Diffusion in concentrated lattice gases. III. Tracer diffusion on a one-dimensional lattice

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The dynamical process of the diffusion of tagged particles in a one-dimensional concentrated lattice gas is investigated. The particles are noninteracting except that double occupancy is forbidden. The mean-square displacement of a tagged particle is calculated for all times by an approximate theory and compared to results from Monte Carlo simulations. The overall agreement is quite good. For an infinite chain and for large time t the mean-square displacement is found to increase proportionally to $t^{1/2}$ in agreement with existing results. For periodic chains it increases as $2D_{\rm tr}t$ for large times, with a coefficient of tracer diffusion $D_{\rm tr}$ inversely proportional to the number of particles on the chain. This, too, is in agreement with the results of older calculations. In the case of hard reflecting walls finally the mean-square displacement asymptotically approaches a constant, which can be calculated simply.

I. INTRODUCTION

In this paper we study tracer diffusion on a linear chain, the sites of which are partly occupied by identical particles. The average rate of occupancy of a site equals c, the *concentration* of particles, and no double occupancy is allowed. The dynamics of the system consists of a hopping process, where the transition rate of each particle to an empty neighboring site equals Γ. Alternatively the system may be interpreted as an Ising-spin system with occupied sites corresponding to one spin direction and empty sites to the other one. In this case, the dynamics consists of spin exchange between neighboring sites of oppposite spins at the constant rate Γ, which is known as Kawasaki dynamics[1] in the limit of infinite temperature. In this limit the collective diffusion of this model is trivial, and the diffusion constant entering Fick's law is simply[1,2]

$$D=\Gamma a^2 , \tag{1.1}$$

where a is the spacing between the sites. Tracer diffusion, in this case, however, is completely different from tracer diffusion in higher dimensional lattice gases, where, under most conditions, the tracer-diffusion constant exists and the mean-square displacement of a tagged particle increases linearly with time, after some initial period. The circumstance that particles can never pass each other, known especially in the biophysical literature as *single-filing condition,* severely restricts their freedom to move over large distances, and thereby dramatically influences the properties of tracer diffusion. For many years this has intrigued researchers from various disciplines, resulting in polychromatic literature. To our knowledge the first field in which our present problem raised interest was that of biophysics, where Hodgkin and Keynes[3] (see also Heckmann[4]) introduced the single-filing concept to describe diffusion through very narrow pores in membranes. Here a central problem is that of tracer diffusion through pores of finite length. The main result, implicit in the work of Hodgkin and Keynes and elaborated on by E. J. Harris,[5] Lea,[6] and Rickert,[7] gives the ratio between tracer- and collective-diffusion coefficients (or, equivalently, between tracer-diffusion coefficient and permeability) as

$$D_{\rm tr}=\frac{\kappa_T D}{c}\langle (N_c+1)^{-1}\rangle , \tag{1.2}$$

where $D_{\rm tr}$ is the tracer-diffusion coefficient, N_c is the number of particles in the channel besides the tracer or tagged particles, and the angular brackets indicate an equilibrium average. Furthermore, κ_T is an isothermal compressibility, defined as

$$\kappa_T=\frac{\partial c}{\partial(\beta\mu)} , \tag{1.3}$$

where μ is the collective chemical potential and $\beta=(k_B T)^{-1}$ with T the temperature and k_B Boltzmann's constant. Levitt[8] gives a general thermodynamic proof of this result. An experimental check of (1.2) was made by Rosenberg and Finkelstein,[9] who in turn could use this equation to estimate average numbers of molecules in membrane pores. Notice that in the limit of an infinitely long channel $D_{\rm tr}$ becomes zero.

Among mathematicians the interest in one-dimensional diffusion problems subject to a single-filing condition arose with a publication of Harris's[10] work. He considered a one-dimensional system of Brownian particles with hard-core interactions. The latter may be defined by constructing independent Brownian paths and interchanging particle labels pairwise whenever two trajectories inter-

sect each other. Harris showed that in the thermodynamic limit the mean-square displacement of a labeled Brownian particle increases for long times as

$$\langle[\Delta x(t)]^2\rangle = 2S\left[\frac{Dt}{\pi}\right]^{1/2}, \tag{1.4}$$

where S is the average spacing between the particles and the collective-diffusion constant D is identical to the diffusion coefficient for a single noninteracting Brownian particle. Moreover, he proved that the spatial distribution of a tagged particle starting at the origin approaches a Gaussian for long times. The absence in (1.4) of a linear term in t implies again that for the infinite system the coefficient of tracer diffusion vanishes. Under appropriate scalings of space and time, the lattice gas becomes identical to Harris's system in the limit $c \to 0$, as will be discussed further in Sec. III. Remarkably, Levitt[11] in a short paper rederived Harris's result in a more physical language, allowing furthermore for a class of independent particle processes more general than the Wiener process considered chiefly by Harris. Spitzer wrote a paper on interactions of Markov processes[12] that has become well known among mathematicians. In this paper he posed several problems and, inspired by the work of Harris, made the conjecture that for all c the mean-square displacement of a tagged particle in our lattice gas would grow proportional to $t^{1/2}$ for long times.

In the late seventies the problem was taken up by solid-state physicists interested in superionic conduction, independently of previous work. Richards[13] found by Monte Carlo simulations that the mean-square displacement of a tagged particle increases proportionally to $t^{1/2}$ for long times, and he gave some qualitative arguments to explain this behavior. Fedders[14] obtained similar asymptotic behavior by a diagrammatic Green's-function technique. Correcting the coefficient obtained by Richards he found the asymptotic law, valid for large times,

$$\langle[\Delta x(t)]^2\rangle = \frac{2(1-c)}{c}a^2\left[\frac{\Gamma t}{\pi}\right]^{1/2}. \tag{1.5}$$

In the limit $c \to 0$ this is in agreement with (1.3), as follows from (1.4) and the identification $S = a/c$. Alexander and Pincus[15] gave a very simple and elegant explanation of the result (1.5). They noticed that, under the single-filing condition, the derivative of the displacement with respect to the particle label is directly proportional to the collective particle density. Hence, if the time evolution of the latter is described by Fick's law with the diffusion constant D, one obtains a mean-square displacement, which in general would be of the form

$$\langle[\Delta x(t)]^2\rangle = \frac{2\kappa_T}{c^2}a\left[\frac{Dt}{\pi}\right]^{1/2}. \tag{1.6}$$

In our case κ_T equals $c(1-c)$, and D is given by (1.1), so (1.6) reduces to (1.5) indeed.

Along the mathematical line Arratia[16] recently proved (1.5) rigorously, and in addition established, for general c, the asymptotically Gaussian behavior of the spatial distribution of a tagged particle starting at the origin.

The new element in this paper is that the mean-square displacement of a tagged particle is investigated for all times, both by an approximate theory and by Monte Carlo simulations. The theory is developed in Sec. II. For the infinite system, we find agreement both with (1.4) and with exact expansions for the short-time behavior.[17] In Sec. III we compare our theoretical predictions with the result of Monte Carlo simulations. The agreement is found to be quite good for all times and for all concentrations.

We have also investigated the influence of boundaries on our results. Most interesting is the case of periodic boundary conditions. In this case the center of mass may diffuse around the chain. Consequently, if displacement is measured by following a particle around the ring, the mean-square displacement becomes linear in time again, for large times. The dependence of $D_{\rm tr}$ on system size is found to satisfy (1.2) indeed. A slight extension of the theory for infinite systems yields a prediction for the mean-square displacement for all times in the periodic systems. This also is worked out in Sec. II and compared to Monte Carlo results in Sec. III.

In the case of finite chains with reflecting boundary conditions the mean-square displacement reaches an asymptotic value for large times, which is calculated in Sec. II and compared to numerical simulations in Sec. III. Under these boundary conditions our approximate theory becomes rather cumbersome, due to the breaking of shift invariance. It becomes simple again under a further approximation, which is good in the limit of large N. In Sec. IV finally we make some concluding remarks.

