

Cooperative Diffusion in One-Dimensional Lattice Gases

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We obtain exact time-power series through 11th order for cooperative diffusion in a one-dimensional lattice gas with nearest-neighbor interactions. In the high-temperature limit (single-site exclusion one) mean field theory is exact and the model is soluble for arbitrary initial conditions. The exact solution is used to recast the time-power series for a general temperature as a series in the appropriate function obtained from the high-temperature limit. We discuss why more conventional methods of extracting power-law exponents for the asymptotic long-time behavior do not work well for this model.

KEY WORDS: Cooperative diffusion; kinetic Ising Model; time-power series; singularities.

1. INTRODUCTION

In the present paper we explore the use of exact power series in the time to describe the evolution of a one-dimensional lattice gas with nearest-neighbor interactions to equilibrium via a site-hopping mechanism (diffusion). Specifically, no two particles can occupy the same lattice site at the same time (excluded volume) and particles on nearest-neighbor lattice sites experience an attractive interaction (clustering tendency). Employing matrix techniques similar to those used in previous studies on homogeneous lattice gases,⁽¹⁻³⁾ we obtain a finite number of the exact coefficients in the time series.

One can imagine molecules adsorbed on a linear lattice, as illustrated in Fig. 1a. The number of particles on the lattice is fixed and we consider the internal diffusion of the molecules by the mechanism of hopping from a given site to a neighboring unoccupied site, as illustrated by the arrows

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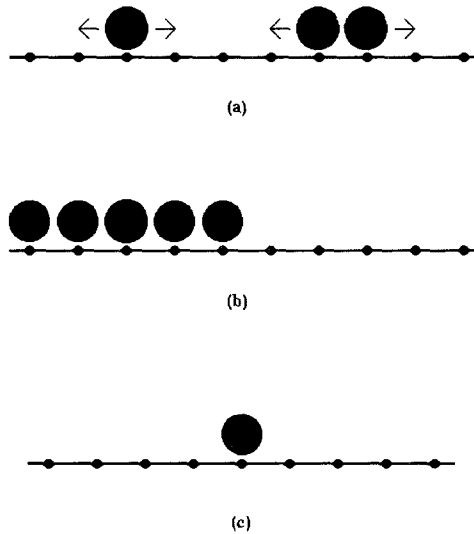
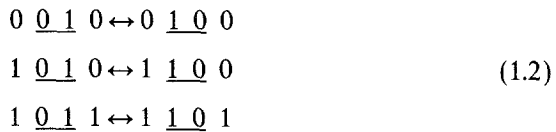


Fig. 1. (a) Illustration of the diffusion of particles on a 1D lattice where the particles can hop to nearest-neighbor unoccupied sites. (b) Illustration of the initial condition where the left half of the lattice is occupied and the right half is vacant. (c) Initial condition of a single particle at a given site.

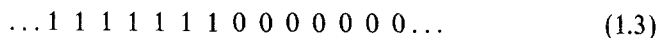
in Fig. 1. Letting 0 and 1 represent, respectively, lattice sites unoccupied and occupied by a particle, then the basic reaction is the switching of a 0 and a 1 as follows:



Incorporating the influence of nearest-neighbor particles, one has three basic different types of reaction (where the sites involved in the switch of state are underlined):



The specific process that we will study is the evolution toward a uniform density of the “two-phase” state where, at zero time, half of the lattice is filled and the other half is empty (as illustrated in Fig. 1b):



We give the coefficients in the time-power series for the species on either side of the original phase boundary through 11th order in the time. We will

label the sites in the neighborhood of the boundary between all 1's and all 0's as follows:

$$\begin{array}{cccccccc}
 \text{(occupancy of site)} & \dots & 1 & & 1 & & 1 & & 0 & & 0 & & 0 & \dots \\
 \text{(site number)} & \dots & (-3) & & (-2) & & (-1) & & (0) & & (1) & & (2) & \dots
 \end{array} \tag{1.4}$$

Thus we begin with the initial condition

$$\begin{aligned}
 P_m(t=0) &= 1 & (m < 0) \\
 P_m(t=0) &= 0 & (m \geq 0)
 \end{aligned} \tag{1.5}$$

while at infinite time the density is uniform (there can be no equilibrium phase boundary in the one-dimensional nearest-neighbor Ising model)

$$P_m(t = \infty) = 1/2 \quad (\text{all } m) \tag{1.6}$$

We will focus attention on the density at the original boundary; specifically we consider the following function [the subscript x refers to the temperature-dependent Boltzmann factor between nearest-neighbor occupied lattice sites; see (2.3)]

$$q_x = 2P_{-1} - 1 = \begin{cases} 1 & \text{as } t \rightarrow 0 \\ 0 & \text{as } t \rightarrow \infty \end{cases} \tag{1.7}$$

which, as indicated, will decay to zero at long times. For magnetic systems q_x is the magnetization. We anticipate that the function q_x will decay as a power law in the time (as illustrated for the high-temperature limit in Fig. 2)

$$q_x \sim t^{-\gamma} \tag{1.8}$$

We have recently been successful in extracting power-law exponents from time-power series for the growth of Eden clusters,⁽⁴⁾ $A + B \rightarrow 0$ type reaction-diffusion systems,⁽⁵⁾ and aggregation processes obeying the Smoluchowski equation (with general sum or product kernels).⁽⁶⁾ For all present system, involving diffusion alone, we utilize yet another approach as follows.

In the high-temperature limit (where excluded volume is retained, but the nearest-neighbor attractive interactions vanish) one can solve the diffusion problem exactly for the one-dimensional lattice gas for arbitrary initial conditions (arbitrary density) in terms of appropriate functions for single-particle random walks (illustrated in Fig. 1c). We will refer to the high-temperature limit of the function q_x described in (1.7) simply as q . We

thus know q exactly. One of the known properties of the high-temperature limit is its asymptotic behavior at large t ,

$$q \sim t^{-1/2} \quad (1.9)$$

where in the infinite-temperature limit one has $\gamma = 1/2$ as expected for diffusion. Using the function q , we can convert the time-power series for q_x into an expansion in terms of q in the following form:

$$[1 - q_x] = \sum_{n=1}^{\infty} a_n [1 - q]^n \quad (1.10)$$

Given a finite number of terms in the time-power series for q_x we can obtain the same number of terms in the expansion of (1.10). The asymptotic properties of q_x can be explored as a function of q [whose asymptotic behavior is known from (1.9)].

