Study of a Lorentz-gas based on correlated walks[a]

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The dynamics of a Lorentz-gas molecule is simulated in terms of correlated walks on cubic lattices. For a finite lattice with reflecting boundary, the ergodicity is established so that the probability distribution in position and direction approaches a stationary state which is homogeneous (site-independent) and isotropic (direction-independent). Exact expressions for probability distribution in direction are obtained for simple, body-centered, and face-centered cubic lattices. They approach equilibrium exponentially with a different number of relaxation times depending on the lattice. The directional probabilities for a single-site lattice with reflecting boundary approach equilibrium in an oscillatory manner. The Boltzmann H-function for this system, however, shows a monotonic behavior, and coincides with the H-function for the same system with periodic boundary. The parameters in the model, step length and unit time, can be eliminated in the kinetic theoretical limit. In this limit, the diffusion coefficient calculated for the lattice reproduces the result by means of the Boltzmann equation within the restriction imposed on the directions of the movement.

I. INTRODUCTION

In the conventional random walks in one dimension,[1] the walker is allowed to move right or left on a line with the probabilities of steps given at random. In 1951 Goldstein proposed and studied a correlated walk model in which the step probabilities depend on the direction of the previous step.[2] Gillis and others obtained several interesting results on the correlated walks in n dimensions.[3] Manning applied the model for the study of atomic diffusion in crystals.[4] These works appear to have been buried in a huge amount of literature directed toward the random walks, proper and with self-avoiding restriction.[4,5] In our recent works, we have reported applications of correlated walks to various physical phenomena, including the conformation of polymers,[6] atomic diffusion in cubic crystals with impurities,[7] and the phase transition in Ising systems.[8]

In the present paper we establish a close connection between correlated walks and the Lorentz gas model. The following results are obtained.

(a) The correlated walks on a cubic lattice simulate the dynamics of a Lorentz gas molecule in a substantial manner. Only the directions of the movement are restricted to the nearest-neighbor directions associated with the chosen lattice.

(b) The diffusion coefficient obtained from the exact expression (3.6) for the mean square displacement, reproduces the result by means of the Boltzmann equation (2.2) within the aforementioned restriction on the directions. In particular, the diffusion coefficient is given in terms of the diffusion-relaxation rate Γ_1, which

incorporates the loss and gain processes with the well-known factor $(1 - \cos\theta)$, where θ is the scattering angle.

(c) The ergodic property of the Lorentz-gas-correlated-walk model is established for a *finite* lattice with reflecting boundary. At whatever lattice site and in whatever direction the particle (correlated walker) may start initially, the probability distribution approaches a stationary state that is "homogeneous" (site-independent) and "isotropic" (direction-independent) [see Eq. (5.1)].

(d) The approach to equilibrium of a "homogeneous" system is studied by calculating explicitly the probability distributions in direction, (4.8), (6.10), and (6.17), respectively, for simple cubic (sc), body-centered cubic (bcc), and face-centered cubic (fcc) lattices. The approach is of the exponential-decay type with a different number of relaxation times. All relaxation times approach the same value if the interaction is hard-sphere-like, so that the differential cross section should become isotropic.

(e) The approach to equilibrium as a whole may be studied in terms of the Boltzmann H-function [Eq. (4.12)]. This function calculated explicitly as a function of time shows a monotonic decrease to a stationary value.

(f) The probabilities in direction [Eq. (5.3)] for a single-site lattice with reflecting boundary show *oscillatory* approach to equilibrium. The H-function for this system however shows a monotonic behavior and happens to have the same H-function as that for the single-site lattice with periodic boundary. In spite of the difference in boundary, the probabilities for both cases are characterized by the same relaxation times.

Features (c)–(f) should also hold for the solutions of the Boltzmann equation with analogous initial and boundary conditions. It is significant that exact results are obtained for the lattice model of the Lorentz gas (the present model) while the Boltzmann equation for the same gas is more difficult to solve.

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In Sec. II we set up a correlated walk model on the sc lattice appropriate for the Lorentz gas. From the exact expression (3.6) for the mean square displacement, the diffusion coefficient is calculated in Sec. III. In the kinetic theoretical limit, Eqs. (3.14) and (3.15), in which the unit time τ and the step length a_0 in the model are eliminated while the speed and the mean free path of the Lorentz-gas particle are kept constant, the diffusion coefficient essentially reproduces the result by means of the Boltzmann equation. In Sec. IV, we study the approach to equilibrium of a homogeneous system by calculating the distribution functions in direction. Correlated walks on a finite lattice with reflecting boundary are discussed in Sec. V. In Sec. VI, correlated walks on bcc and fcc lattices are set up and discussed. A brief summary is given in Sec. VII.

II. LORENTZ GAS AND CORRELATED WALKS

In the so-called Lorentz gas model, particles move independently of each other in a potential field of fixed scatterers. The Hamiltonian H of the system is given by

$$H = \sum_{j=1}^{N} \frac{p_j^2}{2m} + \sum_{j=1}^{N} \sum_{\alpha=1}^{N_I} v(\mathbf{r}_j - \mathbf{R}_\alpha) , \qquad (2.1)$$

where $\mathbf{R}_1$, $\mathbf{R}_2$, ..., $\mathbf{R}_{N_I}$ are the positions of N_I scatterers.

In the calculation of thermodynamic properties of the particles, it is assumed that the positions of scatterers $\{\mathbf{R}_\alpha\}$ are distributed at random and characterized by the average density $n_I \equiv N_I/\Omega$ alone.