II. CALCULATION OF THE VELOCITY AUTOCORRELATION FUNCTION

A. Low concentration of vacancies

The anomalous $t^{1/2}$ long-time behavior of the mean-square displacement of a tagged particle on the linear chain is easily understood in the limiting case of very small vacancy concentration. In this case we may assume that each of the vacancies present in the chain performs a random walk, virtually uninfluenced by the others present. (This implies that we consider the vacancies as being able to pass each other.) The displacement of a tagged particle after a given time t can be denoted as $a[n_{rl}(t)-n_{lr}(t)]$, where $n_{rl}(t)$ is the number of vacancies that were to the right of the particle at time 0 and are to the left of it at time t, and $n_{lr}(t)$ is defined analogously. Since the vacancies exhibit normal diffusive behavior with a mean-square displacement increasing proportionally to t for large times, both $n_{lr}(t)$ and $n_{rl}(t)$ increase asymptotically as $t^{1/2}$. Of course, on the average $n_{rl}(t)-n_{lr}(t)$ equals zero, but the fluctuations of this quantity are typically of the order of $t^{1/4}$. Hence the mean-square displacement of particle 1, given by the average value $a^2\langle[n_{rl}(t)-n_{lr}(t)]^2\rangle$, increases as $t^{1/2}$ for large time.

For a more quantitative analysis we consider the (unnormalized) velocity autocorrelation function, which is directly related to the mean-square displacement by the following chain of identities:

$$\frac{d^2}{dt^2}\langle[x(t)-x(0)]^2\rangle=2\frac{d}{dt}\langle V(t)[x(t)-x(0)]\rangle \quad (2.1a)$$

$$=2\frac{d}{dt}\langle V(0)[x(0)-x(-t)]\rangle \quad (2.1b)$$

$$=2\langle V(0)V(-t)\rangle \quad (2.1c)$$

$$=2\langle V(t)V(0)\rangle\ . \quad (2.1d)$$

In the transitions from (2.1a) to (2.1b) and from (2.1c) to (2.1d) we used time-translation invariance of the equilibrium average. In the Laplace domain, (2.1) becomes

$$\tilde{C}(s)=\frac{s^2}{2}\langle[\Delta x(s)]^2\rangle\ . \quad (2.2)$$

A small conceptual problem is that in the model under consideration the particles are assumed to jump instantaneously, hence a velocity connected to these jumps is not defined in the usual sense. However, one may define a *generalized velocity* by assigning to a jump, say in the forward direction, occurring at the instant t_0,

$$V(t)=a\delta(t-t_0) \quad (2.3)$$

The time integral of this quantity obviously describes the time dependence of $x(t)$ correctly.

The calculation of $C(t)$ for the case of small vacancy concentration is relatively simple. First of all a nonzero initial velocity exists only if, just at $t=0$, the tagged particle makes a jump, hence we may restrict ourselves to situations where such an initial jump occurs. The effective velocity, due to initial jumps to the right, equals $(1-c)\Gamma a$, the product of the jump frequency and the distance crossed in the jump. One way to understand this is by considering the case where the jumps occur at a constant velocity $a/\Delta t$ and last a time Δt, and pass to the limit $\Delta t\to 0$. Similarly the effective velocity due to the initial jumps to the left equals $-(1-c)\Gamma a$.

The self-correlation function of the initial jump yields a contribution $2(1-c)\Gamma a^2\delta(t)$ to the velocity autocorrelation function. This contribution is most easily understood again by considering the case where jumps happen at constant speed $a/\Delta t$ and passing to the limit $\Delta t\to 0$. The factor of 2 results from the two possible jump directions.

In performing the initial jump the tagged particle changes positions with a vacancy, which will be called the special vacancy, since it plays an important role in our calculations. For $t>0$ a nonzero contribution to the velocity autocorrelation arises only if just at time t the tagged particle and the special vacancy change positions again. Contributions from jumps of the other vacancies past the tagged particle cancel on the average, since to lowest order in $1-c$ the vacancies move independently of each other, and the distribution of the vacancies other than the special vacancy just after the initial jump, is symmetric with respect to the position of the tagged particle. The special vacancy describes, to lowest approximation in $1-c$, a random walk with an exponential waiting-time distribution

$$\psi(t)=2\Gamma\exp(-2\Gamma t)\ . \quad (2.4)$$

The probability to find it after a time t at a distance of n lattice units away from its starting position is given for this process by[18]

$$P(n,t)=\exp(-2\Gamma t)I_n(2\Gamma t)\ , \quad (2.5)$$

where I_n denotes a Bessel function of imaginary argument. Suppose the initial jump of the special vacancy is to the left. Then the probability density for a jump to the right of the special vacancy past the tagged particle at time t equals $\Gamma P(0,t)$ and that for a jump to the left $\Gamma P(1,t)$. The respective contributions to the velocity autocorrelation function of the tagged particle are $-(1-c)\Gamma^2a^2P(0,t)$ and $(1-c)\Gamma^2a^2P(1,t)$. If, in addition, we sum over the two initial jump directions and add the contribution from the self-correlation of the initial jump, we find the total result

$$C(t)=2(1-c)\Gamma^2a^2\{\delta(\Gamma t)-\exp(-2\Gamma t)\times[I_0(2\Gamma t)-I_1(2\Gamma t)]\}\ . \quad (2.6)$$

The coefficient of self-diffusion can be obtained from this expression in the usual way[19] by integrating $C(t)$ from zero to infinity. As anticipated it is found to be zero. The long-time behavior of $C(t)$ is of the form[20]

$$C(t)\approx-(1-c)\Gamma^2a^2(2\pi)^{-1/2}(2\Gamma t)^{-3/2}\ . \quad (2.7)$$

The mean-square displacement of the tagged particle is obtained directly with the aid of Eq. (2.1) as

$$\langle[\Delta x(t)]^2\rangle=2(1-c)\Gamma a^2\int_0^t d\tau\exp(-2\Gamma\tau)I_0(2\Gamma\tau) \quad (2.8a)$$

$$\approx 2(1-c)a^2(\Gamma t/\pi)^{1/2} \quad (2.8b)$$

B. General concentrations

At general concentrations the picture sketched above remains qualitatively the same. However, we must be more careful about taking into account mutual influences among the vacancies. For example, if we would impose the rule that vacancies cannot pass each other, just as the particles, then, if the special vacancy would be just to the left of the tagged particle, it would prevent other vacancies which are further to the left from jumping past the tagged particle. Hence the velocity autocorrelation function would not be determined by jumps of the special vacancy past the tagged particle alone. We are completely free, however, to let the vacancies jump among each other as we please, since such jumps are physically inconsequential, and we can use this freedom to save the simplifying feature that all nonvanishing contributions to the velocity autocorrelation function stem from jumps of the special vacancy past the tagged particle.

Consider the situation just after the initial jump. If we would take out the special vacancy, the system would be on the average mirror symmetric, with the tagged particle as the reflection center. This is a consequence of the absence of correlations between the particles. Furthermore, if we let the system evolve in time, this average symmetry is conserved. A consequence of this symmetry is that

after taking out the special vacancy, the average velocity of the tagged particle would be zero for all times larger than zero, in spite of our knowledge about the initial jump. Hence beyond the initial δ function, no further contributions to the velocity autocorrelation function would arise.

