\Gamma' = \Gamma$. It has been found by Richards[16] from numerical simulations that the mean-square displacement of tagged particles increases with $t^{1/2}$ for large times. This result implies that no tracer diffusion coefficient exists. The presence of the neighboring particles which the tracer cannot pass is responsible for the strong correlations in its random walk. On the other hand, the numerical simulations indicate that the WTD behave qualitatively similarly to the three-dimensional case. They can be properly normalized, and also their first moment exists,

$$\int_0^\infty dt\, t\left[\psi_b(t) + \psi_f(t)\right] = \bar{t} = \left[2(1-c)\Gamma\right]^{-1} \tag{13}$$

Under these conditions, the approximation of correlated consecutive jumps predicts a mean-square displacement proportional to t, in disagreement with the actual behavior. Fedders[17] could derive an expression for the asymptotic mean-square displacement (see below) from a rather complicated diagrammatic approach.

Recently Van Beijeren gave an approximate derivation[2] of the velocity autocorrelation function of a tagged particle on the linear chain from random-walk considerations. His derivation discerns the role of the special vacancy in establishing the correct backward correlations. Hence the dynamics of the special vacancy is treated explicitly. The following expression for the velocity autocorrelation function is obtained:

$$C(s) = (1-c)\Gamma a^2 \left\{ \frac{\zeta}{c^2 + (1-c)\zeta + c\left[c^2 + 2(2-c)\zeta + \zeta^2\right]^{1/2}} \right\}^{1/2} \tag{14}$$

where $\zeta = s/2\Gamma$. The following asymptotic behavior of the mean-square displacement results:

$$\langle x^2 \rangle_t(t) = \begin{cases} 2(1-c)\Gamma a^2 t & \Gamma t \ll 1 \\ \dfrac{2(1-c)}{c} a^2 \left(\dfrac{\Gamma t}{\pi} \right)^{1/2} & \Gamma t \gg 1 \end{cases} \tag{15}$$

[2] This derivation will be published together with the numerical simulations in Ref. 18.

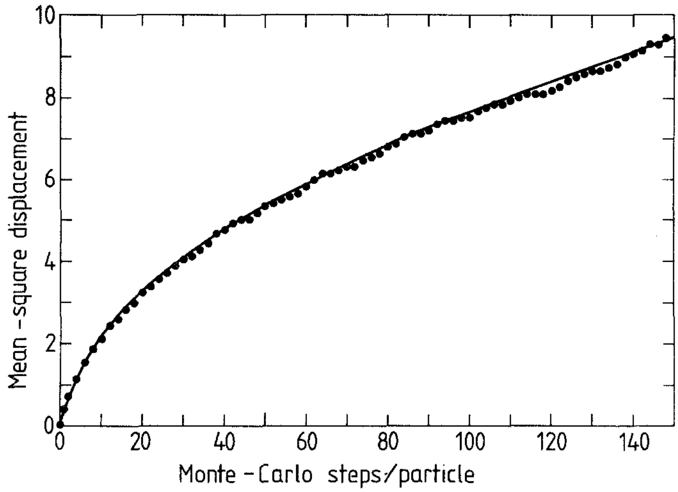

Fig. 3. Mean-square displacement of tagged particles on a linear chain. Points: numerical simulation with 32000 sites, $c = 0.5068$, and periodic boundary conditions. The line indicates the theory.

The long-time behavior is identical with that found by Fedders.[17] For intermediate times, $\langle x^2 \rangle(t)$ can be found by numerical inverse Laplace transformation of $2\tilde{C}(s)/s^2$. The result is compared with the numerical simulation in Fig. 3. Both results agree quite well, although there is a small but systematic deviation of the simulations to lower values at intermediate times. Data for other concentrations, and a discussion of the influence of boundary conditions, will be given in a forthcoming publication.[18]

In summary, there exists an alternative approximate theory for the velocity autocorrelation function of tagged particles in the one-dimensional lattice gas. It accounts for the correlations inherent in this random-walk problem and compares well with the numerical simulations.

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