If this density n_I is low and the potential v has a short range, any given particle will be scattered *elastically* by one scatterer at a time. In this case, the following Boltzmann equation should hold[9]:

$$\frac{\partial f(\mathbf{r}, \mathbf{v}, t)}{\partial t} + \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{r}} = 2\pi n_I v \int_0^\pi d\theta \sin\theta \, I(v, \theta)$$

$$\times [\, f(\mathbf{r}, \mathbf{v}', t) - f(\mathbf{r}, \mathbf{v}, t)] , \qquad (2.2)$$

where $I(v, \theta)$ represents the differential scattering cross section and θ, the scattering angle, that is, the angle between $\mathbf{v}$ and $\mathbf{v}'$. Since only elastic scatterings enter here, each group of particles with a definite speed (and hence energy) will move independently of any other group. In then follows that Eq. (2.2) can be solved separately for each group of particles with the same speed. It is further known that the diffusion coefficient D calculated from (2.2) is given by[9]

$$D = \frac{1}{3} \left\langle \frac{v^2}{\Gamma_0} \right\rangle_0 , \qquad (2.3)$$

where

$$\Gamma_0(v) = 2\pi n_I v \int_0^\pi d\theta \sin\theta \, I(v, \theta)[1 - \cos\theta] \qquad (2.4)$$

is the diffusion relaxation rate, and the brackets $\langle \, \rangle_0$ represent the thermal average.

We now propose to simulate the dynamics of the particles in terms of correlated walks as follows. Let us take an sc lattice with a spacing a_0. A particle is allowed to move on the lattice sites with the same speed
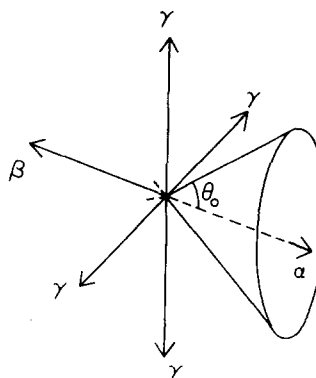

FIG. 1. The particle, after hitting a scatterer, will move forward, sideways, or backward with the probabilities α, γ, or β, respectively.

v and only along the cubic axes, that is, in the six directions $(x_+, x_-, y_+, y_-, z_+, \text{and } z_-$ directions). Impurities (scatterers) will now be distributed on lattice sites at random; each site is occupied by impurity with the same probability. If the particle hits a scatterer, which happens with probability q, it will move forward, reverse, or turn with the following probabilities:

$$\alpha_0(\text{forward}) = \frac{\int_0^{\theta_0} d\theta \, \sin\theta I(v, \theta)}{\int_0^\pi d\theta \, \sin\theta I(v, \theta)}$$

$$\beta_0(\text{reverse}) = \frac{\int_{\pi-\theta_0}^\pi d\theta \, \sin\theta I(v, \theta)}{\int_0^\pi d\theta \, \sin\theta I(v, \theta)} \qquad (2.5)$$

$$\gamma_0(\text{turn}) = \tfrac{1}{4}(1 - \alpha_0 - \beta_0) ,$$

where θ_0 is chosen such that the partial forward scattering corresponds to one sixth of the total solid angle 4π:

$$\tfrac{4}{6}\pi = 2\pi \int_0^{\theta_0} d\theta \, \sin\theta$$

or

$$\theta_0 = \cos^{-1}(\tfrac{2}{3}) . \qquad (2.6)$$

See Fig. 1.

If the particle does not hit the scatterer, which should happen with the probability $1 - q$, it should continue to move in the same direction.

In summary, the particle moves on the lattice with correlated directions as follows. It may proceed in the same direction as the previous direction with the probability $\alpha \equiv q\alpha_0 + (1 - q)$, turn back with the probability $\beta \equiv q\beta_0$, or turn at right angles (four possible directions) with the probability $\gamma \equiv q\gamma_0$.

It is clear that the dynamics of the particle moving on the lattice is very similar to that of the Lorentz gas particle. The major difference lies in the fact that the directions of the particle in our lattice model are restricted to the six general directions. If one is interested in the macroscopic properties of the gas, the step length a_0, which appears in the model, can be eliminated in a reasonable manner as we will see in Sec. III.

III. DIFFUSION COEFFICIENT

According to the rules prescribed in Sec. II the particle moves on the lattice one step per unit time:

$$\tau \equiv a_0/v \ . \tag{3.1}$$

Let $P_a(x, y, z, N)$ be the probability that the particle arrives at the site (xa_0, ya_0, za_0) with the direction a at the time $N\tau$. The six directions will be named by

$$(x_+, x_-, y_+, y_-, z_+, z_-) \equiv (1, 2, 3, 4, 5, 6) \ . \tag{3.2}$$

The probabilities of arrival with direction, P_a, will satisfy the following equations:

$P_1(x, y, z, N)$

$$= \alpha P_1(x-1, y, z, N-1) + \beta P_2(x-1, y, z, N-1)$$

$$+ \gamma \sum_{b=3, 4, 5, 6} P_b(x-1, y, z, N-1) \tag{3.3}$$

and similar equations for $P_2, \dots, P_6$. These difference equations may be solved subject to given initial conditions.

