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Diffusion in Lattices with Anisotropic Scatterers

J. B. T. M. Roerdink,[1] K. E. Shuler,[2] and G. F. Lawler[3]

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We study diffusion in lattices with periodic and random arrangements of anisotropic scatterers. We show, using both analytical techniques based upon our previous work on asymptotic properties of multistate random walks and computer calculation, that the diffusion constant for the random arrangement of scatterers is bounded above and below at an arbitrary density ρ by the diffusion constant for an appropriately chosen periodic arrangement of scatterers at the same density. We also investigate the accuracy of the low-density expansion for the diffusion constant up to second order in the density for a lattice with randomly distributed anisotropic scatterers. Comparison of the analytical results with numerical calculations shows that the accuracy of the density expansion depends crucially on the degree of anisotropy of the scatterers. Finally, we discuss a monotonicity law for the diffusion constant with respect to variation of the transition rates, in analogy with the Rayleigh monotonicity law for the effective resistance of electric networks. As an immediate corollary we obtain that the diffusion constant, averaged over all realizations of the random arrangement of anisotropic scatterers at density ρ, is a monotone function of the density.

KEY WORDS: Random walks on periodic and random lattices; anisotropic scatterers; bounds for the diffusion constants; density expansion; monotonicity law.

1. INTRODUCTION

We continue studies on the asymptotic properties of multistate random walks with particular reference to the effect of the spatial arrangement of the different internal states on the diffusion constants. We consider

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(i) periodic arrangements, where the lattice is constructed by periodically repeating a unit cell which contains a certain number of inequivalent sites; (ii) random arrangements, where the transition probabilities at each site are chosen independently from a certain probability distribution; and (iii) a mixed case, random-periodic arrangements, where the lattice is constructed from a unit cell, but the transition probabilities at the sites within a unit cell are chosen at random. Building on the results of previous studies,[1-3,7] we specifically address here the case of anisotropic scatterers on a 2D square lattice, where the probabilities of positive jumps equal those of negative jumps. If we denote the stepping probabilities from site k on the lattice in the positive and negative horizontal directions by p_k^+ and p_k^-, respectively, and those in the vertical directions by q_k^+ and q_k^-, then these anisotropic scatterers are characterized by the equalities $p_k^+ = p_k^- := p_k$, $q_k^+ = q_k^- := q_k$ (with $2p_k + 2q_k = 1$), but $p_k \neq q_k$, in general. In the cases of random-periodic and random arrangements we restrict ourselves to Bernoulli distributions of scatterers, i.e., $p_k = a$ with probability ρ and $p_k = a'$ with probability $1-\rho$, with $0 \leqslant a,\ a' \leqslant 1/2$.

We concentrate on the *diffusion constants*, which for a d-dimensional lattice with space directions $j = 1,..., d$ are defined by

$$D_j = \lim_{n \to \infty} \{\langle r_j^2(n)\rangle - \langle r_j(n)\rangle^2\}/2n, \qquad j = 1,..., d$$

where $r_j(n)$ is the displacement in direction j after n steps and the brackets denote an average over all realizations of the walk. In our case, where $p_k^+ = p_k^-$, $q_k^+ = q_k^-$, we have $\langle r_j(n)\rangle = \langle r_j(0)\rangle$.

It is easy to see[1,2] that different periodic configurations of scatterers, which are of two types, "impurities" ($p_k = a$) and "host sites" ($p_k = a'$), even with the same density of impurities, can give rise to different diffusion constants. In the random case, however, with probability one all realizations of a random configuration (e.g., $p_k = a$ with probability ρ and $p_k = a'$ with probability $1-\rho$, $0 < a,\ a' < 1/2$) give the same diffusion constants.[3] Here we study the diffusion constants as a function of the density ρ of impurities and:

(i) Give a conjecture as to the optimal arrangement of impurities to minimize (maximize) the horizontal diffusion constant D_x of periodic arrangements with a fixed density of impurities. The constant D_x is easy to compute for these optimal arrangements, giving a conjectured $D_x^{(\min)}(\rho)$ and $D_x^{(\max)}(\rho)$. This is analogous to the result for the effective dielectric constant ε_{eff} of a two-component material, which has been rigorously established to be bounded above and below at all densities ρ of one of the components by the dielectric constants corresponding to composites with simple, periodic geometries.[4-6]

(ii) Prove that the average diffusion constant for the random-periodic arrangement with density ρ on a unit cell with N sites, denoted by $\overline{D_x^{(N)}}(\rho)$, lies between the bounds $D_x^{(\min)}(\rho)$ and $D_x^{(\max)}(\rho)$ mentioned above [note that $\overline{D_x^{(N)}}(\rho)$ is well defined by ref. 3]. Here the bar denotes the average over configurations of scatterers.