We will proceed as follows. In the next section we outline the calculation of the exact time-power series for our one-dimensional lattice gas with nearest-neighbor interactions. Then we review the solution for the high-temperature limit, using Glauber's method. It will turn out that for excluded volume only (infinite temperature), mean field theory is exact for this model. We next review the mean field approximation at general temperature as applied to our model (where it is not exact). We then illustrate the function expansion of (1.10) and give numerical examples. Finally, in the discussion we outline why other, more direct approaches to the calculation of the power-law exponent do not work in this case.

2. EXACT POWER SERIES IN THE TIME

We have previously discussed the kinetic parameters for the one-dimensional Ising model in terms of breaking and forming bonds; our treatment follows that work.⁽²⁾ We will take the activation energy ε^\ddagger to break a nearest-neighbor bond as a fraction (varying from zero to one) of the bond energy

$$\varepsilon^\ddagger = -\alpha\varepsilon \quad (2.1)$$

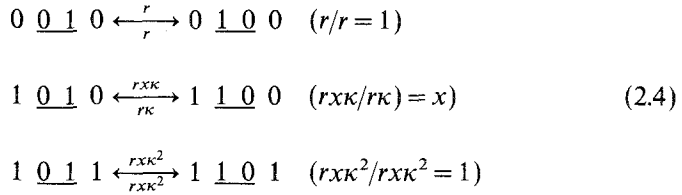
so that the rate factor associated with breaking a bond becomes

$$\kappa = x^{-\alpha} \quad (2.2)$$

where

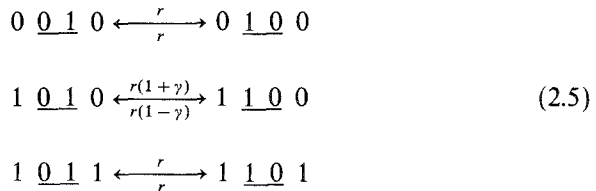
$$x = \exp(-\varepsilon/kt) \quad (2.3)$$

is the equilibrium Boltzmann factor for forming a nearest-neighbor bond. If κ is the rate factor for breaking a bond, then by detailed balance $x\kappa = x^{1-\alpha}$ must be the rate factor for forming a bond. Taking r as the basic rate parameter for diffusion (site hopping) with no nearest-neighbor bonds being formed or broken, one then has the specific rate constants for the reactions in (1.2):



The ratio of the forward to the backward rate constants for each process is indicated; notice that, as required by detailed balance, only the middle reaction results in a net change in the number of bonds.

Another scheme for the rate parameters is one similar to that introduced by Glauber⁽⁷⁾ for the change of a single spin influenced by states of neighboring spins:



where, again from detailed balance,

$$\frac{1+\gamma}{1-\gamma} = x
 \tag{2.6}$$

Note that in the scheme of (2.5) an isolated particle and an isolated hole (0-state) diffuse at the same rate.

To obtain exact series expansions in the time for the occupation probabilities of sites on a linear lattice with the initial condition of (1.3), one observes that to obtain n exact derivatives of the occupation probabilities one need consider only configurations involving n moves or less [relative to the initial configuration of (1.3)]. Indicating the number of

moves by subscripts, the following species (showing all configurations involving 2 moves or less)

$$\begin{aligned}
 (S_0) & \quad + + + - - - \\
 (S_1) & \quad + + - + - - \\
 (S_{2a}) & \quad + + - - + - \\
 (S_{2b}) & \quad + - + + - -
 \end{aligned} \tag{2.7}$$

are described by the following differential equations [using the rate parameters of (2.4); we let the symbol S_k designate both a lattice configuration and its probability]:

$$\begin{aligned}
 \frac{dS_0}{dt} &= (x\kappa)S_1 - (\kappa)S_0 \\
 \frac{dS_1}{dt} &= (\kappa)S_0 - (1 + x\kappa + x\kappa^2)S_1 + S_{2a} + (x\kappa^2)S_{2b} \\
 \frac{dS_{2a}}{dt} &= S_1 + \dots \\
 \frac{dS_{2b}}{dt} &= (x\kappa^2)S_1 + \dots
 \end{aligned} \tag{2.8}$$

The site occupation probabilities [using the labeling of (1.3)] are given in terms of the S_k , for example,

$$\begin{aligned}
 P_{-1} &= S_0 + S_{2b} + \dots \\
 P_0 &= S_1 + S_{2b} + \dots \\
 P_1 &= S_{2a} + \dots
 \end{aligned} \tag{2.9}$$

where the additional terms indicated, but not shown, are for species involving more than two moves.

To obtain a power series in the time, we follow procedures previously outlined.^(1,2) The relations in (2.9) can be generalized by introducing a row vector \mathbf{s} , whose general k th element is the probability of the S_k lattice configuration, and a column vector \mathbf{v}_m whose general k th element is the occupation number (0 or 1) of the m th lattice site in lattice configuration S_k . One then has

$$P_m = \mathbf{s} \cdot \mathbf{v}_m \tag{2.10}$$

Equations (2.8) can be written in terms of the vector \mathbf{s} as follows:

$$\frac{d\mathbf{s}}{dt} = -\mathbf{s}\mathbf{W} \tag{2.11}$$

where \mathbf{W} is the appropriate matrix of rate parameters. Writing the S_k as power series in time

$$S_k = \sum_{n=0}^{\infty} S_k^{(n)} t^n / n! \tag{2.12}$$

then, on taking successive derivatives, evaluated at $t=0$, one has (where $\mathbf{s}^{(n)}$ is a vector whose general element is $S_k^{(n)}$)

$$\mathbf{s}^{(n)} = (-1)^n \mathbf{s}^{(0)} \mathbf{W}^n \tag{2.13}$$

Finally, writing $P_m(t)$ as a power series in the time

$$P_m(t) = \sum_{n=0}^{\infty} P_m^{(n)} t^n / n! \tag{2.14}$$

where

$$P_m^{(n)} = \left(\frac{d^n P_m}{dt^n} \right)_{t=0} \tag{2.15}$$

one has [combining (2.10)–(2.14)]

$$P_n^{(m)} = (-1)^m \mathbf{s}^{(0)} \mathbf{W}^m \mathbf{v}_n P_m^{(n)} = (-1)^n \mathbf{s}^{(0)} \mathbf{W}^n \mathbf{v}_m \tag{2.16}$$