We want to define the dynamics of the vacancies, including the special one, among themselves in such a way that at all times by taking out the special vacancy one would restore the symmetry mentioned above. The way to do this is as follows: At each instant of time the special vacancy belongs to a cluster of vacancies of size greater than or equal to 1. Call this cluster the special-vacancy cluster. As all other clusters of vacancies, the special-vacancy cluster may grow or shrink by units of size 1, due to jumps of vacancies into or out of the cluster. As long as the size of the special-vacancy cluster is larger than unity, we could take out the special vacancy without influencing these growth and shrinking processes at all. If the special-vacancy cluster is of unit size, its growth still does not depend on the presence of the special vacancy, but of course it cannot shrink any more if the special vacancy is taken out. Hence we define the following dynamics for the special vacancy: It remains constrained to the special-vacancy cluster as long as the latter is larger than unity and it may jump, with jump rate Γ in either direction, whenever the special-vacancy cluster has shrunk to size 1. Of course, after each jump the special vacancy belongs to a new special-vacancy cluster. By this definition the dynamics of all nonspecial vacancies is completely uninfluenced by the special one, hence the average symmetry of the system on taking out the special vacancy is guaranteed for all times. As a consequence, $C(t)$ is determined exactly by jumps of the special vacancy across the tagged particle.

As in the extremely dilute case, the special vacancy performs a random walk among the particles, but now its waiting-time distribution is given by the probability of the special-vacancy cluster to shrink to 0 size. Therefore we cannot expect the waiting-time distribution to be independent of the past. For example, just after a jump of the special vacancy the growth rate of the new special-vacancy cluster is smaller than average, since on one side it is bounded by two neighboring occupied sites.

Such memory effects cannot simply be taken into account exactly, or even systematically. Therefore we have calculated the waiting-time distribution $\psi(t)$ for the special vacancy, ignoring these effects completely. The calculation starts from three basic assumptions.

(i) Immediately after a jump of the special vacancy the special-vacancy cluster has size $m \geq 1$, with probability

$$P(m)=c(1-c)^{m-1} . \tag{2.9}$$

(ii) The rate of growth of a vacancy cluster from size m to $m+1$ is $2(1-c)\Gamma$.

(iii) The rate of shrinking of a vacancy cluster from size m to size $m-1$ is 2Γ.

In fact (iii) is exact, but in (i) and (ii) all knowledge of the past is ignored. The problem of calculating the waiting-time distribution starting from the above three assumptions is equivalent to the solution of an asymmetric random-walk problem with an absorbing boundary at the origin. In the Laplace domain the solution is straightforward and well known,[21] therefore we defer the details to Appendix A and just quote the result here,

$$\tilde{\psi}(s)=\frac{c\nu}{[1-\tilde{X}(s)](2-c)(\nu+s)-(1-c)\nu} , \tag{2.10}$$

with

$$\nu=2\Gamma(2-c) \tag{2.11}$$

and

$$\tilde{X}(s)=\frac{1}{2}-\frac{\nu}{2(s+\nu)(2-c)}\left\{c^2+(2-c)^2\left[\frac{2s}{\nu}+\left\lfloor\left(\frac{s}{\nu}\right)^2\right\rfloor\right]\right\}^{1/2} . \tag{2.12}$$

To calculate the velocity autocorrelation function $\tilde{C}(s)$ we need an expression for $\tilde{P}(n,s)$, the Laplace transform of the probability density for the special vacancy to arrive at site n at time t, having made an initial jump to site 0 at time 0. For the symmetric random walk with waiting-time distribution ψ this expression is well known[22] and reads

$$\tilde{P}(n,s)=[1-\tilde{\psi}^2(s)]^{1/2}\left(\tilde{\psi}/\{1+[1-\tilde{\psi}^2(s)]^{1/2}\}\right)^{|n|} . \tag{2.13}$$

A short derivation is presented in Appendix A. Assume that the initial jump of the special vacancy was directed to the left. Then the contribution to $\tilde{C}(s)$ due to final jumps to the right is equal to $-(1-c)\Gamma a^2\frac{1}{2}\tilde{\psi}(s)\tilde{P}(0,s)$. In this expression the factor $(1-c)\Gamma$ is the initial jump rate again; $\frac{1}{2}\tilde{\psi}(s)\tilde{P}(0,s)$ describes the probability for a return of the special vacancy to the left of the tagged particle, followed by a jump to the right, and the factor $-a^2$ stems from the Laplace transforms of the initial and final velocity. The contribution from final jumps to the left is found similarly as $(1-c)\Gamma a^2\frac{1}{2}\tilde{\psi}(s)\tilde{P}(1,s)$. Both these contributions must be multiplied by a factor of 2 because of the two possible directions of the initial jump. Finally the self-correlation of the initial jump yields a contribution $(1-c)\Gamma a^2$ again. Taking all contributions together and substituting (2.13) for $\tilde{P}(0,s)$ and $\tilde{P}(1,s)$ we obtain the result

$$\tilde{C}(s)=(1-c)\Gamma a^2([1-\tilde{\psi}(s)]/[1+\tilde{\psi}(s)])^{1/2} \tag{2.14a}$$

$$=(1-c)\Gamma a^2\left[\frac{\zeta}{c^2+(1-c)\zeta+c[c^2+2(2-c)\zeta+\zeta^2]^{1/2}}\right]^{1/2} , \tag{2.14b}$$

where we introduced the dimensionless Laplace transform variable $\zeta = s/(2\Gamma)$.

Some comments on the result are in place. Firstly, the coefficient of self-diffusion is zero for all c, as follows from

$$\lim_{s\to 0} \tilde{C}(s) = 0 \ . \tag{2.15}$$

Secondly, $\tilde{C}(s)$ has a finite limit for $s \to \infty$,

$$\lim_{s\to\infty} \tilde{C}(s) = (1-c)\Gamma a^2 \ . \tag{2.16}$$

This limit results solely from the self-correlation of the initial jump. It may be interpreted as an infinite-frequency diffusion coefficient. The fact that it is nonzero is an artifact of the model, resulting from the assumption of instantaneous jumps. For realistic systems (2.16) should apply to frequencies which are much larger than the jump frequency but much smaller than the inverse of the duration of a jump.

The asymptotic small-s behavior of $C(s)$ is of the form

$$\tilde{C}(s) \approx \frac{1-c}{c}\Gamma a^2 \left[\frac{s}{4\Gamma}\right]^{1/2} , \tag{2.17}$$

corresponding to a $t^{-3/2}$ long-time tail in the time domain again. The crossover between the large-s behavior (2.16) and the small-s behavior (2.17) occurs in the region

$$\zeta_c \approx \frac{c^2}{2(2-c)} \tag{2.18}$$

or, in the time domain, for

$$t_c \approx \frac{2-c}{c^2\Gamma} \ . \tag{2.19}$$

The mean-square displacement follows from (2.14) and (2.3) as

$$\langle [\Delta x(s)]^2 \rangle = \frac{(1-c)a^2}{2\Gamma\zeta^{3/2}} \left[\frac{1}{c^2+(1-c)\zeta + c[c^2+2(2-c)\zeta+\zeta^2]^{1/2}}\right]^{1/2} . \tag{2.20}$$

In the time domain, the short- and long-time behavior are readily obtained as

$$\langle [\Delta x(t)]^2 \rangle \approx 2(1-c)\Gamma a^2 t \quad \text{(small } t\text{)} , \tag{2.21a}$$

$$\langle [\Delta x(t)]^2 \rangle \approx \frac{2(1-c)}{c} a^2 \left[\frac{\Gamma t}{\pi}\right]^{1/2} \quad \text{(large } t\text{)} . \tag{2.21b}$$

Again, the crossover time is of the order t_c.

