Second moment for cooperative diffusion in one-dimensional hard-particle lattice gases

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The diffusion of hard particles that span an arbitrary number of lattice sites on a one-dimensional lattice can be expressed in terms of a differential equation that contains one term that represents the random walk of independent particles and another term that represents the interaction of particles. The cooperative term involves the gradient of the pair distribution at the distance of closest approach. The moments of the particle distribution can then be expressed as a set of recursion relations that involve moments of the pair distribution at closest approach. For the case of the second moment this reduces to an equation involving the zeroth moment of the pair distribution for particles spanning a single lattice site which is known exactly. The independent-walk part of the second moment has the usual linear dependence with time while the cooperative part introduces a contribution that varies as $\sqrt{t}$. [S1063-651X(96)03811-1]

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I. INTRODUCTION

Diffusion plays an important role in many physical processes. The standard linear diffusion equation in continuous space treats the average random motion of independent particles, while the interaction between particles generally introduces some kind of nonlinear terms. Solutions are known for some special classes of nonlinear diffusion equations [1], such as Burger's equation [2]. In this paper we consider one of the simplest examples of cooperative diffusion, namely, the motion of hard particles on a one-dimensional lattice, for which we obtain a modified diffusion equation. As is the case for the cooperative dynamics in many systems, the problem of finding the moments of the distribution is simpler than solving the complete problem [3,4] and in this case we are able to give a general solution for the second moment.

In Fig. 1 we illustrate a sample configuration of particles on a one-dimensional lattice where the particles cover an arbitrary number ν of lattice sites. One can think of this model as one involving particles of fixed length where the lattice is made increasingly finer with lattice spacing $\delta=1/\nu$. The equilibrium properties of such a system were treated for general δ by Lee and Yang [5] in their famous paper on the connection between phase transitions and the zeroes of the grand partition function. The dynamics for general δ is more complicated and only the case of $\delta=1$ [as illustrated in Fig. 1(b)] has been solved [6]. In the present paper we obtain an expression for the second moment of the particle distribution for general ν (or δ) for the initial condition of a group of close-packed particles with a finite second moment. The kind of process we will use to illustrate the cooperative diffusion of particles is illustrated in Fig. 2 where we have a close-packed group of M particles at zero time. As time increases these particles diffuse out in both directions and the second moment of the distribution increases.

We will approach this problem as follows. In Sec. II we review briefly the application of Glauber's approach for diffusion to the special case of $\nu=1$ since we will find that the second moment for general ν can be expressed in terms of the properties of the $\nu=1$ system. Then, in Sec. III, we construct the differential equation for diffusion for general ν. This equation contains one set of terms that represents the diffusion of independent particles and another involving the pair distribution at the distance of closest approach that represents the cooperative part of the process. In Sec. IV we form the moments of the distribution and find that we can obtain an exact expression for the second moment in terms of the zeroth moment of the pair distribution for the case $\nu=1$ which we construct in Sec. V. We discuss the contribution of the cooperative nature of the process to diffusion in Sec. VI.

II. SOLUTION FOR $\nu=1$

In this section we review the solution for one-dimensional lattice diffusion with $\nu=1$, as illustrated in Fig. 1(b). The solution for this model was first given by Kutner [6] in 1981; a review of the subject is available [7]. Here we use the method of Glauber [8] which has been applied to this model [9]. Glauber's method was devised to treat the one-dimensional Ising model where at each site of a one-dimensional lattice there was a spin that could have two orientations. Here the two states are the state of occupancy of a lattice site, occupied by a particle $(+1)$ and unoccupied (-1). We let the variable σ_m represent the state of site m,

$$\sigma_m = \pm 1. \tag{2.1}$$

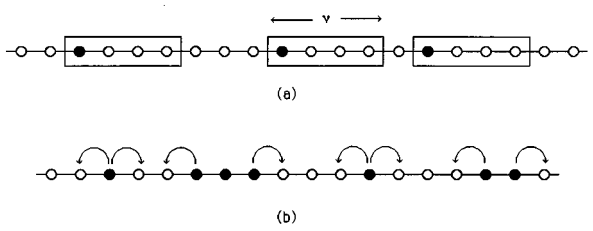

FIG. 1. Hard particles on a one-dimensional lattice. (a) Illustration of the case where the particle spans four sites ($\nu=4$). The reference site keeping track of the location of the particle is shown in black. (b) A sample configuration of particles for the case $\nu=1$ illustrating the allowed hops to nearest-neighbor sites.