All of the species S_k as in (2.7) are easily generated by computer, as is the matrix \mathbf{W} ; the series are then obtained by simple matrix multiplication. For calculating exactly the first m derivatives requires a square matrix of linear dimension 4, 7, 12, 19, 30, 45, 61, 83, 111, and 143 for $n=2$ to $n=11$, respectively. The matrices thus get large, but we are able to determine a fairly large number of exact coefficients in the time power series. We have determined all of the coefficients $P_m^{(n)}$ for lattice sites in the vicinity of the original boundary through $n=11$; these are available from the authors on request. For example, the first three coefficients for the lattice sites immediately on either side of the original boundary [as defined in (1.3)] are (where $w = \kappa x$)

$$\begin{aligned} P_{-1}^{(0)} &= 1, & P_{-1}^{(1)} &= -\kappa, & P_{-1}^{(2)} &= \kappa^2 + w\kappa + w\kappa^2 \\ P_{-1}^{(3)} &= -(-\kappa^2 + \kappa^3 + w\kappa + 3w\kappa^2 + w\kappa^3 + w^2\kappa + 2w^2\kappa^2 + 2w^2\kappa^3) \\ P_0^{(0)} &= 0, & P_0^{(1)} &= \kappa, & P_0^{(2)} &= -(\kappa + \kappa^2 + w\kappa) \\ P_0^{(3)} &= 2\kappa + \kappa^2 + \kappa^3 + 2w\kappa + 3w\kappa^2 - w\kappa^3 + w^2\kappa + w^2\kappa^2 \end{aligned} \tag{2.17}$$

3. THE HIGH-TEMPERATURE LIMIT

In this section we will apply the method of Glauber⁽⁷⁾ to obtain a stochastic model of relaxation in a system where the basic reaction is given by the process of (1.1), i.e., single-particle site hopping. The method of Glauber has been applied by Kawasaki⁽⁸⁾ to the switching of nearest-neighbor spins in the magnet, a model that is the exact equivalent of particle diffusion. We will follow Glauber's notation closely. We let σ_m be a double-valued variable indicating the state of occupancy of the m th site on the lattice. The quantity σ can have the values $+1$ (indicating an occupied site) and -1 (indicating a vacant site); since we will make use of the mathematical properties of σ , this choice is more useful than letting 1 and 0 represent the occupancy of a site. Let $P\{\sigma\}$ be the *a priori* probability of a particular lattice configuration, $\{\sigma\}$ being a vector of σ values giving the state of occupancy of all the sites on the lattice. Then the master equation for the time rate of change of $P\{\sigma\}$ is

$$\begin{aligned} \frac{dP\{\sigma\}}{dt} = & -\sum_n w_n(\sigma_n, \sigma_{n+1}) P(\sigma_1 \cdots \sigma_n \sigma_{n+1} \cdots) \\ & + \sum_n w_n(-\sigma_n, -\sigma_{n+1}) P(\sigma_1 \cdots -\sigma_n -\sigma_{n+1} \cdots) \end{aligned} \quad (3.1)$$

where $w_n(\sigma_n, \sigma_{n+1})$ is the transition probability for the reaction $(\sigma_n, \sigma_{n+1}) \rightarrow (-\sigma_n, -\sigma_{n+1})$. Equation (3.1) can be written more compactly as

$$\frac{dP\{\sigma\}}{dt} = -\sum_n \sum_{\alpha=\pm 1} \alpha w_n(\alpha\sigma_n, \alpha\sigma_{n+1}) P(\sigma_1 \cdots \alpha\sigma_n, \alpha\sigma_{n+1} \cdots) \quad (3.2)$$

Multiplying by σ_m and summing over $\{\sigma\}$, one finds

$$\frac{d\langle\sigma_m\rangle}{dt} = -2 \sum_{\{\sigma\}} \sigma_m (w_m + w_{m-1}) P\{\sigma\} \quad (3.3)$$

The asymmetric form of (3.3) results from our choice of describing the switching as involving sites m and $m+1$; we alternatively could have chosen $m-1$ and m . On using symmetric w 's, the resulting equation will of course be symmetric, as we will see shortly.

In Glauber's original work he treated the case of the change of a single σ value (flip of a single spin in the magnet or the addition, or adsorption, of a particle in the lattice gas). His basic analog of (3.3) has the form

$$\frac{d\langle\sigma_m\rangle}{dt} = -2 \sum_{\{\sigma\}} \sigma_m w_m^* P\{\sigma\} \quad (3.4)$$

where w_m^* is the transition probability in lattice gases for the adsorption-desorption process. If both adsorption-desorption and switching (diffusion) processes can occur simultaneously, then one obtains

$$\frac{d\langle\sigma_m\rangle}{dt} = -2 \sum_{\{\sigma\}} \sigma_m (w_m^* + w_m + w_{m-1}) P\{\sigma\} \quad (3.5)$$

The presence of internal diffusion will effect the rate of adsorption even if the system is uniform (readjusting microconfigurations on the lattice influences the sites available for adsorption).

In the high-temperature limit one has $x = 1$ and $\kappa = 1$, which reduces the kinetics to a study of independent particles, the only interaction being the restriction that only one particle can occupy a given site (which means, of course, that a particle cannot move to a neighboring site if it is already occupied). In this case the transition probability for the process given in (1.1) for a one-dimensional lattice gas is

$$w_m = \frac{1}{2} r \sigma_m (\sigma_m - \sigma_{m+1}) \quad (3.6)$$

which is zero for the $(m, m + 1)$ configurations $(++)$ and $(--)$ and is r (the basic rate parameter for switching) for $(-+)$ and $(+-)$. Using (3.6) in (3.3) yields

$$\frac{d\langle\sigma_m\rangle}{d(rt)} = \langle\sigma_{m-1}\rangle - 2\langle\sigma_m\rangle + \langle\sigma_{m+1}\rangle \quad (3.7)$$

Since

$$\langle\sigma_m\rangle = P_m - (1 - P_m) \quad (3.8)$$

where P_m is the *a priori* probability site m is occupied, (3.7) can be written as

$$\frac{dP_m}{d(rt)} = P_{m-1} - 2P_m + P_{m+1} \quad (3.9)$$

Equation (3.9) is the differential equation for the symmetric random walk of a single particle,

$$\dots(m-1) \overset{r}{\leftarrow} (m) \overset{r}{\rightarrow} (m+1)\dots \quad (3.10)$$

Thus, many-body diffusion of independent particles on a lattice where multiple particle occupancy of a site is forbidden is given exactly by the superposition of single-particle random walks. In addition, the solution for

diffusion on two- and three-dimensional lattices is obtained by simply taking the products of the probability distributions for independent random walks in each dimension.