The regime of small particle concentration is of some special interest. For short times the tagged particle will not see its neighboring particles in most cases and hence performs a regular random walk with exponential waiting-time distribution. Only after a time of the order t_c, which may be interpreted now as the average time a tagged particle needs to meet one of its neighbors, the particle will "notice" it cannot pass its neighbors, and a crossover to the long-time behavior will take place. However, for small c the crossover does not occur immediately; from (2.14) one sees that there is an intermediate regime, characterized by $c^2 < \zeta < 1$, where $\tilde{C}(s)$ behaves dominantly as

$$\tilde{C}(s) \approx \Gamma a^2 (1 - c\zeta^{-1/2}) \ . \tag{2.22}$$

This implies that for $1 < 2\Gamma t < c^{-2}$ the mean-square displacement should behave roughly as

$$\langle [\Delta x(t)]^2 \rangle \approx a^2 [2\Gamma t - \tfrac{4}{3}\pi^{1/2} c (2\Gamma t)^{3/2}] , \quad 1 < 2\Gamma t < c^{-2} . \tag{2.23}$$

In the two limiting cases $c \to 0$ and $c \to 1$ we expect our expression (2.14) for the velocity autocorrelation function to become exact, since then the neglect of memory effects in determining the waiting-time distribution for the special vacancy appears to be justified. For $c \to 1$ this is so because we have the case treated in Sec. II A; the dynamics of the special vacancy becomes uninfluenced by the other vacancies and reduces to a simple random walk with exponential waiting-time distribution. In the case $c \to 0$ both the special-vacancy cluster and the neighboring clusters of vacancies are almost always very large. Therefore we expect that memory effects, which do typically arise from situations in which the special vacancy cluster or one of its neighbors are of size 0 or 1, extend over an insignificant fraction of the total waiting time only.

In the limit $c \to 1$ one may check these properties by comparing (2.6) and (2.14). Indeed in this limit an inverse Laplace transform of (2.14) reproduces (2.6) up to corrections of the order $1-c$. In the limit $c \to 0$ we should reproduce Harris's results[10] if we introduce scaled variables $\xi = cx/a$, $\sigma = \zeta/c^2$, and $\tau = 2\Gamma c^2 t$. One then finds from (2.20), by passing to the limit $c \to 0$,

$$\langle [\Delta\xi(\sigma)]^2 \rangle = \frac{1}{\sigma^{3/2}} \left[\frac{1}{1+\sigma+(1+4\sigma)^{1/2}}\right]^{1/2} , \tag{2.24}$$

and for the long-time behavior of the mean-square displacement this yields

$$\langle [\Delta\xi(\tau)]^2 \rangle = \left[\frac{2\tau}{\pi}\right]^{1/2} . \tag{2.25}$$

The last result is in agreement with those of Harris, but Harris does not give any explicit results to which (2.24) can be compared for general σ. Hence this equation seems to establish a new result for a system of Brownian particles with mutal hard-core repulsion on a line.

C. Short-time expansions

Short-time expansions for the mean-square displacement, the velocity autocorrelation function, and other correlation functions of interest may be obtained through an iterative solution of the master equation describing the hopping process we are considering. The details will appear in a separate paper by one of the authors[17]; here we merely quote the result for the mean-square displacement:

$$\langle[\Delta x(t)]^2\rangle = a^2[\,2(1-c)\Gamma t - 2c(1-c)(\Gamma t)^2 + \tfrac{4}{3}c(1-c)(1+\tfrac{1}{2}c)(\Gamma t)^3 - \tfrac{1}{6}c(1-c)(8+c+c^2)(\Gamma t)^4 + \tfrac{1}{30}c(1-c)(40-10c+4c^2+c^3)(\Gamma t)^5 + O((\Gamma t)^6)] \quad (2.26)$$

This may be compared to the short-time expansion one obtains from our approximate expression (2.20) by expanding in powers of ζ^{-1} and applying an inverse Laplace transform. The result is

$$\langle[\Delta x(t)]^2\rangle_{\text{approx}} = a^2[\,2(1-c)\Gamma t - 2c(1-c)(\Gamma t)^2 + \tfrac{4}{3}c(1-c)(1+\tfrac{1}{2}c)(\Gamma t)^3 - \tfrac{1}{3}c(1-c)(4+c^2)(\Gamma t)^4 + \tfrac{1}{30}c(1-c)(40-20c+12c^2+3c^3)(\Gamma t)^5 + O((\Gamma t)^6)]\,. \quad (2.27)$$

Upon comparing (2.26) and (2.27) one discovers the following features.

(i) The first three terms in the expansions are identical.

(ii) In the limits $c\to 0$ and $c\to 1$ all coefficients become the same in the two expansions, not just in the sense that they appraoch zero in these limits, but the ratios of corresponding coefficients approach unity.

(iii) For $0<c<1$ the coefficients of t^4 and t^5 are different in both expansions. The relative differences are largest for $c\approx\frac{1}{2}$. For this value of c the approximate coefficient of t^4 is about 3% larger than the exact one and the approximate coefficient of t^5 is about 8% smaller than the exact one. The fact that the first deviating coefficient in the approximate series is too large suggests that this series overestimates the mean-square displacement.

(iv) In the limits $c\to 0$ and $c\to 1$ the coefficients in the Laplace transforms of (2.26) and (2.27) reduce to those of the Taylor expansions for

$$\langle[\Delta x(s)]^2\rangle = \frac{2a^2\Gamma}{s}\left[1-\frac{c}{2}-\frac{c}{2}\left[1+\frac{4}{\zeta}\right]^{1/2}\right], \quad (2.28)$$

$$\langle[\Delta x(s)]^2\rangle = \frac{2(1-c)a^2\Gamma}{s^2}\left[1+\frac{2}{\zeta}\right]^{-1/2}, \quad (2.29)$$

respectively. These equations can be obtained from (2.20) by taking the appropriate limits. Equation (2.28) corresponds to the intermediate-time behavior (2.23) and (2.29) is the complete expression for $c\to 1$.

D. Periodic boundary conditions

Consider a chain of N sites, put on a ring, such that site N is neighboring site 1, and let there be M particles on the chain; hence $c=M/N$. It turns out that the mean-square displacement of a tagged particle, measured by following the particle around the ring (hence *not* modulo the ring length) grows proportional to t for large times.

This is most easily understood again in the case of low vacancy concentration; in fact, we may turn to the case where just one vacancy is present. In performing its random walk this vacancy will cycle around the ring erratically. If we count clockwise cycles positive and counterclockwise cycles negative, the number of complete cycles made by the vacancy after a time t much larger than the average time needed for one cycle, will have a normal distribution with a width proportional to $t^{1/2}$. The displacement of a tagged particle during time t just equals, up to a difference of ± 1, the number of cycles made by the vacancy, hence its mean-square displacement grows as t. The time scale on which this behavior becomes manifest is the average time the vacancy needs to make one cycle. It is proportional to N^2. Hence for large N the mean-square displacement of a tagged particle will exhibit a crossover on this time scale from an increase as $t^{1/2}$, the infinite system behavior, to an increase proportional to t, a normal diffusive behavior. Another way to interpret this behavior is as a diffusion of the system of all particles around the ring.

Calculation of the velocity autocorrelation function for general concentration can be done in complete analogy to the calculation for the infinite system. There are three important modifications, however.

(i) The rate for an initial jump in a given direction is $(1-c)\Gamma N/(N-1)$ instead of $(1-c)\Gamma$, because the knowledge that the tagged particle is at a given position increases the probability of finding a vacancy at a neighboring position by a factor $N/(N-1)$.

(ii) The waiting-time distribution $\psi(t)$ for jumps of the special vacancy depends on the system size N for similar reasons. This we will ignore in our calculations.

(iii) Velocity correlations may arise from jumps to the special vacancy past the tagged particle after making a number of cycles around the ring. Mathematically this is equivalent to letting the special vacancy make a random walk on a periodic infinite lattice with period N and concentration c, and counting the jumps past all particles labeled $kcN+1$, $k=0,\pm 1,\pm 2,\ldots$.