We also consider the low-density expansion for the horizontal diffusion constant in the random case, henceforth denoted by $D_x^{(R)}(\rho)$,

$$D_x^{(R)}(\rho) = b_0 + b_1\rho + b_2\rho^2 + b_3\rho^3 + \cdots \tag{1.1}$$

It is not known whether this expansion actually exists to all orders (although it is expected to). However, in ref. 3 it was proved that

$$D_x^{(R)}(\rho) = \lim_{N\to\infty} \overline{D_x^{(N)}}(\rho) \tag{1.2}$$

i.e., the constant for the random case is the limit of the random-periodic case as the size of the unit cell tends to infinity. Since $\overline{D_x^{(N)}}(\rho)$ is a polynomial in ρ for all N, we can expand it,

$$\overline{D_x^{(N)}}(\rho) = b_{0,N} + b_{1,N}\rho + b_{2,N}\rho^2 + \cdots + b_{N,N}\rho^N$$

and hope that

$$b_j = \lim_{N\to\infty} b_{j,N} \tag{1.3}$$

In ref. 2 the limit in (1.3) was computed for $j=1$. In ref. 7 the case $j=2$, $a'=1/4$ was considered, and it was shown that (1.3) holds for $j=1$ and $j=2$, $a'=1/4$. The coefficient b_2 was expressed in terms of some probabilities for simple random walk which could not be evaluated explicitly. In this paper we make an approximate calculation of $\lim_{N\to\infty} b_{2,N}$ which we expect to be an approximation for b_2. We also consider the limiting case $a=0.5$, $a'=0$ [in this case it is not even known rigorously that $D_x^{(R)}(\rho)$ exists], and evaluate the limits in (1.3) exactly for $j=0, 1, 2$. We then compare the expansions to numerical results obtained by the cell method described in Section 2 of this paper.

Finally, we discuss a *monotonicity law* in analogy with the Rayleigh monotonicity law for the effective resistance R_{eff} of electric networks, which states that if any resistance of a circuit is increased, the new effective resistance R'_{eff} between any two points can only have increased, i.e., $R'_{\text{eff}} \geqslant R_{\text{eff}}$. We note that this law has an equivalent formulation in terms of escape probabilities for *reversible*[4] Markov chains.[8] Although in the case

[4] In the physical literature this property is usually denoted by the term "detailed balance."[11]

of anisotropic scatterers the embedded Markov chain defined on the N sites in the unit cell (see ref. 1) is not reversible, nevertheless the following monotonicity result has been established[14] for this case. Consider a periodic 2D lattice where the unit cell contains N distinct anisotropic scatterers. To the kth scatterer in the unit cell we assign transition probabilities p_k $(0 < p_k < 1/2)$ in the positive and negative x directions, and $q_k = 1/2 - p_k$ in the positive and negative y directions. Then, if the horizontal diffusion constant for the random walk on this lattice is denoted by $D_x^{(N)}(p_1, p_2, ..., p_N)$, it can be shown[14] that

$$\partial/\partial p_k \, D_x^{(N)} = N\pi_k^2 > 0 \qquad (k = 1, ..., N) \tag{1.4}$$

where $\{\pi_k\}$ is the stationary occupation probability of site k of the embedded Markov chain on the set of the N sites of the unit cell. The positivity of π_k is a consequence of the fact that all nearest neighbors are connected by positive transition probabilities, i.e., the walk is irreducible. It follows that an increase in any of the horizontal transition probabilities p_k leads to an increase in $D_x^{(N)}$. The effect on the vertical diffusion constant $D_x^{(N)}$ does not require separate discussion, since[2]

$$D_x^{(N)} + D_y^{(N)} = 1/2 \tag{1.5}$$

Here we apply this monotonicity law to the random-periodic and random cases, where impurities (defined by $p_k = a$) are interspersed with host sites (defined by $p_k = a' < a$) with density ρ of impurities. We give the bound

$$\overline{D_x^{(N)}}(\rho + \Delta\rho) - \overline{D_x^{(N)}}(\rho) \geqslant (a - a') c^{-4} \, \Delta\rho [N/(N+1)]^2$$

where $c = \max\{a/a', \ (1/2 - a')/(1/2 - a)\}$. Since $D_x^{(R)}(\rho)$ is the limit of $\overline{D_x^{(N)}}(\rho)$, this implies

$$D_x^{(R)}(\rho + \Delta\rho) - D_x^{(R)}(\rho) \geqslant (a - a') c^{-4} \, \Delta\rho$$

This shows that both $\overline{D_x^{(N)}}(\rho)$ and $D_x^{(R)}(\rho)$ are (strictly) monotonic functions of the density ρ.