In what follows we will take $r = 1$, which is equivalent to scaling time so as to introduce a new variable $t' = rt$ (for simplicity, we drop the prime).

To incorporate specific initial conditions, it is more convenient to deal with conditional probabilities. Let $P(n(0)|m(t))$ be the conditional probability that a particle is a site n at time t having started at site m at $t = 0$. Then for a single-particle symmetric random walk $P(n|m)$ obeys the same differential-difference equation as P_m ,

$$\frac{dP(n|m)}{dt} = P(n|m-1) - 2P(n|m) + P(n|m+1) \tag{3.11}$$

which has the solution

$$P(n(0)|m(t)) = e^{-2t} I_{m-n}(2t) \tag{3.12}$$

where I_{m-n} is the modified or imaginary Bessel function. The general solution for the average site density, P_m , is then given by

$$P_m(t) = \sum_n P_n(0) P(n(0)|m(t)) \tag{3.13}$$

where $P_n(0)$ are the arbitrary initial site densities.

If we consider the special initial conditions of (1.3), i.e.,

$$\begin{aligned} P_n(0) &= 0 & (n \geq 0) \\ P_n(0) &= 1 & (n < 0) \end{aligned} \tag{3.14}$$

then combining (3.12)–(3.14), one has

$$\begin{aligned} P_m(t) &= e^{-2t} \sum_{n=-1}^{-\infty} I_{m-n}(2t) \\ &= e^{-2t} \sum_{k=m+1}^{\infty} I_k(2t) \end{aligned} \tag{3.15}$$

Using the following properties of the imaginary Bessel functions⁽⁹⁾

$$\begin{aligned} I_k &= I_{-k} \\ e^{-2t} \sum_{k=-\infty}^{\infty} I_k(2t) &= 1 \end{aligned} \tag{3.16}$$

we find that (3.15) becomes

$$P_m(t) = \frac{1}{2} + \frac{1}{2}e^{-2t}I_0(2t) - e^{-2t} \sum_{n=0}^m I_n(2t) \quad (m \geq 0)$$

$$P_{-m} = 1 - P_{m-1}$$
(3.17)

The first few specific cases of (3.17) are

$$P_0 = \frac{1}{2} - \frac{1}{2}e^{-2t}I_0(2t)$$

$$P_1 = \frac{1}{2} - \frac{1}{2}e^{-2t}I_0(2t) - e^{-2t}I_1(2t)$$

$$P_2 = \frac{1}{2} - \frac{1}{2}e^{-2t}I_0(2t) - e^{-2t}I_1(2t) - e^{-2t}I_2(2t)$$
(3.18)

and

$$P_{-1}(t) = \frac{1}{2} + \frac{1}{2}e^{-2t}I_0(2t)$$
(3.19)

Using the definition of (1.7), we then have

$$q = e^{-2t}I_0(2t)$$
(3.20)

The general form of the modified Bessel function is

$$I_n(2t) = t^n \sum_{k=0}^{\infty} \frac{t^{2k}}{k!(k+n)!}$$
(3.21)

while the asymptotic form⁽⁹⁾ for large t is

$$I_n(2t) = \frac{e^{2t}}{(4\pi t)^{1/2}} \left[1 + \frac{\mu-1}{16t} + \frac{(\mu-1)(\mu-9)}{2!(16t)^2} - \frac{(\mu-1)(\mu-9)(\mu-25)}{3!(16t)^3} + \dots \right]$$
(3.22)

where

$$\mu = 4n^2$$
(3.23)

The expansion of $q(t)$ about the origin is then

$$q(t) = 1 - 2t + 6t^2/2! - 20t^3/3! + 70t^4/4! - 252t^5/5! + 924t^6/6! - 3432t^7/7! + 12,870t^8/8! - 48,620t^9/9! + 184,756t^{10}/10! - 705,432t^{11}/11! + \dots$$
(3.24)

In the limit of $x \rightarrow 1$, the series for general x described in Section 2 for q_x reduce to the above series. At large t , the asymptotic form of $I_0(2t)$ is given by⁽⁹⁾

$$I_0(2t) = \frac{e^{2t}}{(4\pi t)^{1/2}} \left(1 + \frac{1}{16t} + \frac{9}{512t^2} + \frac{75}{8192t^3} + \dots \right)$$
(3.25)

giving for $q(t)$

$$q(t) \sim (0.2821) \frac{1}{\sqrt{t}} \left[1 + (0.0625) \frac{1}{t} + (0.01758) \frac{1}{t^2} + (0.009155) \frac{1}{t^3} + \dots \right] \tag{3.26}$$

In Fig. 2 we compare the exact $q(t)$, giving the decay of the boundary probability in the high-temperature limit, given by (3.20) and shown as a solid curve, with the approximation (solid diamonds)

$$q(t) \sim (0.2821)t^{-1/2} \tag{3.27}$$

In Eq. (3.27), $q(t) \rightarrow \infty$ as $t \rightarrow 0$; otherwise (3.27) is a remarkably good approximation to the exact function over a large range of t values. We note that q is also the probability that an isolated particle (e.g., as shown in Fig. 1c) remains at a given lattice site as a function of time.