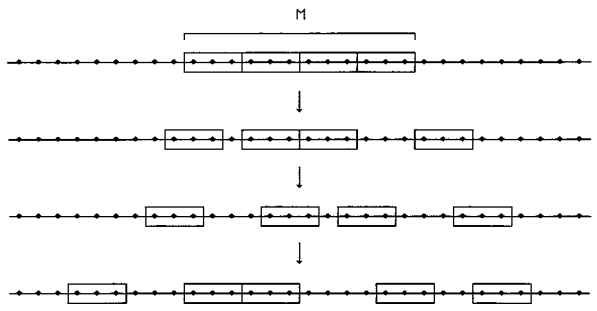

FIG. 2. Illustration of an initial close-packed block of M particles (here with $\nu=3$) that with time diffuse out along the lattice in both directions.

The rules for the hard-particle system are that if there is a particle at site m, then the closest another particle can get to the reference particle is $m\pm\nu$ where ν measures the size (number of sites spanned by) the particle. The basic dynamic process in our diffusion model is the hopping from one lattice site to another which we can represent by the following reaction:

$$(-+)\leftrightarrow(+-). \tag{2.2}$$

Following Glauber we can write the differential equation for the time evolution of the average value of σ_m as

$$d\langle\sigma_m\rangle/dt=-2\sum_{\{\sigma\}}\sigma_m[w(m-1,m)+w(m,m+1)]P\{\sigma\}. \tag{2.3}$$

The two terms involving w in (2.3) represent the exchange of a particle at site m with either site $(m-1)$ or $(m+1)$, as illustrated in Fig. 3(a). For the case of $\nu=1$ we have [9]

$$w(m,m+1)=\tfrac{1}{2}(1-\sigma_m\sigma_{m+1}), \tag{2.4}$$

which is zero for the nearest-neighbor σ combinations $(++)$ and $(--)$ and one for $(-+)$ and $(+-)$. Using (2.4) in (2.3) gives

$$d\langle\sigma_m\rangle/dt=\langle\sigma_{m-1}\rangle-2\langle\sigma_m\rangle+\langle\sigma_{m+1}\rangle. \tag{2.5}$$

We can write the average sigma as

$$\langle\sigma_m\rangle=P_m-(1-P_m), \tag{2.6}$$

where P_m is the *a priori* probability that a particle will be found at site m. Using (2.6) in (2.5) we have

$$dP_m/dt=P_{m-1}-2P_m+P_{m+1}, \tag{2.7}$$

which is the differential equation for independent particles hopping on a one-dimensional lattice

$$\cdots\leftrightarrow(m-1)\leftrightarrow(m)\leftrightarrow(m+1)\leftrightarrow\cdots. \tag{2.8}$$

One then has the general solution for an arbitrary initial configuration of particles

$$P_m(t)=\sum_n P_n(0)P(n_0|m_t), \tag{2.9}$$

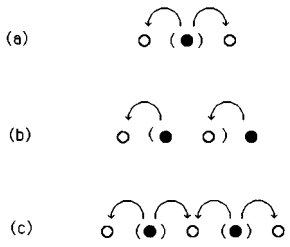

FIG. 3. Illustration of allowed hops for the case of $\nu=1$. The sites being monitored are in parentheses. (a) Allowed moves for a singlet. (b) Allowed moves for a nearest-neighbor doublet.

where $P_n(0)$ is the initial distribution of particles and $P(n_0|m_t)$ is the conditional probability that given a particle at site n at $t=0$ the particle is at site m at time t. The conditional probabilities are given by [9]

$$P(n_0|m_t)=e^{-2t}I_{m-n}(2t), \tag{2.10}$$

where $I_n(2t)$ is the imaginary Bessel function. If we specialize to the case where the initial probabilities are either zero or one, then we have

$$P_m(t)=e^{-2t}\sum_n I_{m-n}(2t), \tag{2.11}$$

where the sum is over the initial sites containing particles.