Let us first consider the case in which, at the initial time $N=0$, the particle arrives at the origin with the direction $a=1$; this can be expressed by

$$P_a(x, y, z, 0) = \delta_{x,0}\,\delta_{y,0}\,\delta_{z,0}\,\delta_{a,1} \ . \tag{3.4}$$

For small N, the solution may be worked out by drawing appropriate diagrams. The analytic solution for a general N is difficult to obtain. It is, however, known that moments such as

$$\langle r^2 \rangle \equiv \sum_a \sum_x \sum_y \sum_z (x^2+y^2+z^2) P_a(x, y, z, N) \tag{3.5}$$

can be obtained in terms of the solutions of the one-dimensional correlated walks.[7] The result for $\langle r^2 \rangle$ is as follows:

$$\frac{\langle r^2 \rangle}{a_0^2} = \frac{1+\Delta}{1-\Delta}\,N - \frac{2\Delta}{(1-\Delta)^2}\,(1-\Delta^N) \ , \tag{3.6}$$

where

$$\Delta \equiv \alpha - \beta \ . \tag{3.7}$$

For large N, the first term dominates except when $\alpha=1$, in which case $\langle r^2 \rangle$ equals $N^2 a_0^2$. The mean square displacement at the time $N\tau$ is connected with the diffusion coefficient D by[10]

$$\langle r^2 \rangle = 6DN\tau \quad \text{for large } N \ . \tag{3.8}$$

Using this relation, we obtain

$$D = \frac{1}{6}\,\frac{1+\Delta}{1-\Delta}\,a_0^2\tau^{-1} \ . \tag{3.9}$$

The diffusion coefficient D obtained here depends on the model parameters (a_0, τ), which may be eliminated in the following manner.

In the Lorentz gas model there exists a definite collision rate $1/\tau_0$ given by

$$1/\tau_0 = n_I v\sigma \ , \tag{3.10}$$

where

$$\sigma \equiv 2\pi \int_0^\pi d\theta \, \sin\theta \, I(v, \theta) \tag{3.11}$$

is the total cross section. The mean free path defined by

$$l \equiv v\tau_0 = (n_I\sigma)^{-1} \tag{3.12}$$

does not depend on the speed of the moving particle. The probability of moving without suffering collision, is proportional to the distance L traveled and should be given by L/l for small L. We may therefore postulate that the probability q of hitting a scatterer after the length of travel a_0 is given by

$$q = a_0/l = a_0 n_I \sigma \ , \tag{3.13}$$

which is valid for small a_0. Let us now define the *kinetic-theoretical limit*:

$$a_0 \to 0 \ , \quad \tau \to 0 \ , \tag{3.14}$$

such that

$$a_0/\tau = v \ (\text{speed}) = \text{finite} \ ,$$
$$(n_I\sigma)^{-1} = l \ (\text{mean free path}) = \text{finite} \ . \tag{3.15}$$

In this limit, the diffusion coefficient D is reduced to

$$D = \frac{1}{3}\,\frac{v^2}{\Gamma_1} \ , \tag{3.16}$$

where

$$\Gamma_1 \equiv n_I v\sigma(1 - \alpha_0 + \beta_0) \ . \tag{3.17}$$

If the distribution of particles is given, Eq. (3.16) should be averaged with the distribution. It should be noted that the result [Eqs. (3.16) and (3.17)] is in essential agreement with the standard formula given by Eqs. (2.3) and (2.4) based on the Boltzmann equation. In fact, if we assume that the particle will be scattered forward, backward, or sideways, the Boltzmann formula [Eqs. (2.3) and (2.4)] reduces to Eqs. (3.16) and (3.17). The contribution of the gain term, that is, the integral with the factor $\cos\theta$ in Eq. (2.4), is represented by the terms involving α_0 and β_0. That is,

$$\Gamma_1 = n_I v\sigma(1 - \langle\cos\theta\rangle_{\text{sc}}) \ , \tag{3.18}$$

where

$$\langle\cos\theta\rangle_{\text{sc}} \equiv \alpha_0 \cos 0 + 4\gamma_0 \cos(\tfrac{1}{2}\pi) + \beta_0 \cos(\pi) = \alpha_0 - \beta_0 \ . \tag{3.19}$$

IV. APPROACH TO EQUILIBRIUM OF A HOMOGENEOUS SYSTEM

Let us consider a "homogeneous" state in which the particle distribution does not change from place to place. If such a condition is realized at some time, it will be maintained thereafter. We will study the evolution of the directional probabilities in the present section.

Let us assume that at the initial time $N=0$ the particles arrive at any and every lattice site with the direction 1 with the same probability. This initial condition can be expressed by

$$P_a(x, y, z, 0) = C\delta_{a,1} \ , \tag{4.1}$$

where C is a positive constant. Let us solve the difference equations (3.3) under this condition.

Since the solutions do not depend on the position coordinates (x, y, z), we drop these coordinates and introduce new probabilities $\{p_a\}$ by

$$P_a(N) \equiv Cp_a(N) \tag{4.2}$$

with the normalization

$$\Sigma_a p_a(N) = 1 . \tag{4.3}$$

Let us construct a row matrix, called a *state vector*, representing the probability distribution $p_a(N)$ by

$$\mathbf{p} \equiv (p_1, p_2, \ldots, p_6) . \tag{4.4}$$

The initial condition corresponding to Eq. (4.1) is given by

$$\mathbf{p}(0) = (1, 0, 0, \ldots, 0) . \tag{4.5}$$

Using Eq. (3.3), we obtain

$$\mathbf{p}(N) = \mathbf{p}(N-1) \cdot \mathbf{T} , \tag{4.6}$$

where $\mathbf{T}$ represents the *transition matrix* given by

$$\mathbf{T} \equiv \begin{pmatrix} \alpha & \beta & \gamma & \gamma & \gamma & \gamma \\ \beta & \alpha & \gamma & \gamma & \gamma & \gamma \\ \gamma & \gamma & \alpha & \beta & \gamma & \gamma \\ \gamma & \gamma & \beta & \alpha & \gamma & \gamma \\ \gamma & \gamma & \gamma & \gamma & \alpha & \beta \\ \gamma & \gamma & \gamma & \gamma & \beta & \alpha \end{pmatrix} . \tag{4.7}$$