We note in passing that the generalization of (3.5) to higher-order expectation values is

$$\begin{aligned} & d\langle \sigma_i \sigma_j \dots \rangle / dt \\ &= -2 \sum_{\{\sigma\}} \sigma_i \sigma_j \dots [(w_i + w_{i-1}) + (w_j + w_{j-1}) + \dots + w_i^* + w_j^* + \dots] P\{\sigma\} \end{aligned} \tag{3.28}$$

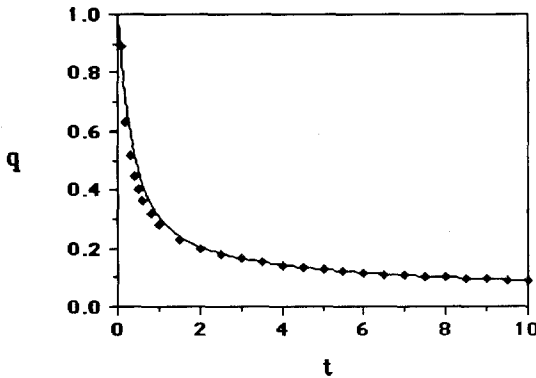


Fig. 2. Probability of a single particle (initial condition of Fig. 1c) remaining at the initial site, which is the same as the function q_x of (1.7) in the high-temperature limit. The solid curve is the exact solution of (3.20), while the solid diamonds are the approximation of (3.27).

Restricting the system to diffusion only (setting $w^* = 0$) and using (3.6) for w , one finds

$$\langle \sigma_i \sigma_j \dots \rangle = \langle \sigma_i \rangle \langle \sigma_j \rangle \dots \tag{3.29}$$

The factorization of (3.29) is the basic assumption of mean field theory, which we see is exact in the high-temperature limit for our model.

4. MEAN FIELD APPROXIMATION

In the previous section we found that in the high-temperature limit the mean field assumption, Eq. (3.29), was in fact exact. In this section we construct the necessary equations to obtain the mean field approximation at a general temperature for cooperative diffusion relative to the results obtained with the exact series expansions. We begin by constructing the differential equations for diffusion using Glauber’s approach. The basic unit for cooperative diffusion in one dimension, is a quartet of contiguous sites, which we label as follows:

$$\sigma_{m-1} \sigma_m \sigma_{m+1} \sigma_{m+2} \tag{4.1}$$

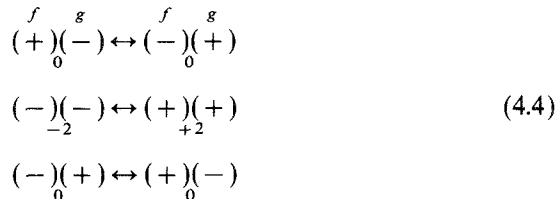
where $\sigma_i = \pm 1$, indicating the presence or absence of a particle at site i . We introduce the functions

$$\begin{aligned} f_m &= \sigma_{m-1} \sigma_m \\ g_m &= \sigma_{m+1} \sigma_{m+2} \end{aligned} \tag{4.2}$$

which have the property

$$\begin{aligned} f, g &= +1 && \text{for like } \sigma\text{'s} \\ f, g &= -1 && \text{for unlike } \sigma\text{'s} \end{aligned} \tag{4.3}$$

The basic diffusion reactions of (1.2) have the following structure in terms of the appropriate f and g factors (the numbers below a doublet give the sum, $f + g$):



One observes that in order only the proper switching reactions, one requires the factor w_m of (3.6), while in order to assign the correct γ terms of (2.5), one needs the following factor:

$$u_m = 1 - (\gamma/2)(f_m + g_m) \quad (4.5)$$

The differential equation for cooperative diffusion using the Glauber-like assignment of parameters given in (2.5) is then

$$\frac{d\langle\sigma_m\rangle}{dt} = -2 \sum_{\{\sigma\}} \sigma_m (w_m u_m + w_{m-1} u_{m-1}) \quad (4.6)$$

which gives [setting the basic diffusion parameter r of (2.5) equal to one]

$$\begin{aligned} dq_m/dr &= (q_{m-1} - 2q_m + q_{m+1}) \\ &+ (\gamma/2)(-q_{m-2} + q_{m-1} + q_{m+1} - q_{m+2} + s_{m-1} + 2s_m + s_{m+1}) \end{aligned} \quad (4.7)$$

where [with (3.8) this is q of (1.7)]

$$q_m = \langle\sigma_m\rangle, \quad s_m = \langle\sigma_{m-1}\sigma_m\sigma_{m+1}\rangle \quad (4.8)$$

In the high-temperature limit $x = 1$ one has, from (2.6), $\gamma = 0$, in which case (4.7) reduces to (3.7).

Using the simplest form of closure (mean-field approximation) gives

$$s_m = q_{m-1}q_mq_{m+1} \quad (4.9)$$

From (3.8) we have the relation

$$P_m = (1 + q_m)/2 \quad (4.10)$$

For the border site $m = -1$ [see (1.4)] one has

$$\begin{aligned} P^{(0)} &= 1, & P^{(1)} &= -(1 - \gamma), & P^{(2)} &= 3(1 - \gamma) \\ P^{(3)} &= -10(1 - \gamma)(1 + 3\gamma/5) \end{aligned} \quad (4.11)$$

while the mean-field equations of (4.7) and (4.9) yield

$$\begin{aligned} P^{(0)} &= 1, & P^{(1)} &= -(1 - \gamma), & P^{(2)} &= 3(1 - \gamma)(1 - \gamma) \\ P^{(3)} &= -10(1 - \gamma)[(1 - \gamma)^2 - 4\gamma(1 - \gamma)] \end{aligned} \quad (4.12)$$

One sees that the mean-field approximation gives the derivatives exact only through the first derivative.

In order to treat the more general case of the transition probabilities used in (2.4) for the special case of $\alpha = 1/2$, the following factor is required:

$$u_m = \left(\frac{1 - f_m g_m}{2} \right) + \left(\frac{1 + f_m g_m}{2} \right) \left\{ \frac{1}{2} \left[1 + \left(\frac{f_m + g_m}{2} \right) \right] \frac{1}{\sqrt{x}} + \frac{1}{2} \left[1 - \left(\frac{f_m + g_m}{2} \right) \right] \sqrt{x} \right\} \tag{4.13}$$

Using the w_m of (3.6) with (4.13) in (4.6) gives the required differential equation:

$$\begin{aligned} dq_m/dt = & aq_{m-1} - 2(a-b)q_m + aq_{m+1} - b(q_{m-2} + q_{m+2}) \\ & + b(s_{m-1} - 2s_m + s_{m+1}) \\ & + (1-a+b)[s'_m(-2, -1, 1) - s'_m(-2, 0, 1) \\ & - s'_m(-1, 0, 2) + s'_m(-1, 1, 2)] \end{aligned} \tag{4.14}$$

where

$$a = \frac{1}{2}(1 + \sqrt{x}), \quad b = \frac{1}{4}(\sqrt{x} - 1/\sqrt{x}) \tag{4.15}$$

and

$$s'_m(i, j, k) = \langle \sigma_{m+i} \sigma_{m+j} \sigma_{m+k} \rangle \tag{4.16}$$