One could proceed in a similar manner for $\nu>1$, constructing the appropriate w_m functions and obtaining the analog of (2.5). In fact this leads to rather complicated equations and in this case it is simpler to approach the differential equations in a direct manner. The reason that the case $\nu=1$ can be solved is that two particles can switch places (''go through one another'') as if they were truly independent. This does not alter the mathematics since the identity of the particles is immaterial. But it does scramble the initial order on the lattice.

III. DIFFERENTIAL EQUATIONS FOR $\nu>1$

In Eq. (2.6) we gave the relation between $\langle\sigma_m\rangle$ and P_m. In this section we will find that it is more convenient to express the differential equations directly in terms of the P_m and in this case it is easier to use the indices 0 and 1 to represent a vacant and occupied lattice site (Glauber's method used the mathematical properties of $+1$ and -1). In order to change the probability of occupancy of site m we must consider jumps where neighboring particles move onto the site (increasing the probability of occupancy) and also jumps where a particle at site m moves to neighboring sites (decreasing the probability of occupancy). The four possible moves are illustrated in Fig. 4(a) for the case of $\nu=4$. Now with $\nu>1$ we must stipulate that the requisite stretch of unoccupied sites be present in order for an allowed move to take place. The differential equation illustrated in Fig. 4(a) can be written as follows (again for $\nu=4$ where the parentheses enclose ν sites spanned by a particle):

$$dP_m/dt=P((10_m00)0)+P(0(000_m1))-P((1_m000)0)-P(0(0001_m)). \tag{3.1}$$

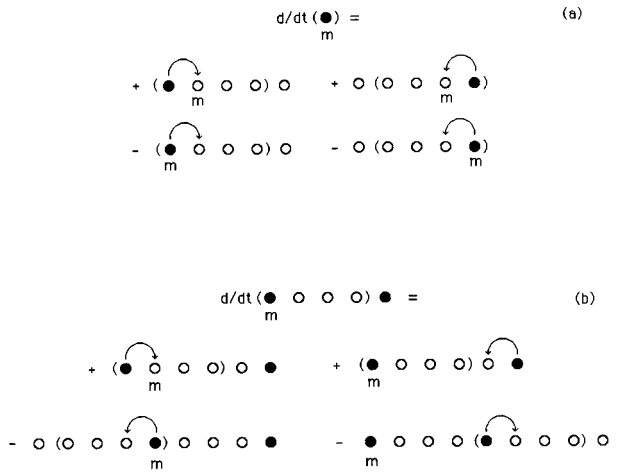

FIG. 4. The contributions to the differential equation for particles with $\nu=4$ at site m. (a) Moves contributing to the rate equation for the singlet. (b) Moves contributing to the rate equation for the nearest-neighbor doublet.

We can rewrite (3.1) using the identity

$$P((1_m000)0)+P((1_m000)1)=P((1_m000))=P_m. \tag{3.2}$$

The equality on the left hand side follows from the general identity

$$P(s\ 0)+P(s\ 1)=P(s), \tag{3.3}$$

where s is any fixed sequence (sequence s must be followed by something and the only two possibilities are 0 and 1). The equality on the right hand side follows since if there is a particle at site m then because of the extent of excluded volume the 0's indicated must follow. Rearranging (3.2) we have

$$P((1_m000)0)=P_m-P((1_m000)1). \tag{3.4}$$

It is useful now to define the quantity

$$Q_m=P((1_m000)1). \tag{3.5}$$

This is the probability that two particles are at the distance of closest approach and is related to the discrete pair distribution function through the relation $g_m=Q_m/P_m$. Using (3.4) and (3.5) in (3.1) we obtain

$$\begin{aligned} dP_m/dt=&P_{m-1}-2P_m+P_{m+1}+(Q_{m-\nu}-Q_{m-\nu+1})\\ &+(Q_m-Q_{m-1}). \end{aligned} \tag{3.6}$$

The first set of terms involving P_{m-1}, P_m, and P_{m+1} is identical with (2.7) for the case of $\nu=1$ which is equivalent to the diffusion of independent particles. But now for $\nu>1$ we have the additional terms involving Q, the pair distribution, that represent the cooperative nature of diffusion for $\nu>1$. The combinations of terms in (3.6) can be identified as the finite difference (discrete space) approximations to the following derivatives:

$$\begin{aligned} P_{m-1}-2P_m+P_{m+1}&\approx\frac{\partial^2P(x,t)}{\partial x^2},\\ Q_m-Q_{m-1}&\approx\frac{\partial Q(x,t)}{\partial x}. \end{aligned} \tag{3.7}$$

As ν gets larger (or, with particle size fixed, the grid gets finer), these approximations become more accurate and in the limit of $\delta\to0$ we get the continuum limit. Then in continuous space

$$\frac{\partial P(x,t)}{\partial t}=\frac{\partial^2P(x,t)}{\partial x^2}+\frac{\partial Q(x,t)}{\partial x}-\frac{\partial Q(x-c,t)}{\partial x}, \tag{3.8}$$

which is the familiar diffusion equation with extra terms involving the variation of the probability of closest approach along the lattice.