The matrix equation (4.6) has the standard form of a finite Markoff chain equation.[11] With the initial condition [Eq. (4.5)], it can be solved in an elementary manner. The results are as follows:

$$p_1(N) = \tfrac{1}{6} [1 + 3(\alpha - \beta)^N + 2(\alpha + \beta - 2\gamma)^N]$$
$$p_2(N) = \tfrac{1}{6} [1 - 3(\alpha - \beta)^N + 2(\alpha + \beta - 2\gamma)^N] \tag{4.8}$$
$$p_3(N) = p_4(N) = p_5(N) = p_6(N) = \tfrac{1}{6} [1 - (\alpha + \beta - 2\gamma)^N] .$$

For a set of values, $\alpha = 0.95$, $\beta = \gamma = 0.01$, the p's are shown by solid lines in Fig. 2. We observe the following properties.

(a) Unless $\alpha = 1$, in which case the particle moves always in the same direction (no scattering), the prob-
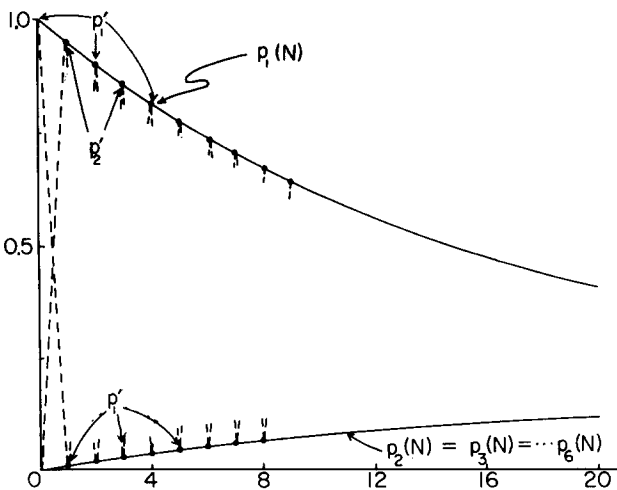
FIG. 2. Directional probabilities $(p_1, p_2, \ldots)$ as a function of of N. The solutions [Eq. (4.8)] with $\alpha = 0.95$ and $\beta = \gamma = 0.01$ are joined by solid lines. The solutions [Eq. (5.3)] with reflecting boundary are joined by broken lines.
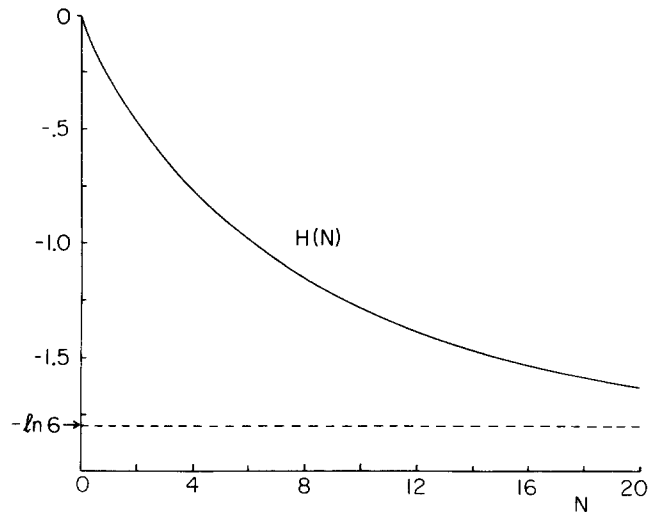
FIG. 3. Boltzmann H-function [Eq. (4.12)] defined with the directional probability distribution p as a function of time $N\tau$. $\alpha = 0.95$; $\beta = \gamma = 0.01$.

ability distribution approaches a stationary state in which all "momentum" states are occupied by the same probability $\tfrac{1}{6}$. Since, all states $a = 1, 2, \ldots, 6$ can be viewed as states of equal energy, we may interpret the above result as the manifestation of the *ergodicity*.

(b) The distribution approaches equilibrium *exponentially* with *two relaxation times*. In the kinetic theoretical limit defined by Eqs. (3.14) and (3.15), Eqs. (4.8) become

$$p_1(t) = \tfrac{1}{6}(1 + 3e^{-\Gamma_1 t} + 2e^{-\Gamma_2 t})$$
$$p_2(t) = \tfrac{1}{6}(1 - 3e^{-\Gamma_1 t} + 2e^{-\Gamma_2 t}) \tag{4.9}$$
$$p_3(t) = \cdots = p_6(t) = \tfrac{1}{6}(1 - e^{-\Gamma_2 t}) ,$$

where

$$t \equiv N\tau , \tag{4.10}$$

and

$$\Gamma_2 \equiv n_I v \sigma [1 - \langle P_2(\cos\theta) \rangle_{sc}] \equiv n_I v \sigma (1 - \alpha_0 - \beta_0 + 2\gamma_0) , \tag{4.11}$$

where P_2 represents the Legendre polynomial of degree 2. The relaxation time $\tau_1 \equiv \Gamma_1^{-1}$ is the same as that defined in Eq. (3.17), which characterizes the diffusion. The second relaxation time $\tau_2 \equiv \Gamma_2^{-1}$ has the same order of magnitude as τ_1, but in general differs from the latter. Only in the case of hard sphere interaction, for which $\alpha_0 = \beta_0 = \gamma_0$, do both relaxation times agree in value. We further note that the relaxation time τ_2 characterizes the growth of the probabilities $p_3, \ldots, p_6$ of those states that have directions perpendicular to the direction of the initially populated state $a = 1$.