In the high-temperature limit as $x \rightarrow 1$ one has

$$\sqrt{x} \sim 1 + \gamma', \quad 1/\sqrt{x} \sim 1 - \gamma' \tag{4.17}$$

giving

$$a = 1 + \gamma'/2, \quad b = \gamma'/2, \quad a - b = 1, \quad 1 - a + b = 0 \tag{4.18}$$

Using (4.18) in (4.14) with $\gamma = \gamma'$ reduces (4.14) to (4.7). Of course the Glauber form is exact for all temperatures; it is only as one approaches the high-temperature limit that the forms of (4.14) and (4.7) become equivalent. In the high-temperature limit, we have from (4.15) that $a = 1$ and $b = 0$, in which case (4.14) reduces to (3.7).

In principle it is not difficult to go beyond the mean field approximation by using higher-order closure approximations. The basic rate equation involves contiguous quartets of lattice sites. Thus in the mean field approximation the basic assumption is that quartet probabilities can be written as

$$P_{\sigma_j \sigma_j \sigma_k \sigma_l} = P_{\sigma_i} P_{\sigma_j} P_{\sigma_k} P_{\sigma_l} \tag{4.19}$$

in analogy with (4.9). A higher-order level of closure is obtained by writing the quartet probability as a Markov chain, e.g.,

$$P_{\sigma_i \sigma_j \sigma_k \sigma_l} = P_{\sigma_i} P(\sigma_i | \sigma_j) P(\sigma_j | \sigma_k) P(\sigma_k | \sigma_l) \quad (4.20)$$

where P_{σ_i} is the *a priori* probability that site i is in state σ_i , while $P(\sigma_i | \sigma_j)$ is the conditional probability that given state σ_i at site i , state σ_j follows at site j .

5. EXPANSIONS IN q

In Section 3 we gave the exact series solution for q_x of (1.7) in the high-temperature limit, which we called q . The exact closed-form solution for q in terms of a Bessel function was given in (3.20); the expansion about $t=0$ was given in (3.24); and the expansion about large t was given in (3.26). For reference we repeat here the beginning terms of the expansion about the origin,

$$q = 1 - 2t + 6t^2/2! + \dots \quad (5.1)$$

In Section 2 we outlined the construction of the exact series for finite temperatures. The function q_x begins [see (1.7) and (2.17)]

$$q_x = 1 - 2\kappa t + 2(1 + x + x\kappa)(\kappa t)^2/2! + \dots \quad (5.2)$$

We then introduce the following function (with a similar definition for y_x in terms of q_x)

$$y = 1 - q = \begin{cases} 0 & \text{as } t \rightarrow 0 \\ 1 & \text{as } t \rightarrow \infty \end{cases} \quad (5.3)$$

From (5.1) and (5.2) one has y_x and y , respectively, as series in t . One can then eliminate t between the two functions and give y_x as a series in y . We will use $y(\kappa(t))$ so as to make the first terms (initial slopes) in y and y_x identical. As an example, for the case of $x=4$ and $\alpha=1/2$, one finds

$$\begin{aligned} y_x = & y - y^2 + (0.625) y^3 + (0.11458) y^4 + (0.00521) y^5 + (0.04431) y^6 \\ & + (0.04680) y^7 + (0.05289) y^8 + (0.05823) y^9 + (0.06328) y^{10} \\ & + (0.06797) y^{11} + \dots \end{aligned} \quad (5.4)$$

One sees that the series is quite well behaved; the beginning terms dominate and the coefficients of the higher-order terms are small and of uniform sign.

One can proceed in a similar manner for the case of the mean field approximation. We use the mean field approximation of (4.9) in (4.14) and obtain a recursion relation for the coefficients in the time-power series, in analogy with (5.2). We then define a quantity y_{mf} , in analogy with y of (5.3), and then expand y_{mf} in powers of y . Again using the case of $x = 4$ and $\alpha = 1/2$ as an example, one finds (no y^2 term)

$$\begin{aligned}
 y_{mf} = & y - (0.125) y^3 - (0.19271) y^4 - (0.04115) y^5 + (0.03828) y^6 \\
 & + (0.08317) y^7 + (0.07737) y^8 + (0.06207) y^9 + (0.04646) y^{10} \\
 & + (0.03868) y^{11} + \dots
 \end{aligned}
 \tag{5.5}$$

As with (5.4), the beginning terms dominate and the coefficients of the higher-order terms are well behaved.

In Fig. 3 we show y_x and y_{mf} as a function of y as given by the truncated series of (5.4) and (5.5), respectively. The dashed parts of the curves are extrapolations to the known limit $y_x = y_{mf} = 1$ at the point $y = 1$. One notes that as y is increased one has

$$y > y_{mf} > y_x
 \tag{5.6}$$

that is, the mean field approximation overestimates the rate of decay to the equilibrium state. As $x \rightarrow 1$ ($T \rightarrow \infty$) one would have

$$(T \rightarrow \infty) \quad y = y_{mf} = y_x
 \tag{5.7}$$

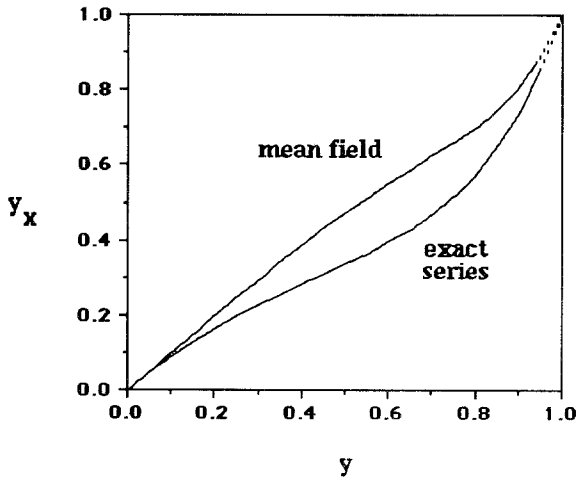


Fig. 3. The function $y_x = 1 - q_x$ [with q_x defined in (1.7)], for cooperative diffusion as a function of the corresponding quantity $y = 1 - q$ (with q the higher-temperature limit of q_x). The curve marked “exact series” is obtained from Eq. (5.4), while the mean-field curve is a plot of Eq. (5.5). The dashed portion of the curves is an extrapolation to the known limit.