In order to solve (3.6) we need a differential equation for the Q_m. This is constructed in analogy with the process used for (3.1); the reactions that increase or decrease Q_m are illustrated in Fig. 4(b) (again for $\nu=4$). The differential equation then is

$$\begin{aligned} dP((1_m000)1)/dt=&P((10_m00)01)+P((1_m000)01)\\ &-P(0(0001_m)0001)\\ &-P(1_m000(1000)0). \end{aligned} \tag{3.9}$$

Using the identities

$$\begin{aligned} &P((1_m000)(1000)0)+P((1_m000)(1000)1)\\ &\quad=P((1_m000)(1000))=P((1_m000)1) \end{aligned} \tag{3.10}$$

we obtain

$$\begin{aligned} dP((1_m000)1)/dt=&P((1_m000)01)-P((1_m000)1)\\ &+P((1_{m-1}000)01)-P((1_m000)1)\\ &+P((1_m000)(1000)1)\\ &+P((1_{m-\nu}000)(1000)1). \end{aligned} \tag{3.11}$$

Defining

$$\begin{aligned} R_m&=P((1_m000)01),\\ S_m&=P((1_m000)(1000)1) \end{aligned} \tag{3.12}$$

then the differential equation of (3.9) can be written

$$dQ_m/dt=(R_m-Q_m)+(R_{m-1}-Q_m)+S_{m-\nu}+S_m. \tag{3.13}$$

So the rate of change of the two-particle correlation Q is given in terms of another two-particle correlation (R) and three-particle correlation S. We then require differential equations for R and S which require higher order particle correlations, and so on, giving an infinite hierarchy of equations.

We will not try to solve this hierarchy of equations explicitly but instead will focus attention on the moments of the distribution P_m. We will find that the second moment

can be expressed in terms of the zeroth moment of the distribution Q_m which we can calculate in general.

When the system is at equilibrium all of the probabilities in (3.13) are independent of position on the lattice and we obtain the result

$$Q=R+S. \tag{3.14}$$

IV. MOMENTS OF P_m

We consider the power moments of the distribution P_m,

$$\mu_n=\sum_m m^n P_m. \tag{4.1}$$

We consider the initial condition where M sites are occupied by particles in a symmetric fashion about the center site as illustrated in Fig. 2. Thus we have for all time

$$\mu_0=M \quad \text{and} \quad \mu_{\text{odd}}=0. \tag{4.2}$$

Taking the time derivative of (4.1) and using (3.6) for dP_m/dt we have

$$d\mu_n/dt=\sum_m m^n(P_{m-1}-2P_m+P_{m+1}) + \sum_m m^n(Q_{m-\nu}-Q_{m-\nu+1}+Q_m-Q_{m-1}). \tag{4.3}$$

Since the sum is over an infinite number of sites we can shift the summation index as follows (for example):

$$\sum_m m^n P_{m-1}=\sum_m (m+1)^n P_m. \tag{4.4}$$

Then we can write (4.3) as

$$d\mu_n/dt=\sum_m P_m[(m+1)^n-2m^n+(m-1)^n] + \sum_m Q_m[(m+\nu)^n-(m+\nu-1)^n+m^n -(m+1)^n]. \tag{4.5}$$