(c) In order to see the global approach to equilibrium, let us introduce Boltzmann's H function,

$$H(N) \equiv \Sigma_a p_a(N) \ln p_a(N) . \tag{4.12}$$

This function is numerically computed, using the same parameters ($\alpha = 0.95$, $\beta = \gamma = 0.01$) and shown in Fig. 3. The H-function *monotonically* decreases and reaches
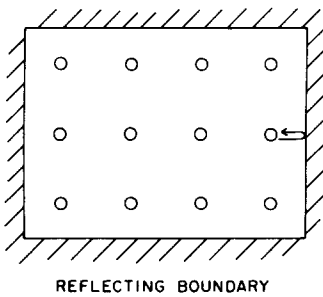
FIG. 4. Finite lattice with a reflecting boundary that is located half a lattice constant away from the outermost lattice points.

REFLECTING BOUNDARY

equilibrium. More discussions will be given in Secs. V–VII.

V. CORRELATED WALKS ON A FINITE LATTICE

Let us consider a lattice with a reflecting boundary (see Fig. 4). The *reflecting boundary* dictates that if the particle leaves an outermost site toward the boundary that is half the lattice constant away, it should return to that site with the direction reversed. Inside the lattice, the same dynamics prescribed by Eqs. (3.3) will be assumed. A general solution with an arbitrary initial condition is hard to obtain. We can, however, obtain the following results.

A. Ergodicity

At whatever site and in whatever direction the particle may start initially, the probability distribution as given by $P_a(x, y, z, t)$ approaches a stationary state, which is "homogeneous" and "isotropic," that is,

$$P_a(x, y, z, N) \rightarrow \text{const} \quad \text{as } N \rightarrow \infty . \tag{5.1}$$

In order to show this property, it is sufficient to observe[11] that some finite powers of the transition matrix, such as T in Eq. (4.7) whose linear dimension has six times the number of lattice points, should exhibit all nonvanishing elements. Such analysis can simply be carried out for a lattice of small size. It is found that this is the case if α, β, and γ are all nonzero (and positive).

It is interesting to note that this *ergodicity* is found for a *finite* lattice without invoking the bulk (or thermodynamic) limit. General questions, such as whether a system approaches equilibrium or not, are believed to depend on the intrinsic elements of dynamics as characterized by step probabilities (or alternatively by the Hamiltonian of the system), and not on the boundary condition.[12] See the following for further discussion.

B. Single-site lattice with a reflecting boundary

Let us take an extreme case in which there exists only one lattice point. This point is surrounded by six reflecting walls. At every unit time the particle should arrive at the same lattice point with a changing direction. Let us consider the state vector $\mathbf{p}' \equiv (p_1', p_2', \ldots, p_6')$, which represents the probability distribution in direction. The dynamics is characterized by the Markoff chain equation (4.6) with the following transition matrix

$$\mathbf{T} \equiv \begin{pmatrix} \beta & \alpha & \gamma & \gamma & \gamma & \gamma \\ \alpha & \beta & \gamma & \gamma & \gamma & \gamma \\ \gamma & \gamma & \beta & \alpha & \gamma & \gamma \\ \gamma & \gamma & \alpha & \beta & \gamma & \gamma \\ \gamma & \gamma & \gamma & \gamma & \beta & \alpha \\ \gamma & \gamma & \gamma & \gamma & \alpha & \beta \end{pmatrix} . \tag{5.2}$$

We assume the same initial condition as before, that is, Eq. (4.5). The solutions for this case are given by

$$p_1'(N) = \tfrac{1}{6}[1 + 3(\beta - \alpha)^N + 2(\alpha + \beta - 2\gamma)^N]$$

$$p_2'(N) = \tfrac{1}{6}[1 - 3(\beta - \alpha)^N + 2(\alpha + \beta - 2\gamma)^N] \tag{5.3}$$

$$p_3'(N) = p_4'(N) = p_5'(N) = p_6'(N) = \tfrac{1}{6}[1 - (\alpha + \beta - 2\gamma)^N] .$$

First, we note that all probabilities approach the same value, $\tfrac{1}{6}$, as N tends to infinity. This is a manifestation of the ergodicity as discussed earlier.

The present solutions [Eqs. (5.3)] have a close connection to the solutions [Eqs. (4.8)], which were obtained with the homogeneity assumption. The condition of homogeneity, that is, site independence, for the probabilities P_a is equivalent to assuming the periodic boundary condition for a "single-site" lattice. A closer look indicates that the two solutions [Eqs. (4.8)] and [Eqs. (5.3)] are mutually obtainable with the interchange: $\alpha \rightleftarrows \beta$.

When $\alpha \gg \beta$, the probabilities $p_1'(N)$ and $p_2'(N)$ oscillate violently for the reflecting boundary as shown in Fig. 2, and the same quantities smoothly approach equilibrium for the periodic boundary. In spite of this difference, the H-function $H(N)$ is found to be the *same* for *both* boundaries, and it shows a monotonic approach to the equilibrium value equal to $-\ln 6$ (see Fig. 3). In other words, our system approaches equilibrium with the same rate for both boundaries. While the coincidence of the H-function may be accidental, the same relaxation times τ_1 and τ_2 should characterize the evolution of the directional probabilities for a general boundary. It is also interesting to note that despite the oscillatory evolution of the probabilities $p_1'(t)$ and $p_2'(t)$, the H-function is smooth and monotonic.