The value of x used in Fig. 3 represents only a very moderate degree of cooperative interaction. The value $x=4$, from (2.3), corresponds to $-\varepsilon/kT=1.34$, which is typical of a weak van der Waals interaction. One sees in Fig. 3 that the mean field approximation does not give a very good description of the time evolution of the cooperative system in our one-dimensional system. As mentioned at the end of Section 4, a higher form of closure beyond mean field would undoubtedly give better results.

From Fig. 3 it appears that y_x goes to one linearly with y (i.e., there is no tendency for the function to hook in to the value $y_x=1$ with either infinite or zero slope). If this is so, then we have

$$(t \rightarrow \infty) \quad q_x \sim q \quad (5.8)$$

From (3.27) we know that q varies as $t^{-1/2}$ for large t . Thus, if we accept (5.8), we have

$$(t \rightarrow \infty) \quad q_x \sim t^{-1/2} \quad (5.9)$$

6. DISCUSSION

In the previous section we saw that expansions of q_x in terms of q , the high-temperature limit, are useful for cooperative diffusion. Here we explore why more direct approaches to the extraction of the power-law exponent do not work well in this case. We will focus on the high-temperature limit, since we know the exact solution in terms of a Bessel function [Eq. (3.20)], the series expansion about $t=0$ [Eq. (3.21)], and the asymptotic series for large t [Eq. (3.22)].

One straightforward approach⁽⁴⁾ would be to introduce the Euler transform

$$s = t/(1+t), \quad t = 1/(1-s) \quad (6.1)$$

which maps the infinite interval $t=0$ to ∞ onto the finite interval $s=0$ to 1. From (5.9) we expect $q(s)$ to have the form

$$q(s) \sim (1-s)^\gamma \quad (6.2)$$

where we know that $\gamma=1/2$. Taking the logarithmic derivative of $q(s)$, one has [defining $\Theta(s)$]

$$(1-s)d \ln(q)/d \ln(s) = -\Theta(s) \quad (6.3)$$

$$(\lim s \rightarrow 1) \quad \Theta(s) \rightarrow \gamma = 1/2$$

Using the series of (3.21), one obtains (no square term)

$$\begin{aligned} \Theta(s) = & 2s - 2s^3 - 3s^4 - 2s^5 + 1(1/3)s^6 + 6s^7 + 9(33/72)s^8 \\ & + 8(1/3)s^9 + (11/60)s^{10} - 14(1/6)s^{11} + \dots \end{aligned} \tag{6.4}$$

We can then construct Padé approximants to $\Theta(s)$. For example, using the first six terms of (5.14), we obtain

$$\Theta(s) \cong 2s \left[\frac{1 - (26/15)s + (3/5)s^2 + (7/30)s^3}{1 - (26/15)s + (8/5)s^2} \right] \tag{6.5}$$

The exact form $\Theta(t)$ is given by

$$\Theta(t) = 2t \left(1 - \frac{I_1(2t)}{I_0(2t)} \right) \tag{6.6}$$

Using (6.6) and (3.22), we find that the asymptotic form of $\Theta(s)$ is

$$s \rightarrow 1, \quad \Theta(s) = \frac{1}{2} + \frac{1}{16}(1-s) + \dots \tag{6.7}$$

The exact behavior of $\Theta(s)$ is shown in Fig. 4a, while the Padé approximant of (6.5) is shown in Fig. 4b. The main feature of Fig. 4a is that $\Theta(s)$ goes through a maximum before leveling off to the asymptotic value of $\gamma = 1/2$. While the Padé approximant reproduces the maximum accurately, it does not go to the proper limit as $s \rightarrow 1$; increasing the number of terms in the approximants increases the accuracy with which the curve fits the maximum, but does not improve the estimate of $\Theta(s = 1)$. Thus the information contained in the series is used to construct the maximum, but does not offer a reliable estimate of the exponent $\gamma = 1/2$. Thus, even though it looks like the $t^{-1/2}$ form in Fig. 2 is a remarkably good approximation to the exact form, the logarithmic slope only gives the correct exponent as $t \rightarrow \infty$.

Another way to evaluate the exponent γ is as follows. We use the function $y = 1 - q$ and the t series of (3.24) for q . We also introduce the scaled time

$$t' = 2t \tag{6.8}$$

but for simplicity we will henceforth drop the prime. Equation (3.24) then gives $y = y(t)$, which we can invert to give t as a function of y . From (3.27) the asymptotic form of $t = t(y)$ is

$$t \sim \left(\frac{1}{1-y} \right)^{1/\gamma} \tag{6.9}$$

We can write t formally as a power series in y as

$$t = \sum_{n=1}^{\infty} \alpha_n y^n \tag{6.10}$$

the first terms of which are

$$t = y + 0.75y^2 + 0.7083y^3 + 0.7292y^4 + 0.7833y^5 + 0.8619y^6 + \dots \tag{6.11}$$

One sees that this series is very well behaved, all of the coefficients being positive. If the singularity at $y = 1$ determines the radius of convergence of the function, then the ratios of successive coefficients