We define the moments of Q_m as

$$\alpha_n=\sum_m m^n Q_m. \tag{4.6}$$

As illustrated in Fig. 5(a) the configuration of nearest-neighbor pairs is symmetric about the origin. For the nearest-neighbor pairs (the Q_m) we shift the value of m to $(m+\nu/2)$, i.e., we measure moments from the center of the doublet, as illustrated in Fig. 5(b). Then we have

$$\alpha_n'=\sum_m (m+\nu/2)^n Q_m. \tag{4.7}$$

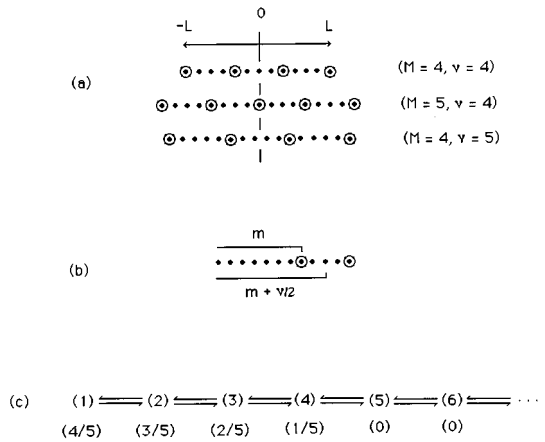

FIG. 5. (a) Illustration of the symmetric initial conditions for various M and ν. (b) Illustration of the shift by $\nu/2$ for calculating the moments of the doublet distribution. (c) Illustration of the equivalent random walk process represented by Eq. (5.12). The numbers in parentheses are the initial probabilities of independent random walkers for the case of $\nu=5$.

Starting with a symmetric configuration about the origin as illustrated in Fig. 5(a) all of the even moments α_n' are zero. The relations between the first few α_n and α_n' are

$$\alpha_0'=\alpha_0,$$
$$\alpha_1'=\alpha_1+(\nu/2)\alpha_0=0 \quad \text{or} \quad \alpha_1=-(\nu/2)\alpha_0, \tag{4.8}$$
$$\alpha_2'=\alpha_2+\nu\alpha_1+(\nu^2/4)\alpha_0=\alpha_2-(\nu^2/4)\alpha_0.$$

Then we have

$$d\mu_2/dt=2\mu_0+2(\nu-1)\alpha_0, \tag{4.9}$$

$$d\mu_3/dt=0, \tag{4.10}$$

$$d\mu_4/dt=2\mu_0+12\mu_2+(\nu-1)(\nu^2-2\nu+2)\alpha_0 + 12(\nu-1)\alpha_2'. \tag{4.11}$$

We see that if $\nu=1$ the μ_n can then be obtained simply by successive integration of a set of recursion relations. For $\nu>1$ the moments of P_m depend on the moments of Q_m. For the special case of μ_2 we have

$$\mu_2(t)=\mu_2(0)+2Mt+2(\nu-1)\int_0^t \alpha_0(s)ds. \tag{4.12}$$

We can determine $\mu_2(t)$ exactly if we know α_0. But α_0 is

$$\alpha_0=\sum_m Q_m. \tag{4.13}$$

Now this quantity does not depend on the position of the particles on the lattice but simply depends on how many nearest-neighbor contacts there are. So one can remove the obligatory 0's and reduce the calculation to that of α_0 for the case of $\nu=1$. And we know the solution for that case exactly. So we can determine $\mu_2(t)$ exactly, which we turn to now.

V. CALCULATION OF α_0

We need to know the quantity α_0 which can be written in terms of the $P(1_m 1_{m+1})$ for the case $\nu=1$,

$$\alpha_0=\sum_m P(1_m 1_{m+1}). \tag{5.1}$$

The function α_0 for the process illustrated in Fig. 2 has the limits

$$\alpha_0(0)=M-1 \quad \text{and} \quad \alpha_0(\infty)=0. \tag{5.2}$$

To generate an expression for α_0 for general time we return to (2.3) and develop the analog of this equation for the rate of change of doublets. Rate equations for higher order correlations were obtained by Glauber [8] for the one-dimensional Ising model; the dynamics of the two-particle correlation function has been treated by Evans and Hoffman [10]. The processes involved are illustrated in Fig. 3. For the special case of the nearest-neighbor doublet shown in Fig. 3(b) we have

$$d\langle\sigma_m\sigma_{m+1}\rangle/dt=-2\sum_{\{\sigma\}}\sigma_m\sigma_{m+1}[w(m-1,m)+w(m+1,m+2)]P\{\sigma\} \tag{5.3}$$

while for two particles further removed, as illustrated in Fig. 3(c), we have

$$d\langle\sigma_m\sigma_n\rangle/dt=-2\sum_{\{\sigma\}}\sigma_m\sigma_n[w(m-1,m)+w(m,m+1)+w(n-1,n)+w(n,n+1)]P\{\sigma\}, \tag{5.4}$$