VI. CORRELATED WALKS ON bcc AND fcc LATTICES

A. The bcc lattices

A walker is allowed to move from one site to its nearest neighbor with the following rules. It may move in the same direction as that of the previous step with probability α_b, see Fig. 5, turn at $\theta \equiv \cos^{-1}(\tfrac{1}{3})$ with
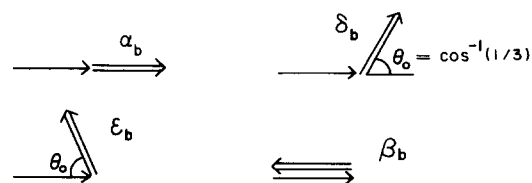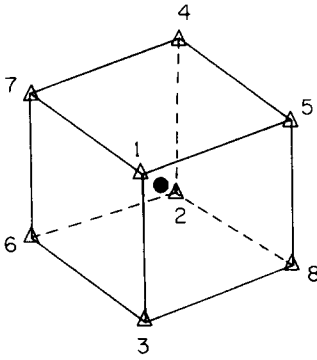

FIG. 5. Step probabilities for the bcc lattice. They are normalized such that $\alpha_b + 3\delta_b + 3\epsilon_b + \beta_b = 1$.

FIG. 6. Nearest-neighbor directions from the center (dot) to eight corners (triangles) are designated by 1, 2, ..., 8.

probability δ_b (there are three possibilities), turn at $\theta = \pi - \cos^{-1}(\frac{1}{3})$ with probability ϵ_b (three possibilities), or reverse with probability β_b. The step probabilities are normalized such that

$$\alpha_b + 3\delta_b + 3\epsilon_b + \beta_b = 1 , \tag{6.1}$$

where various numerical factors correspond to the numbers of possible turns at each angle.

The mean square displacement $\langle r^2 \rangle$ can be calculated in a similar manner, and it can be expressed in the same form as Eq. (3.6) with the following substitution:

$$\Delta_b \equiv \alpha_b + \delta_b - \epsilon_b - \beta_b . \tag{6.2}$$

The diffusion coefficient D for the lattice is given by Eq. (3.9) with the new Δ_b.

The step probabilities α_b, $\beta_b \cdots$ can be related to partial cross sections $\sigma\alpha_{b0}$, $\sigma\beta_{b0}$, $\cdots$ as follows:

$$\alpha_b = 1 - q + q\alpha_{b0} , \quad \beta_b = q\beta_{b0} ,$$
$$\delta_b = q\delta_{b0} , \quad \epsilon_b = q\epsilon_{b0} , \tag{6.3}$$

where

$$\alpha_{b0} \text{ (forward)} \equiv \frac{\int_0^{\theta_b} d\theta \, \sin\theta I(v, \theta)}{\int_0^{\pi} d\theta \, \sin\theta I(v, \theta)}$$

$$\beta_{b0} \text{ (backward)} \equiv \frac{\int_{\pi-\theta_b}^{\pi} d\theta \, \sin\theta I(v, \theta)}{\int_0^{\pi} d\theta \, \sin\theta I(v, \theta)}$$

$$3\delta_{b0} \equiv \frac{\int_{\theta_b}^{\pi/2} d\theta \, \sin\theta I(v, \theta)}{\int_0^{\pi} d\theta \, \sin\theta I(v, \theta)}$$

$$3\epsilon_{b0} \equiv \frac{\int_{\pi/2}^{\pi-\theta_b} d\theta \, \sin\theta I(v, \theta)}{\int_0^{\pi} d\theta \, \sin\theta I(v, \theta)} , \tag{6.4}$$

where

$$\theta_b \equiv \cos^{-1}(\tfrac{3}{4}) . \tag{6.5}$$

In the kinetic-theoretical limit, the diffusion coefficient D becomes

$$D = \frac{1}{3} \frac{v^2}{\Gamma_1^{(b)}} , \tag{6.6}$$

where

$$\Gamma_1^{(b)} \equiv n_I v \sigma (1 - \alpha_{b0} - \delta_{b0} + \epsilon_{b0} + \beta_{b0})$$
$$= n_I v \sigma (1 - \langle \cos\theta \rangle_{\text{bcc}}) . \tag{6.7}$$

The results [Eqs. (6.6) and (6.7)] are similar to Eqs. (3.16) and (3.17), and can be interpreted in an analogous manner. In particular, the diffusion coefficient is given in terms of the relaxation rate $\Gamma_1^{(b)}$.

Let us name the directions of steps by 1, 2, ..., 8 as given in Fig. 6.

Let us assume a homogeneous initial condition:

$$P_a(0) = \delta_{a,1} . \tag{6.8}$$

The state vector $\mathbf{p} \equiv (p_1, p_2, \ldots, p_8)$ satisfies the Markoff chain equation (4.6) with the following transition matrix:

$$\mathbf{T}^{(b)} \equiv \begin{pmatrix} \alpha & \beta & \delta & \epsilon & \delta & \epsilon & \delta & \epsilon \\ \beta & \alpha & \epsilon & \delta & \epsilon & \delta & \epsilon & \delta \\ \delta & \epsilon & \alpha & \beta & \delta & \epsilon & \delta & \epsilon \\ \epsilon & \delta & \beta & \alpha & \epsilon & \delta & \epsilon & \delta \\ \delta & \epsilon & \delta & \epsilon & \alpha & \beta & \delta & \epsilon \\ \epsilon & \delta & \epsilon & \delta & \beta & \alpha & \epsilon & \delta \\ \delta & \epsilon & \delta & \epsilon & \delta & \epsilon & \alpha & \beta \\ \epsilon & \delta & \epsilon & \delta & \epsilon & \delta & \beta & \alpha \end{pmatrix} . \tag{6.9}$$