An analysis similar to the one given in Sec. II B then leads to the following expression for the velocity autocorrelation function:

$$\tilde{C}_p(s,N) = \frac{N}{N-1}(1-c)\Gamma a^2 \times\left[1+\tfrac{1}{2}\tilde{\psi}(s)\sum_{k=-\infty}^{\infty}[\tilde{p}(kcN-1,s)-2\tilde{P}(kcN,s)+\tilde{P}(kcN+1,s)]\right]. \quad (2.30)$$

The first term comes from the self-correlation of the initial jump again; the three terms behind the summation sign contain the contributions from final jumps past particle $kcN+1$ in the opposite direction (negative sign), respectively, the same direction (positive signs) as that of the initial jump past particle 1. By substituting (2.13) we

$$\tilde{C}_p(s,N)=\frac{N}{N-1}(1-c)\Gamma a^2\left[\frac{1-\tilde{\psi}(s)}{1+\tilde{\psi}(s)}\right]^{1/2}\frac{1+q^{cN}}{1-q^{cN}}\ , \tag{2.31}$$

where we introduced

$$q=\frac{\tilde{\psi}(s)}{1+[1-\tilde{\psi}^2(s)]^{1/2}}=\frac{[1+\tilde{\psi}(s)]^{1/2}-[1-\tilde{\psi}(s)]^{1/2}}{[1+\tilde{\psi}(s)]^{1/2}+[1-\tilde{\psi}(s)]^{1/2}}\ . \tag{2.32}$$

Again, we want to make a few comments. First, in the limit $N\to\infty$, (2.31) reduces to (2.14) as it should. For $c=1/N$, the case that only one particle is present in the system, one has $\tilde{C}(s)=\Gamma a^2$, the result for the regular symmetric random walk. The coefficient of tracer diffusion for general c follows as

$$D_{\rm tr}(N)=\lim_{s\to 0}\tilde{C}_p(s,N)=\frac{(1-c)\Gamma a^2}{c(N-1)}\ . \tag{2.33}$$

Notice that this result is independent of the precise form of ψ. Furthermore, Levitt's result (1.2) is seen to be valid, if one observes that for the periodic system the isothermal compressibility is of the from $\kappa_T=c(1-c)N/(N-1)$. It should be stressed, however, that (2.33) defines $D_{\rm tr}$ through the Einstein relation between tracer-diffusion coefficient and mean-square displacement, and *it is not a priori obvious* here that this definition coincides with the usual definition of $D_{\rm tr}$ as the ratio between tracer current and the negative of the tracer gradient, nor is it obvious that the coefficient of tracer diffusion for a periodic system should be the same as for instance that for finite open systems in contact with particle reservoirs. The reason why this is not obvious is that tracer diffusion is driven by bulk fluctuations and the latter are highly sensitive to constraints and boundary conditions. These problems will be pursued in a separate publication.[23]

From (2.29) it follows immediately that the mean-square displacement of a tagged particle satisfies

$$\langle[\Delta x(t)]^2\rangle=\frac{2(1-c)\Gamma a^2}{c(N-1)}t \tag{2.34}$$

for large t.

The crossover from the infinite-system behavior (2.17) to the finite-system limit given in (2.29) is determined by the condition

$$q\approx 1-\frac{1}{cN}\ . \tag{2.35}$$

Inserting (2.10) for $\tilde{\psi}(s)$ and expanding for small s with

$$\tilde{\psi}(s)=1-\frac{s}{2\Gamma c^2}\ , \tag{2.36}$$

one finds that (2.31) is satisfied for $s\approx\Gamma/N^2$. In the time domain this corrresponds to a crossover time of the order N^2/Γ. Indeed, the average time the special vacancy needs to diffuse around the ring is independent of concentration; it is of the order $(cN)^2$ times the average waiting time for a jump of the special vacancy; the latter follows from (2.36) to be equal to $(2\Gamma c^2)^{-1}$.

E. Finite chains with reflecting boundaries

Finite chains with reflecting boundaries can be dealt with in approximately the same way as chains with periodic boundary conditions. A chain of length N maps on to an infinite system with periodicity length $2N$ and symmetry centers between site pairs $[Nk,Nk+1]$, with $k=0,\pm1,\pm2,\ldots$. Owing to the presence of these symmetry centers, the vacancy clusters between the site pairs $[Nk,Nk+1]$ behave differently from the other vacancy clusters. They always contain an even number of vacancies and grow and shrink by units of size 2. The rates for growth and shrinkage are $(1-c)\Gamma$ and Γ, respectively. They are twice as small as the corresponding rates for the other clusters, since diffusion of vacancies through the walls of the system is not allowed. In this case too it is possible to calculate the dynamics of the special-vacancy cluster under the same assumptions as before, but the breaking of translational symmetry makes this calculation much more cumbersome. The calculation becomes simple again if one treats the vacancy clusters near the walls on the same footing as the other clusters, and for large N the error introduced by this approximation is small—of $O(1/N)$. Even under this approximation the velocity autocorrelation function is different for different particles, because the relative positions of the image particles of a given particle depend on the distance of this particle to the walls. If the particles are labeled 1,2, . . . , in natural order and their total number equals cN, the velocity autocorrelation function of particle m can be approximated for large N as

$$\tilde{C}_r(s,m)=\frac{N}{N-1}(1-c)\Gamma a^2\left[1+\tfrac{1}{2}\tilde{\psi}(s)\sum_{k=-\infty}^{\infty}[\tilde{P}(2kcN-1,s)-2\tilde{P}(2kcN,s)+\tilde{P}(2kcN+1,s)-\tilde{P}(2kcN+2m-2,s)\right.$$
$$\left.+2\tilde{P}(2kcN+2m-1,s)-\tilde{P}(2kcN+2m,s)]\right] \tag{2.37}$$

with $\tilde{P}(n,s)$ given by (2.13). Substitution of this equation yields the explicit form

$$\tilde{C}_r(s,m)=\frac{N}{N-1}(1-c)\Gamma a^2\left[\frac{1-\tilde{\psi}(s)}{1+\tilde{\psi}(s)}\right]^{1/2}\times\frac{1+q^{2Nc}-q^{2m-1}-q^{2(cN-m)+1}}{1-q^{2Nc}}\ . \tag{2.38}$$

For small s, (2.38) behaves under the approximation (2.36) for $\tilde{\psi}(s)$, as

$$\tilde{C}_r(s,m)\approx\frac{(2m-1)[2(cN-m)+1](1-c)a^2s}{4(N-1)c^3}\ . \tag{2.39}$$

This implies that for large time the mean-square displace-

ment of particle m according to (2.3) approaches a constant

$$\lim_{t\to\infty}\langle[\Delta x(t)]^2\rangle = 2\frac{N^2}{N-1}a^2\frac{1-c}{c}\rho(1-\rho) \tag{2.40}$$

with $\rho=(m-\frac{1}{2})cN$.

This result may be checked independently, since for large times the initial distribution for the position x_m of particle m becomes uncorrelated from the final distribution. Hence one has

$$\begin{aligned}\langle[x_m(t)-x_m(0)]^2\rangle &= \langle\{[x_m(t)-\langle x_m\rangle] \\ &\quad -[x_m(0)-\langle x_m\rangle]\}^2\rangle \\ &= 2(\langle x_m^2\rangle-\langle x_m\rangle^2)\,. \end{aligned}\tag{2.41}$$