which holds for $n>m+1$. Using the form of w given in (2.4) we have

$$d\langle\sigma_m\sigma_{m+1}\rangle/dt=\langle\sigma_{m-1}\sigma_{m+1}\rangle-2\langle\sigma_m\sigma_{m+1}\rangle+\langle\sigma_m\sigma_{m+2}\rangle \tag{5.5}$$

and

$$d\langle\sigma_m\sigma_{m+k}\rangle/dt=\langle\sigma_{m-1}\sigma_{m+k}\rangle+\langle\sigma_{m+1}\sigma_{m+k}\rangle-4\langle\sigma_m\sigma_{m+k}\rangle+\langle\sigma_m\sigma_{m+k-1}\rangle+\langle\sigma_m\sigma_{m+k+1}\rangle. \tag{5.6}$$

We now define the quantities

$$x_k=\sum_m \sigma_m\sigma_{m+k}, \tag{5.7}$$

where to avoid special conditions at the ends we use periodic boundary conditions. Summing (5.5) and (5.6) over m we then obtain the set of equations

$$\begin{aligned}
dx_1/dt&=-2x_1+2x_2,\\
dx_2/dt&=2x_1-4x_2+2x_3,\\
dx_3/dt&=2x_2-4x_3+2x_4,\\
dx_4/dt&=2x_3-4x_4+2x_5,\\
&\vdots\\
dx_n/dt&=2x_{n-1}-4x_n+2x_{n+1},\\
&\vdots
\end{aligned} \tag{5.8}$$

where the initial conditions are (see Fig. 2)

$$\begin{aligned}
x_n(0)&=N-4n \quad (n<M),\\
x_n(0)&=N-4M \quad (n\geq M).
\end{aligned} \tag{5.9}$$

The relation for $x_1(0)$, for example, is obtained by considering a configuration of M close-packed particles (with $\nu=1$), $\ldots------++++------\ldots$, and counting the number of nearest-neighbor products $\sigma_m\sigma_{m+1}$. For nearest-neighbor sites with like signs ($-$ or $+$) the product is $+1$, but at the border between $-$ and $+$ the product is -1, which represents a change of -2 from the $+1$ product. Since there are two ends of the sequence of M $+$'s we have $x_1(0)=N+2(-2)=N-4$. We next introduce the following new variables:

$$y_n=[x_n-(N-4M)]/4M \tag{5.10}$$

and

$$t'=2t. \tag{5.11}$$

In terms of these variables Eqs. (5.8) and (5.9) become

$$\begin{aligned}
dy_1/dt'&=-y_1+y_2,\\
dy_2/dt'&=y_1-2y_2+y_3,\\
dy_3/dt'&=y_2-2y_3+y_4,\\
&\vdots\\
dy_n/dt'&=y_{n-1}-2y_n+y_{n+1},\\
&\vdots
\end{aligned} \tag{5.12}$$

with the initial conditions

$$y_n(0)=\begin{cases}1-n/M & (n<M)\\ 0 & (n\geq M).\end{cases} \tag{5.13}$$

Equations (5.12) and (5.13) represent a random walk of independent particles on a 1D lattice with reflection at the first site, as illustrated in Fig. 5(c) where the numbers in parentheses show the initial probabilities for $M=5$.

The solution to this set of equations has been given by van Kampen and Oppenheim [11] and later by Schwarz and Poland [12] and is

$$y_n(t')=\sum_{k=1}^{M-1} y_k(0)P(k_0|n_{t'}), \tag{5.14}$$

where

$$P(k|n)=e^{-2t'}[I_{n-k}(2t')+I_{n+k-1}(2t')]. \tag{5.15}$$

Recalling that $t'=2t$ we have

$$y_1(t)=e^{-4t}\sum_{k=1}^{M-1}(1-k/M)[I_{k-1}(4t)+I_k(4t)] \tag{5.16}$$

and

$$x_1(t)=N-4M[1-y_1(t)]. \tag{5.17}$$

Now x_1 is defined in terms of the average correlation of σ_m and σ_{m+1},

$$x_1=\sum_m \langle\sigma_m\sigma_{m+1}\rangle. \tag{5.18}$$

To express x_1 in terms of the probabilities of particle configurations we use the identities (recall that 0 plays the role of -1)