After lengthy calculations, the following solutions are obtained.

$$p_1(N) = \tfrac{1}{8} [1 + 3(\alpha_b + \beta_b - \delta_b - \epsilon_b)^N + (\alpha_b - \beta_b - 3\delta_b + 3\epsilon_b)^N + 3(\alpha_b - \beta_b + \delta_b - \epsilon_b)^N]$$

$$p_2(N) = \tfrac{1}{8} [1 + 3(\alpha_b + \beta_b - \delta_b - \epsilon_b)^N - (\alpha_b - \beta_b - 3\delta_b + 3\epsilon_b)^N - 3(\alpha_b - \beta_b + \delta_b - \epsilon_b)^N]$$

$$p_3(N) = p_5(N) = p_7(N) = \tfrac{1}{8} [1 - (\alpha_b + \beta_b - \delta_b - \epsilon_b)^N - (\alpha_b - \beta_b - 3\delta_b + 3\epsilon_b)^N + (\alpha_b - \beta_b + \delta_b - \epsilon_b)^N] \tag{6.10}$$

$$p_4(N) = p_6(N) = p_8(N) = \tfrac{1}{8} [1 - (\alpha_b + \beta_b - \delta_b - \epsilon_b)^N + (\alpha_b - \beta_b - 3\delta_b + 3\epsilon_b)^N - (\alpha_b - \beta_b + \delta_b - \epsilon_b)^N] .$$

This result is similar to Eqs. (4.8). The most distinctive feature is that the approach to equilibrium is now characterized by three relation rates $(\Gamma_1^{(b)}, \Gamma_2^{(b)}, \Gamma_3^{(b)})$, where

$$\Gamma_1^{(b)} \equiv n_I v \sigma (1 - \langle \cos\theta \rangle_{\text{bcc}}) \equiv n_I v \sigma (1 - \alpha_{b0} + \beta_{b0} - \delta_{b0} - \epsilon_{b0})$$

$$\Gamma_2^{(b)} \equiv n_I v \sigma [1 - \langle P_2(\cos\theta) \rangle_{\text{bcc}}] = n_I v \sigma (1 - \alpha_{b0} - \beta_{b0} + \delta_{b0} + \epsilon_{b0}) \tag{6.11}$$

$$\Gamma_3^{(b)} \equiv n_I v \sigma (1 - \alpha_{b0} + \beta_{b0} + 3\delta_{b0} - 3\epsilon_{b0}) .$$
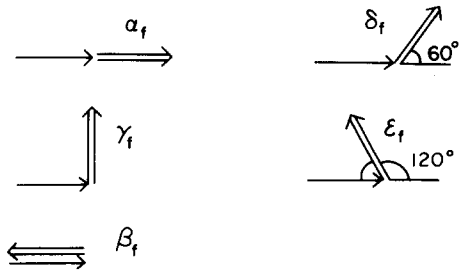
FIG. 7. Step probabilities for the fcc lattice. They are normalized such that $\alpha_f + 4\delta_f + 2\gamma_f + 4\epsilon_f + \beta_f = 1$.
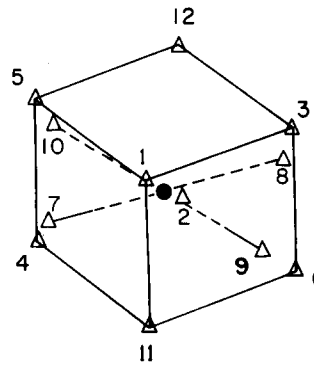

FIG. 8. Twelve nearest-neighbor directions from the center (dot) to corners (triangles) for the fcc lattice are designated by 1, 2, ..., 12.

B. The fcc lattices

The step probabilities for the fcc lattice are shown in Fig. 7. They are normalized such that

$$\alpha_f + 4\delta_f + 2\gamma_f + 4\epsilon_f + \beta_f = 1 \ . \tag{6.12}$$

The mean square displacement $\langle r^2 \rangle$ is found to be expressed in the form [Eq. (3.6)] with the substitution

$$\Delta_f \equiv \alpha_f + 2\delta_f - 2\epsilon_f - \beta_f \ . \tag{6.13}$$

The diffusion coefficient D is given by Eq. (3.9) with

the new Δ_f. In the kinetic-theoretical limit, this quantity D can be expressed in the form [Eq. (3.16)] with the diffusion-relaxation rate

$$\Gamma_1^{(f)} \equiv n_I v \sigma (1 - \alpha_{f0} - 2\delta_{f0} + 2\epsilon_{f0} + \beta_{f0}) \ .$$
$$= n_I v \sigma (1 - \langle \cos\theta \rangle_{fcc}) \tag{6.14}$$

The twelve directions of steps are shown and designated by 1, 2, ..., 12 in Fig. 8. The state vector $\mathbf{p} \equiv (p_1, p_2, \ldots, p_{12})$ obeys the Markoff chain equation (4.6) with the transition matrix