The organization of the paper is as follows. In Section 2 we construct the bounds for the diffusion constants and give a description of the cell method which is used to calculate the diffusion constants numerically. Section 3 contains the low-density expansion up to second order and a comparison with the exact result which is computed numerically. In Section 4 we discuss the monotonicity law and its consequences for the density dependence of $\overline{D_x^{(N)}}(\rho)$ and $D_x^{(R)}(\rho)$.

2. BOUNDS FOR THE DIFFUSION CONSTANTS

An arrangement (or environment) of scatterers on a 2D lattice is a function A from the points of the lattice to $\{R, S\}$. Each site k with $A_k = S$ is a scatterer ($p_k = a$, $q_k = 1/2 - a$) and each site with $A_k = R$ is a regular[5] site ($p_k = a' < a$; $q_k = 1/2 - a'$). Suppose that an arrangement A is periodic with an n_x by n_y rectangular unit cell with $N_S = N_S^A$ scatterers in the cell and hence density $\rho = \rho^A = (n_x n_y)^{-1} N_S$ of scatterers. The calculation of the diffusion constants proceeds as follows.[1] Let the position of the walker on the lattice be indexed by (l, α), where l denotes the translate of the unit cell and α the site within the cell which the walker occupies. The single-step transition probability from site (l', γ) to site (l, α) is denoted by $T^A_{\alpha\gamma}(l - l')$. Then an embedded Markov chain with N states is constructed by ignoring the cell the walker occupies; the corresponding transition matrix $T = T^A$ has matrix elements

$$T_{\alpha\gamma} = \sum_l T_{\alpha\gamma}(l) \tag{2.1}$$

In this section we always assume that the matrix T is irreducible (which is always true if $0 < a$, $a' < 1/2$). Then T has a unique (normalized) right eigenvector corresponding to the eigenvalue $\lambda = 1$, which is denoted by $\pi = \pi^A$. The component π_α represents the equilibrium occupation probability of the walker to be in internal state α. Then, for the lattice with anisotropic scatterers one has the following expressions for the horizontal and vertical diffusion constants[1]:

$$D_x = D_x^A = \sum_\alpha p_\alpha \pi_\alpha, \qquad D_y = D_y^A = \sum_\alpha (1/2 - p_\alpha)\pi_\alpha = 1/2 - D_x \tag{2.2}$$

Let $\lambda_S = \lambda_S^A$ and $\lambda_R = \lambda_R^A$ be the fraction of time spent at scatterers and at regular points in the equilibrium distribution, i.e.,

$$\lambda_S = \sum_{\substack{\alpha \\ A_\alpha = S}} \pi_\alpha, \qquad \lambda_R = 1 - \lambda_S = \sum_{\substack{\alpha \\ A_\alpha = R}} \pi_\alpha \tag{2.3}$$

Then

$$D_x = \lambda_S a + \lambda_R a' \tag{2.4}$$

Different arrangements of scatterers with the same density ρ of scatterers may lead to different values of D_x.[2]

[5] In this section "scatterer" and "regular site" are synonymous with "impurity" and "host site," respectively.

We now ask which arrangements of scatterers lead to the largest and smallest value of D_x, respectively, for a fixed density of scatterers. The answer is suggested by a comparison with the case of a two-component dielectric material. If the two components have dielectric constants ε_1 and ε_2 and densities ρ and $1-\rho$, then one obtains the classical arithmetic and harmonic mean bounds of Wiener[4-6] for the effective dielectric constant ε_{eff} of the material with random microscopic geometry,

$$[\rho\varepsilon_1^{-1} + (1-\rho)\varepsilon_2^{-1}]^{-1} \leqslant \varepsilon_{\text{eff}} \leqslant \rho\varepsilon_1 + (1-\rho)\varepsilon_2 \tag{2.5}$$