$$\begin{aligned}\langle\sigma_m\sigma_{m+1}\rangle&=P(1_m1_{m+1})-P(0_m1_{m+1})-P(1_m0_{m+1})\\&\quad+P(0_m0_{m+1}),\\P(1_m0_{m+1})+P(1_m1_{m+1})&=P(1_m),\\P(0_m1_{m+1})+P(1_m1_{m+1})&=P(1_{m+1}),\\P(1_m0_{m+1})+P(0_m1_{m+1})+P(1_m1_{m+1})+P(0_m0_{m+1})&=1,\end{aligned} \tag{5.19}$$

and we have [where $P_m=P(1_m)$]

$$P(1_m1_{m+1})=\langle\sigma_m\sigma_{m+1}\rangle/4+(P_m+P_{m+1})/2-\tfrac{1}{4}. \tag{5.20}$$

Summing over all m (using periodic boundary conditions) and using relations

$$x_1=\sum_m \langle\sigma_m\sigma_{m+1}\rangle,\quad \sum_m P_m=\sum_m P_{m+1}=M,\quad \sum_m =N \tag{5.21}$$

we have

$$\alpha_0=\sum_m P(1_m1_{m+1})=x_1/4+M-N/4. \tag{5.22}$$

Using (5.17) we have the final result

$$\alpha_0(t)=My_1(t)=e^{-4t}\sum_{k=1}^{M-1}(M-k)[I_{k-1}(4t)+I_k(4t)]. \tag{5.23}$$

The imaginary Bessel functions have the asymptotic form

$$e^{-4t}I_n(4t)\sim\left(\frac{1}{8\pi t}\right)^{1/2}, \tag{5.24}$$

which gives the following asymptotic form for α_0:

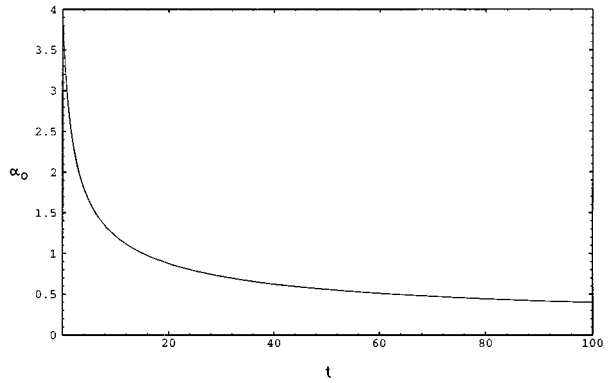

FIG. 6. The function α_0 as a function of time for $\nu=5$. Shown are the exact solution of (5.23) and the approximation of (5.27) which are indistinguishable on the scale shown. The units of time are relative to the basic hopping rate in (2.5).

$$\alpha_0\sim\frac{M(M-1)}{\sqrt{8\pi t}}\quad(t\to\infty). \tag{5.25}$$

As $t\to0$ we have [using (5.12) and (5.13) which are a set of recursion relations for a series in powers of t for the y_n]

$$\alpha_0\sim(M-1)-2t+\cdots\quad(t\to0). \tag{5.26}$$

An approximate form that has both the limits given in (5.25) and (5.26) is

$$\alpha_0=\frac{M(M-1)}{\sqrt{a+8\pi t}+b}, \tag{5.27}$$

where

$$a=\left(\frac{2\pi(M-1)}{M}\right)^2,\quad b=M-\sqrt{a}. \tag{5.28}$$

Figure 6 shows the exact form of α_0 given by (5.23) and compares the result of (5.27). On the scale shown the two relations are virtually indistinguishable. So (5.27) gives all the pertinent features of α_0 (and in particular the correct asymptotic limits as $t\to0$ and $t\to\infty$).