$$r_n = \alpha_n / \alpha_{n-1} \tag{6.12}$$

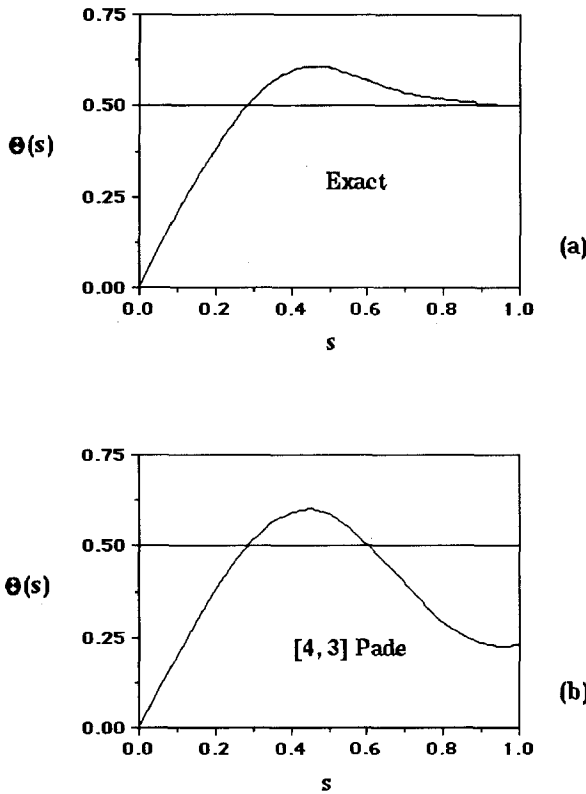


Fig. 4. (a) The exponent $\Theta(s)$ defined by (6.3), using the variable s of (6.1), given exactly in the high-temperature limit by (6.6). (b) The exponent $\Theta(s)$ as given by the Padé approximant of (6.5).

should be asymptotic to the form⁽¹⁰⁾

$$r_n = 1 + \frac{1}{n} \left[\frac{1}{\gamma} - 1 \right] \tag{6.13}$$

The ratios for (6.11) are shown in Fig. 5a for $n=5-20$; the solid curve is (6.13) with $\gamma=1/2$. Using (6.13), one can convert each r_n value into an estimate of γ , γ_n ; these values as a function of $1/n$ for $n=5-20$ are shown in Fig. 5b. One sees that the function is well behaved and the γ_n curve seems to be headed toward the value $\gamma=1/2$ (although oscillations cannot be ruled out, due to singularities in the complex plane).

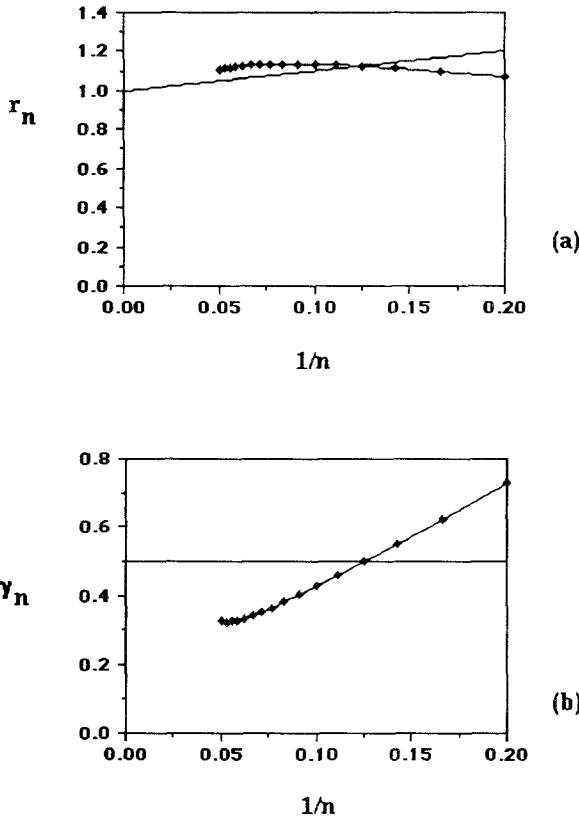


Fig. 5. (a) The ratios of the series defined by (6.11) for the single-particle random walk in the high-temperature limit. The solid line is (6.13) with $\gamma=1/2$. (b) The values of γ as a function of n , γ_n , calculated from the r_n values of Fig. 4a using (6.13). The solid line is the constant value $\gamma=1/2$.

Finally, we return to the case of diffusion at a general temperature. We use our time-power series to construct an accurate representation of $q_x(t)$ over the whole time range. We proceed by applying the s transformation of (6.1) to $q_x(t)$. From (5.9) we expect

$$\begin{aligned} q_x(s) &\sim (1-s)^{1/2} \\ q_x(s)^2 &\sim (1-s) \end{aligned} \quad (6.14)$$

We thus expect $q_x(t)^2$ to be the simpler function. The s -series expansion of q_x^2 is given by ($\alpha = 1/2$ and $x = 4$)

$$\begin{aligned} q_x(s)^2 = &1 - 2s + (2.5)s^2 - (1.5833)s^3 - (0.3646)s^4 + (0.3010)s^5 \\ &- (0.0263)s^6 - (0.0386)s^7 + (0.2910)s^8 + (0.3724)s^9 \\ &+ (0.03935)s^{10} - (0.3834)s^{11} - [0.1075]s^{12} \end{aligned} \quad (6.15)$$

In (6.15) the s^{12} term is added as a correction to force q^2 to go to zero as $s \rightarrow 0$; from (6.14) we expect q_x^2 to go to zero linearly with s . The s^{12} coefficient in square brackets in (6.15) is seen to be a small correction. The function of (6.15) has the exact first 11 derivatives and gives the asymptotic behavior of (6.14). One finds that for this system this procedure of adding on a correction term in fact works as well as or better than the use of Padé approximants. The series truncated at the 11th term, the series with a correction term, and Padé approximants all agree to three significant figures out to about $s = 0.75$. The series with the correction term then agrees well with the mean of the Padé approximants out to about $s = 0.9$. The Padé approximants in general do not go to zero (or even near zero) at $s = 1$. The behavior of the function defined in (6.15) is shown in Fig. 6.

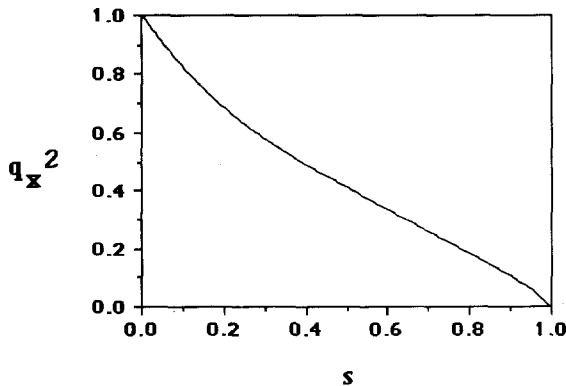


Fig. 6. The function $q_x(s)^2$ of Eq. (6.15) for cooperative diffusion. The curve shown is for $x = 4$ and $\alpha = 1/2$.

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