The right-hand side of this equation can be evaluated by means of elementary combinatorics. The probability of finding particle m at site k, with $m\le k\le N$, is given by

$$W_m(k)=\frac{\begin{bmatrix}k-1\\m-1\end{bmatrix}\begin{bmatrix}N-k\\cN-m\end{bmatrix}}{\begin{bmatrix}N\\cN\end{bmatrix}}\,, \tag{2.42}$$

where the two factors in the numerator count the number of configurations of all particles to the left and right of particle m, respectively, and the denominator counts the total number of particle configurations on the chain. The mean value and the mean square of the position of particle m can be evaluated by generating function techniques; the appropriate generating functions for the problem at hand are given by Netto.[24] The results are as follows:

$$\langle x_m\rangle = ma\left[1+\begin{bmatrix}N\\cN+1\end{bmatrix}\Big/\begin{bmatrix}N\\cN\end{bmatrix}\right], \tag{2.43}$$

$$\begin{aligned}\langle x_m^2\rangle = a^2\Bigg\{m^2\left[\begin{bmatrix}N\\cN\end{bmatrix}+c\begin{bmatrix}N\\cN+1\end{bmatrix}+\begin{bmatrix}N\\cN+2\end{bmatrix}\right] \\ +m\left[(1-c)N\begin{bmatrix}N\\cN+1\end{bmatrix}\right. \\ \left.-(cN+1)\begin{bmatrix}N\\cN+2\end{bmatrix}\right]\Bigg\}\Big/\begin{bmatrix}N\\cN\end{bmatrix}.\end{aligned} \tag{2.44}$$

From this the variance of x_m is obtained directly as

$$\langle x_m^2\rangle-\langle x_m\rangle^2 = a^2\frac{(1-c)(N+1)Nm(cN+1-m)}{(cN+1)^2(cN+2)} \tag{2.45a}$$

$$= a^2\frac{1-c}{c}N\frac{\left[\rho+\frac{1}{2cN}\right]\left[1+\rho+\frac{1}{2cN}\right]\left[1+\frac{1}{N}\right]}{\left[1+\frac{1}{cN}\right]^2\left[1+\frac{2}{cN}\right]}\,. \tag{2.45b}$$

Hence we may conclude that the limiting long-time behavior of the mean-square displacement of particle m is correctly described in (2.40) to leading order in N. Higher-order corrections cannot be taken from this equation, but this was to be expected, since both our use of the same waiting-time distribution $\tilde{\psi}(s)$ for all vacancy clusters and our approximation of $\tilde{\psi}(s)$ by the infinite system value introduced errors of order $1/N$.

Finally one may average (2.45) over m with the result

$$\frac{1}{cN}\sum_{m=1}^{cN}(\langle x_m^2\rangle-\langle x_m\rangle^2) = a^2\frac{(1-c)(N+1)N}{6(cN+1)}\,, \tag{2.46}$$

whereas a similar averaging of (2.40) would yield

$$\frac{1}{cN}\sum_{m=1}^{cN}(\langle x_m^2\rangle-\langle x_m\rangle^2) = a^2\frac{(1-c)[(cN)^2+3cN+\frac{1}{2}]}{6c^3(N-1)}\,. \tag{2.47}$$

III. NUMERICAL SIMULATION

A. Procedure

The simulation of particles in the concentrated lattice gas by Monte Carlo techniques has been comprehensively described in the first paper of this series[25] for the case of diffusion of a three-dimensional fcc lattice. In this section we present some special features of the procedures used for the one-dimensional chains. In order to simulate diffusion on an infinite chain, one long chain was taken and the particles were added randomly to the chain with prescribed *mean* concentration c, as detailed in Ref. 25. Since the occupation probabilities of the sites are uncorrelated no "thermalization" procedure was needed. Periodic boundary conditions were taken for the long chain. Ensembles of short chains were used for the study of boundary effects. Each ensemble consisted of many chains, each having the same length and number of particles. The particles were randomly distributed over the sites of each chain.

In order to achieve good accuracy in determining the mean-square displacement, large numbers of tagged particles must be followed. This argument can be given in quantitative form. The simulations aim at estimating the mean-square displacement of a tagged particle by taking the average of the squared displacements of all particles, which are considered as tagged ones. The magnitude of the deviation of this average from the expectation value is determined by the variance of the squared displacements, which can be related to the fourth moment. Using the

asymptotic law Eq. (1.1) for the mean-square displacement and $\langle [x(t)]^4 \rangle \approx 3 \langle [x(t)]^2 \rangle^2$, one finds that the relative deviations of the squared displacements from the expected values are approximately $(2/M)^{1/2}$ where M is the number of tagged particles. Hence at least 20 000 particles must be taken when an accuracy of 1% is desired. We worked with long chains of at least 32 000 sites; for short chains we created so many members of the ensembles that at least a total of 16 000 particles were present.

B. Results for large chains

Figure 1 shows a typical result of the simulation of self-diffusion of individual particles on the "infinite" linear chain randomly occupied by many particles. One chain with 256 000 sites and 127 928 particles was used. The results for the mean-square displacement agree quite well with the theoretical curve which was obtained by inversion of the Laplace transform of the mean-square displacement, Eq. (2.20). The inversion was performed by application of the fast routine developed by Honig.[26]

The simulated mean-square displacement at $c = 0.5$ appears to be smaller than the theoretical curve at intermediate times ($2\Gamma t \approx 50$—200). Similar systematic deviations of 2—3 % were found in runs with different random-number generators, and at other concentrations. The deviations become small at higher concentrations ($c \geq 0.9$). The observed discrepancy between theory and simulations probably results from the approximations made in the derivation of Eq. (2.20). Its sign agrees with our expectation, based on the short-time expansions (2.26) and (2.27). However, we are not able to assess the errors due to these approximations in a more quantitative way.

In order to demonstrate the agreement of simulation with theory over a wider range of times and for different concentrations, we give in Fig. 2 results for $c = 0.099\,09$, $0.506\,81$, and $0.899\,81$, in a doubly logarithmic representation. The crossover between the asymptotic behaviors for short and large times is nicely seen. Other concentrations showed the same qualitative behavior, and the same overall quality of agreement between theory and simulation. In summary we remark that the theory presented in the preceding section gives a good approximate description of the mean-square displacement of tagged particles in the concentrated linear chain.

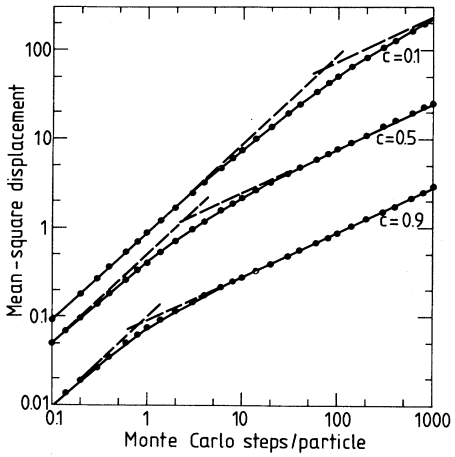

FIG. 2. Mean-square displacement of tagged particles on linear chains with three different concentrations. Solid line, theory; closed circles, numerical simulation; dashed lines, asymptotic behavior.

C. Results for periodic chains

As discussed in Sec. II D the mean-square displacement of a tagged particle in chains with periodic boundary conditions will become a linear function of time, for large times, when the displacement is measured from the starting point without reduction to the original chain. The results of the simulation for 6400 periodic chains of $N = 20$ sites, occupied with $M_p = 10$ particles each, are shown in Fig. 3. One sees linear time behavior after an initial period. The results of the simulation compare well to the theoretical curve, derived from Eq. (2.31) by numerical inversion of the Laplace transform. Also in this case a systematic difference between the theoretical curve and the

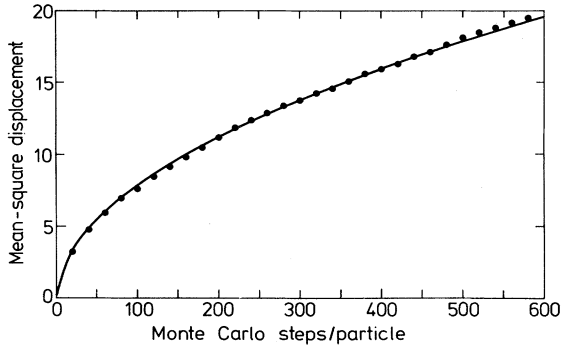

FIG. 1. Mean-square displacement of tagged particles on linear chain. Solid line, theory; closed circles, results of the numerical simulation on a chain with 256 000 sites and 127 928 particles, i.e., $c \approx 0.4997$. One Monte Carlo step corresponds to one attempted jump per particle, i.e., the time is measured in units of $(2\Gamma)^{-1}$.