In particular we see that

$$\alpha_0\sim t^{-1/2}. \tag{5.29}$$

This means that $\mu_2(t)$ of (4.12) has the asymptotic form

$$\mu_2(t)\sim A+Bt+Ct^{1/2}=A+Bt[1+(C/B)t^{-1/2}]\sim A+Bt. \tag{5.30}$$

From (5.30) we see that the effect of cooperativity is to introduce a $\sqrt{t}$ correction to μ_2; the very long-time limit of μ_2 is that for independent units (the particles behave as independent units when they are very far apart). In Fig. 7 we show the behavior of $\mu_2(t)$ for the case $M=5$ and $\nu=5$. We plot the function

$$\Delta\mu_2/M=[\mu_2(t)-\mu_2(0)]/M, \tag{5.31}$$

with $\mu_2(t)$ given by (4.12) using (5.27) for $\alpha_0(t)$. Referring to (5.30), we indicate the contribution arising from the independent diffusion of particles (linear in t), the contribution

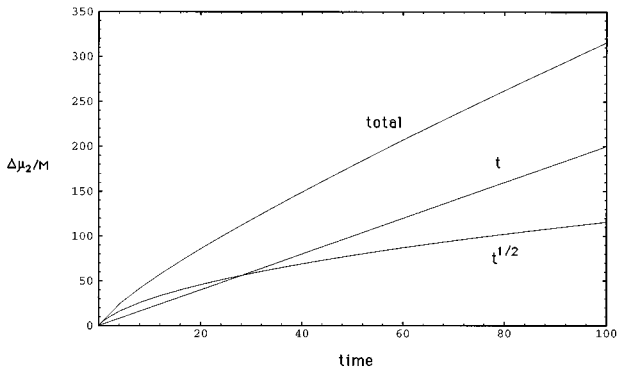

FIG. 7. The time evolution of the second moment for hard particles. The curve marked ''total'' shows the result of (4.12) using (5.27) for $\alpha_0(t)$ for the case $M=5$ and $\nu=5$. The contributions from independent (t) and cooperative interaction ($t^{1/2}$) are indicated. The units of time are relative to the basic hopping rate in (2.5).

arising from the interaction of the particles (varying as the square root of t) and the complete function (labeled ''total'') which is the sum of the two. At long times when the particles have moved far apart from one another the behavior is dominated by independent diffusion. At short times, however, the cooperative nature of the process produces marked deviations from simple diffusion.

VI. DISCUSSION

We have shown that the diffusion of hard particles on a one-dimensional lattice with an arbitrary number of sites occupied by a particle can be written in terms of a differential equation, (3.6), that has one set of terms [the P's in (3.6)] that represents the diffusion of independent particles and another set [the Q's in (3.6)] that reflects the interactions between particles. This division into two sets of effects follows through in the result for the second moment of the particle distribution given by (4.12) where, as illustrated in (5.30), we get a term linear in time from the independent diffusion part and a term varying as the square root of time from the interaction part. From the example shown in Fig. 7 we see that initially the effect of interaction is quite large, even for a small number of particles (5 in Fig. 7) in the initial close-packed cluster. As the particles move away from one another the behavior becomes more and more like that characteristic of independent particles. Our example shows that there are very important nonideal components to diffusion even in our simple one-dimensional model.

We have been able to calculate the second moment of the particle distribution exactly, but not higher moments. The reason that we can make progress with the second moment is that when we form the time derivative of the moments and use (3.6) for the time dependence of the P_m most of the m dependence in m^n cancels and we have the recursion relations illustrated in (4.9) and (4.11) where the time dependence of higher moments is given in terms of lower moments. If one knows the lower moments one simply integrates with respect to time to get the higher moments. For the case of $\nu=1$ we can obtain an arbitrary number of moments. Of course for this case we know the exact solution, given in (2.11), but we do not need to know that to calculate the moments of the distribution recursively. The problem with going beyond μ_2 is seen in the equation for μ_4, (4.11), where we require μ_2 and $\alpha_{2'}$, the second moment of the Q distribution (doublets at closest approach). We could pursue the time dependence of the α_n [or α'_n—see (4.8)] in the same manner but when we use (3.13) for the time dependence of the Q_m we do not get the cancellation of powers of m that leads to a recursion process as was the case with the μ_n. Perhaps there is a way of using identities such as (3.4) to write (3.13) in terms of other species that does lead to a recursion process, but we have not been able to find it.

The second simplification that allowed us to calculate μ_2 is that we require only the time integral of α_0, as shown in (4.12). And $\alpha_0(t)$ is independent of ν so we could obtain this quantity for the case $\nu=1$ which we can solve exactly. All of the higher moments α_n require knowledge of where the particle is on the lattice, involving m^n factors, and hence depend very much on the value of ν.

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