$$\mathbf{T}^{(f)} = \begin{pmatrix}
\alpha & \beta & \delta & \epsilon & \delta & \epsilon & \delta & \epsilon & \delta & \epsilon & \gamma & \gamma \\
\beta & \alpha & \epsilon & \delta & \epsilon & \delta & \epsilon & \delta & \epsilon & \delta & \gamma & \gamma \\
\delta & \epsilon & \alpha & \beta & \gamma & \gamma & \epsilon & \delta & \delta & \epsilon & \epsilon & \delta \\
\epsilon & \delta & \beta & \alpha & \gamma & \gamma & \delta & \epsilon & \epsilon & \delta & \delta & \epsilon \\
\delta & \epsilon & \gamma & \gamma & \alpha & \beta & \delta & \epsilon & \epsilon & \delta & \epsilon & \delta \\
\epsilon & \delta & \gamma & \gamma & \beta & \alpha & \epsilon & \delta & \delta & \epsilon & \delta & \epsilon \\
\delta & \epsilon & \epsilon & \delta & \delta & \epsilon & \alpha & \beta & \gamma & \gamma & \delta & \epsilon \\
\epsilon & \delta & \delta & \epsilon & \epsilon & \delta & \beta & \alpha & \gamma & \gamma & \epsilon & \delta \\
\delta & \epsilon & \delta & \epsilon & \epsilon & \delta & \gamma & \gamma & \alpha & \beta & \delta & \epsilon \\
\epsilon & \delta & \epsilon & \delta & \delta & \epsilon & \gamma & \gamma & \beta & \alpha & \epsilon & \delta \\
\gamma & \gamma & \epsilon & \delta & \epsilon & \delta & \delta & \epsilon & \delta & \epsilon & \alpha & \beta \\
\gamma & \gamma & \delta & \epsilon & \delta & \epsilon & \epsilon & \delta & \delta & \beta & \alpha
\end{pmatrix} \tag{6.15}$$

With the initial condition Eq. (6.8), this equation is solved, and the results are as follows.

$$p_1(N) = \tfrac{1}{12}[1 + 3(\alpha_f - \beta_f + 2\delta_f - 2\epsilon_f)^N + 3(\alpha_f + \beta_f - 2\gamma_f)^N + 2(\alpha_f + \beta_f + 2\gamma_f - 2\delta_f - 2\epsilon_f)^N + 3(\alpha_f - \beta_f - 2\delta_f + 2\epsilon_f)^N] \ ,$$
$$p_2(N) = \tfrac{1}{12}[1 - 3(\alpha_f - \beta_f + 2\delta_f - 2\epsilon_f)^N + 3(\alpha_f + \beta_f - 2\gamma_f)^N + 2(\alpha_f + \beta_f + 2\gamma_f - 2\delta_f - 2\epsilon_f)^N - 3(\alpha_f - \beta_f - 2\delta_f + 2\epsilon_f)^N] \ ,$$
$$p_3(N) = p_5(N) = p_7(N) = p_9(N) = \tfrac{1}{12}[1 + \tfrac{3}{2}(\alpha_f - \beta_f + 2\delta_f - 2\epsilon_f)^N - (\alpha_f + \beta_f + 2\gamma_f - 2\delta_f - 2\epsilon_f)^N - \tfrac{3}{2}(\alpha_f - \beta_f - 2\delta_f - 2\delta_f + 2\epsilon_f)^N] \ ,$$
$$p_4(N) = p_6(N) = p_8(N) = p_{10}(N) = \tfrac{1}{12}[1 - \tfrac{3}{2}(\alpha_f - \beta_f + 2\delta_f - 2\epsilon_f)^N - (\alpha_f + \beta_f + 2\gamma_f - 2\delta_f - 2\epsilon_f)^N + \tfrac{3}{2}(\alpha_f - \beta_f - 2\delta_f + 2\epsilon_f)^N] \ ,$$
$$p_{11}(N) = p_{12}(N) = \tfrac{1}{12}[1 - 3(\alpha_f + \beta_f - 2\gamma_f)^N + 2(\alpha_f + \beta_f + 2\gamma_f - 2\delta_f - 2\epsilon_f)^N] \ . \tag{6.16}$$

A significant feature is that all p's approach equilibrium exponentially, characterized by *four* relaxation times.

VII. REMARKS

In conclusion, we have established a close connection between the Lorentz gas and correlated walks on cubic

lattices. Since our lattice model is easier to handle, we have obtained several exact results; these are enumerated in Sec. I. Some of the results are intuitively obvious. The fact that the ergodicity is proved for a finite lattice is noteworthy. The bulk limit, which had often been thought of as a necessary ingredient for the

irreversibility,[12] is not used here. The irreversibility should depend on the intrinsic microprocesses and not on the initial and boundary conditions. In our model, when $\alpha = 1$ (no scattering), the system is nonergodic. However, as soon as collisions are allowed so that $\alpha < 1$, the system becomes ergodic. The global approach to equilibrium, as studied in terms of the H-function, does not depend on the nature of the boundary condition imposed on our lattice model. In fact, it is possible to show that the H-function for the single-site lattice with a mixed boundary, that is, periodic in one direction and reflecting in other, has the same value. Although such coincidence is viewed as accidental, the fact that the evolution of the directional probabilities is characterized by the same intrinsic relaxation times should hold for a general boundary condition.

Comparative studies of the correlated walks on sc, bcc, and fcc lattices indicate the existence of different numbers of relaxation times $(\tau_1, \ldots, \tau_4)$ that characterize the evolutions of the directional probabilities. This implies that the solutions of the Boltzmann equation, which is equivalent to the continuum limit of the Markoff chain equation (4.6), should involve an indefinite number of relaxation times. The explicitly obtained relaxation times $\tau_1, \ldots, \tau_4$ all agree in value for the hard-sphere interaction.

The evolution of the probabilities of arrival with direction, $P_a(x, y, z, N)$, can be studied from the fundamental difference equations (3.3). This is a much harder problem. The solution of the same problem in one dimension, however, has been obtained and will be reported in a separate paper.[13] This solution is found to depend on the boundary.

A significant merit of correlated walks is that the model can be applied even when the relation between step probabilities and microprocesses cannot be represented simply in terms of the differential cross section. Various phenomena, that can be described in terms of the model were enumerated in Section I.

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