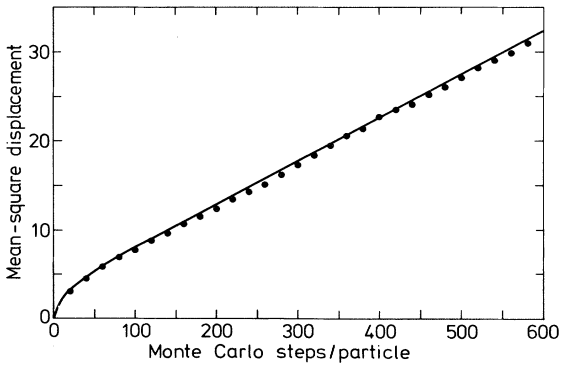

FIG. 3. Mean-square displacement of tagged particles on finite chains of fixed length ($N = 20$) with periodic boundary conditions, for $c = 0.5$. Solid line, theory; closed circles, numerical simulation.

results of the simulation appears at intermediate times, which can probably be attributed to the approximations involved in the derivation of Eq. (2.31).

For further comparison of theory and simulation, we have plotted in Fig. 4 the mean-square displacement of chains with $N=20$ sites, at three concentrations, over a larger time range. Note that the time- and square-displacement ranges are shifted by 1 order of magnitude, compared to Fig. 2. Also this figure exhibits very good agreement between theory and simulation. The crossover between the behavior in the infinite chain and the periodic chain behavior is clearly seen. Table I contains results for the diffusion coefficient $D_{\rm tr}$ determined from the asymptotic linear behavior, for different values of N and M_p. The numerical values have been determined from the simulation by fitting linear behavior to the second half of each simulation. The theoretical values follow from Eq. (2.33). The agreement between simulation and theory is very satisfactory.

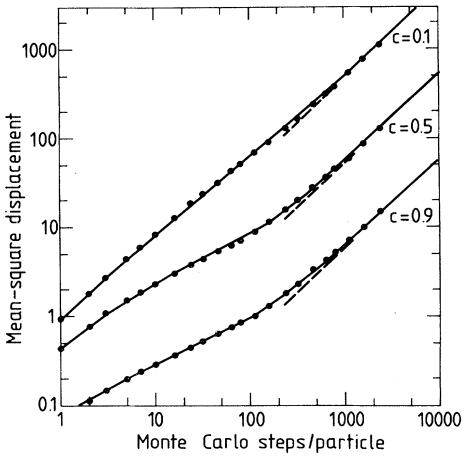

FIG. 4. Mean-square displacement of tagged particles on finite chains with periodic boundary conditions, for three different concentrations. Solid lines, theory; closed circles, numerical simulation; dashed lines, asymptotic long-time behavior.

D. Results for finite chains

The mean-square displacement of a tagged particle in a finite chain must approach a constant value, for large times. Figure 5 presents results for an ensemble of 6400 chains of $N=20$ sites, occupied by $M_p=10$ particles each. Other ensembles with differing chain lengths and particle numbers showed similar qualitative behavior. The numerical results are clearly below the dashed curve, which represents the theoretical mean-square displacement according to Eq. (2.38) after averaging and transformation to the time domain. The simulation does reach with good accuracy the asymptotic mean-square displacement given by Eq. (2.46). The nature of the approximations used to derive Eq. (2.38) has been discussed in Sec. II E, as well as the fact that this equation does not even give the correct asymptotic value for smaller chains, as is exemplified by Fig. 5. The results for all N and M_p are given in Table II. The asymptotic mean-square displacement has been determined from the last-third time interval of each simulation. This range is approximately a factor of 3—9 above the crossover point to the asymptotic behavior. The error ranges represent the square root of the variance. The theoretical values have been calculated from Eqs. (2.41) and (2.46). There is good agreeement between simulation and the calculated asymptotic values for the mean-square displacement, as expected.

The behavior of $\langle(\Delta x)^2\rangle_{\rm as}$ with concentration c and site number N is approximately

$$\langle(\Delta x)^2\rangle_{\rm as}\approx\frac{a^2(1-c)}{3c}N \tag{3.1}$$

TABLE I. Asymptotic diffusion coefficient of tagged particles on finite chains with periodic boundary conditions. Typically 8000 particles were followed in each simulation. The number of Monte Carlo steps is too small for $N=30$ and 40, compared to the other chain lengths.

Chain length	Monte Carlo steps/particle	c	Asymptotic diffusion coefficient Simulation	Theory
6	300	0.5	0.199±0.002	0.200
10	600	0.1	1.00±0.01	1.0 (trivial)
		0.3	0.268±0.003	0.2593
		0.5	0.115	0.1111
		0.7	0.050±0.002	0.0476
		0.9	0.0128±0.0002	0.01235
14	1.200	0.5	0.080±0.001	0.0714
20	2.400	0.1	0.47±0.01	0.4737
		0.3	0.122±0.002	0.1228
		0.5	0.053±0.001	0.0526
		0.7	0.0228±0.0006	0.02256
		0.9	0.0064±0.0001	0.00585
30	1.200	0.5	0.035	0.0345
40	1.500	0.5	0.024	0.0256

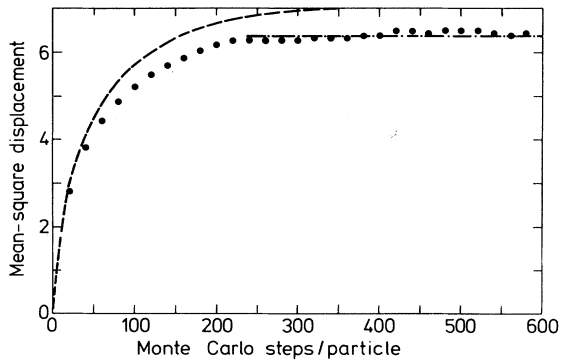

FIG. 5. Mean-square displacement of tagged particles on finite chains of fixed length ($N=20$) with reflecting boundary conditions, for $c=0.5$. Dashed line, theory; closed circles, numerical simulation; dashed-dotted line, asymptotic value according to Eq. (2.4b).

[cf. Eqs. (2.41) and (2.46)]. We will use that equation to derive the crossover from $t^{1/2}$ behavior to a constant mean-square displacement. Comparison of Eqs. (2.21b) and (3.1) yields the crossover time t_f in finite chains

$$2\Gamma t_f=\frac{\pi}{18}N^2 . \tag{3.2}$$

The crossover to the asymptotic behavior in the finite chain is very similar to the crossover in the periodic chain, as could be expected. Again the crossover time is independent of c. The derivation of (3.2) becomes invalid for small c and small N, especially when the mean-square displacement of a particle has not yet developed $t^{1/2}$ behavior.

IV. DISCUSSION

In this paper we have compared the results from an approximate theory and from Monte Carlo simulations for the mean-square displacement of a tagged particle in a purely repulsive one-dimensional lattice gas. For both infinite and periodic systems the agreement was found to be quite good for all times and all concentrations; the discrepancies between theory and simulation never exceeded a few percent. In addition both theory and simulations were found to agree with known asymptotic results for short and long[14–16] times. For systems with reflecting boundaries the Monte Carlo results reproduce the exactly known long-time limit of the mean-square displacement correctly; for this case we have not developed a theory, however, of an accuracy comparable to that of the previous cases. For the periodic system we obtained a coefficient of tracer diffusion inversely proportional to the number of particles, in agreement with previous calculations.[5–8] It is worth noting that an expression for the Green's function $P(n,t)$, describing the probability of finding a particle in an equilibrium system, starting off at the origin at $t=0$, at site n at time t, can be calculated under one additional assumption. This assumption is that the probability for the special vacancy to return to the tagged particle at time t does not depend on the instantaneous position of the latter. The resulting expression for $P(n,t)$ reads

$$P(n,t)=\exp(-\langle[\Delta x(t)]^2\rangle/a^2)I_n\{\langle[\Delta x(t)]^2\rangle/a^2\} . \tag{4.1}$$

This would imply that all cumulants of the moments of displacement, e.g., the fourth cumulant $\{\langle\Delta x(t)]^4\rangle-3\langle[\Delta x(t)]^2\rangle^2\}/a^4$, would be identical to $\langle[\Delta x(t)]^2\rangle/a^2$. This is not confirmed by either short-

TABLE II. Asymptotic mean-square displacement of tagged particles on finite linear chains with reflecting boundary conditions. Typically 8000 particles were followed in each simulation. The number of Monte Carlo steps for $N=40$ is too small, compared to the other chain lengths.

Chain length	Monte Carlo steps/particle	c	Asymptotic mean-square displacements Simulation	Theory
6	150	0.5	1.75	1.75
10	150	0.1	16.6±0.1	16.5
		0.2	9.9±0.1	9.77
		0.3	6.36±0.06	6.42
		0.5	3.14	3.06
		0.7	1.42±0.01	1.375
		0.8	0.85±0.02	0.815
		0.9	0.371±0.009	0.367
20	600	0.1	41.5±0.4	42.0
		0.2	22.3±0.4	22.4
		0.3	14.3±0.2	14.0
		0.5	6.31±0.1	6.36
		0.7	2.88±0.07	2.80
		0.8	1.69±0.03	1.647
		0.9	0.74±0.01	0.737
30	1.200	0.5	9.86	9.69
40	1.500	0.5	12.4	13.02

time expansions or Monte Carlo results, however. Indeed in the latter the fourth cumulant is found to increase as $t^{1/2}$ for long times, but the coefficient is appreciably larger than that for the mean-square displacement, except in the limit $c \to 1$, where (4.1) becomes an exact result. Hence we must conclude that the additional assumption made is too crude.

Further we want to mention the fact, pointed out by Büttiker and Landauer,[27] that a $t^{1/2}$ long-time behavior for the mean-square displacement of a tagged particle is a general phenomenon for one-dimensional systems subject to a single-filing constraint but exhibiting normal collective diffusion. The easiest way to understand this is by the arguments of Alexander and Pincus.[15] As further examples of such systems Büttiker and Landauer mention the damped harmonic-oscillator chain,[28] the sine-Gordon chain,[29,27] and de Gennes's reptation model of polymers.[30] The last example is closely related to a model of a random walk on a random walk, discussed by Kehr and Kutner.[31]

Generalizations of the method presented here for the calculation of the velocity autocorrelation function of a tagged particle are, in general, not straightforward. In the case of Kawasaki dynamics at finite temperature, where besides the hard-core repulsion, a nearest-neighbor energy is present, the situation resulting on taking out the special vacancy is not on average symmetric any more and the cluster dynamics becomes much more complicated than in the case of infinite temperature. In higher dimensions one cannot, even at infinite temperature, take out the special vacancy without disturbing the lattice symmetry. Only in the limit $c \to 1$ is the situation always simple, because one only has to study a simple random walk of an isolated vacancy. This has been used extensively for calculations of the so-called correlation factor,[32] which measures the reduction of the coefficient of tracer diffusion due to memory effects in the velocity autocorrelation function.

ACKNOWLEDGMENTS

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APPENDIX: CLUSTER AND SPECIAL-VACANCY DYNAMICS

We calculate the waiting-time distribution for the special-vacancy cluster to shrink to zero under the following three assumptions.

(i) Initially the probability for the cluster to be of a size m equals $c(1-c)^{m-1} m \geq 1$.

(ii) The rate of growth from m to $m+1$ is $2\Gamma(1-c)$.

(iii) The rate of decrease from m to $m-1$ is 2Γ for $m \geq 1$.

We consider the process as a random walk on the natural numbers with an absorbing boundary at the origin. The waiting-time distributions ψ^+ and ψ^- for jumps to the right (increasing numbers) and to the left, respectively, are both Poissonian and have the form

$$\psi^+(s) = \frac{(1-c)\nu}{(2-c)(s+\nu)} , \tag{A1a}$$

$$\psi^-(s) = \frac{\nu}{(2-c)(s+\nu)} , \tag{A1b}$$

where $\nu = 2(2-c)\Gamma$ is the overall jump frequency. Let $\tilde{X}(s)$ be the Laplace transform of the probability density for a first return to a given site, for example m, after an excursion to the right. It satisfies

$$\tilde{X}(s) = \psi^+(s)\psi^-(s) \sum_{n=0}^{\infty} [\tilde{X}(s)]^n \tag{A2a}$$

$$= \psi^+(s)\psi^-(s) \frac{1}{1-\tilde{X}(s)} . \tag{A2b}$$

The nth term that occurs in the series occurring in (A2a) results from all paths consisting of one jump from m to $m+1$, followed by n excursions to the right returning to $m+1$, and a final jump from $m+1$ to m. The solution of (A2b) for $\tilde{X}(s)$ is given in (2.12). The probability density for reaching site $m-1$ for the first time starting from site m is found as the product of the probability density for making an arbitrary number of excursions to the right from site m, followed by one jump to the left, i.e.,

$$\tilde{P}(m-1 \mid m,s) = \tilde{\psi}^-(s) \sum_{n=0}^{\infty} \tilde{X}^n(s) = \frac{\tilde{\psi}^-(s)}{1-\tilde{X}(s)} . \tag{A3}$$

From this the probability to reach the origin starting from site m is obtained as

$$\tilde{P}(0 \mid m,s) = \tilde{P}(m-1 \mid m,s)\tilde{P}(m-2 \mid m-1,s) \cdots \tilde{P}(0 \mid 1,s) = \left[\frac{\psi^-(s)}{1-\tilde{X}(s)} \right]^m . \tag{A4}$$

Finally the waiting-time distribution $\tilde{\psi}(s)$ follows as

$$\tilde{\psi}(s) = \sum_{m=1}^{\infty} (1-c)^{m-1} c \tilde{P}(0 \mid m,s) = c \frac{\tilde{\psi}^-(s)[1-\tilde{X}(s)]^{-1}}{1-(1-c)\tilde{\psi}^-(s)[1-\tilde{X}(s)]^{-1}} , \tag{A5}$$

which is identical to (2.10).

The derivation of (2.13) is very similar. In this case the waiting-time distributions for jumps in both directions are given by $\frac{1}{2}\tilde{\psi}(s)$. Then the Laplace transforms of the probability density for a first return from the right (or left) to an arbitrary site m, if at the initial time the vacancy just arrived at m, is found from the equation

$$\tilde{Y}(s) = \tfrac{1}{4}\tilde{\psi}^2(s) \frac{1}{1-\tilde{Y}(s)} \tag{A6}$$

with the solution

$$\tilde{Y}(s) = \tfrac{1}{2}\{1-[1-\tilde{\psi}^2(s)]^{1/2}\} . \tag{A7}$$

Then the probability to arrive at site $m+n$ starting just after a jump to site m is obtained as

$$\tilde{P}(n,s)=\left[\frac{\frac{1}{2}\tilde{\psi}(s)}{1-\tilde{Y}(s)}\right]^{n}\frac{1}{1-2\tilde{Y}(s)} . \tag{A8}$$

The factor $[\frac{1}{2}\tilde{\psi}/(1-\tilde{Y})]^2$ is obtained in the same way as (A4); the factor $(1-2\tilde{Y})^{-1}$ results from the possibility of making an arbitrary number of excursions returning to n in both directions after the first arrival at this site.

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