The microscopic geometries corresponding to the bounds in (2.5) are very simple periodic arrangements, i.e., parallel layers of dielectric material which are perpendicular (lower bound) or parallel (upper bound) to the applied electric field, where each layer consists of a single component. Motivated by this result, we *conjecture* that, since we have chosen the horizontal stepping probability from a scatterer to be larger than that of a regular site, scatterers should be arranged horizontally (vertically) in order to maximize (minimize) D_x. This leads to configurations as depicted in Fig. 1a and 1b, where we put all scatterers on rows or columns, respectively. We can only obtain completely filled rows (columns) if the total number N_S of scatterers is an integer multiple of n_x (n_y). Computation of the diffusion constants for these configurations is easy because it reduces to a one-dimensional problem. For example, in the case of Fig. 1a, which is associated with the minimal value of D_x, the reduced unit cell is that of Fig. 1c with n_x sites in a horizontal row. The corresponding diffusion constant $D_x^{(\min)}$ can be obtained by standard methods (see, e.g., ref. 2, Section 2.1):

$$D_x^{(\min)} = N\left\{\sum_{k=1}^{N} p_k^{-1}\right\}^{-1}$$

Since $p_k = a$ for the N_s scatterers and $p_k = a'$ for the $N - N_s$ regular sites, we find

$$D_x^{(\min)}(\rho) = [a^{-1}\rho + a'^{-1}(1-\rho)]^{-1} \tag{2.6}$$

It is easy to see that the horizontal diffusion constant corresponding to Fig. 1b is the same as the vertical diffusion constant of Fig. 1a with a replaced by $1/2 - a$ and a' by $1/2 - a'$. Hence, using (2.2),

$$D_x^{(\max)}(\rho) = \tfrac{1}{2} - [(\tfrac{1}{2}-a)^{-1}\rho + (\tfrac{1}{2}-a')^{-1}(1-\rho)]^{-1} \tag{2.7}$$

Notice that (2.6) and (2.7) only depend on the density of scatterers, not on the particular way in which the rows (columns) of scatterers are arranged in the unit cell.

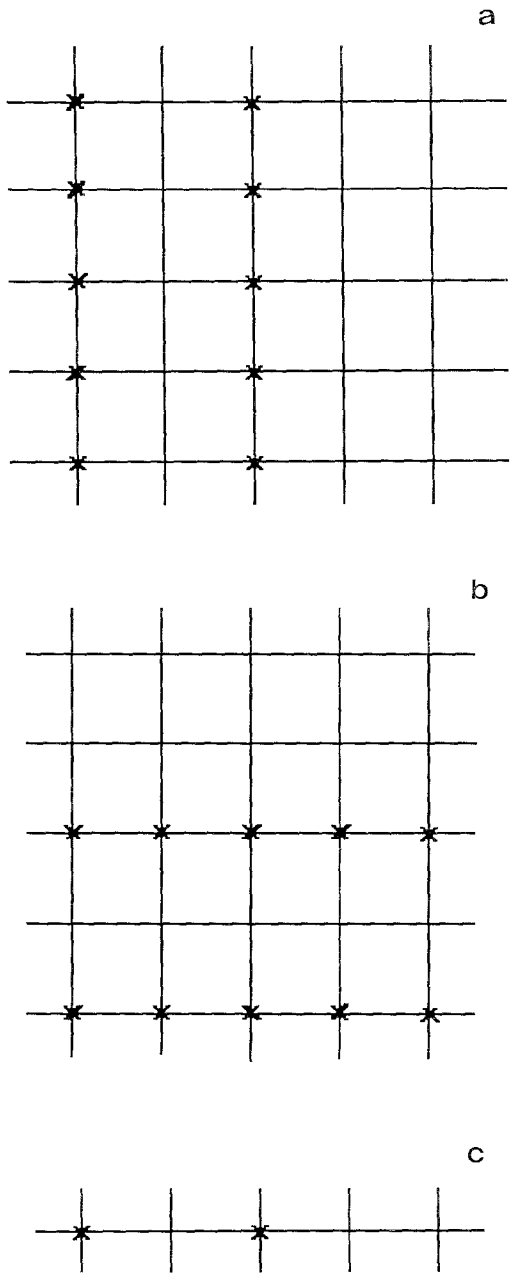


Fig. 1. (a) Unit cell with scatterers arranged columnwise. (b) Unit cell with scatterers arranged rowwise. (c) Reduced unit cell corresponding to (a).

Although we are unable to prove that (2.6) and (2.7) are bounds for all configurations with a given density ρ, we can prove that the *average* diffusion constant for the random-periodic arrangement satisfies these bounds, i.e., if $\overline{D_x^{(N)}}(\rho)$ denotes the average diffusion constant for a random periodic $\sqrt{N}\times\sqrt{N}$ array and $a \geqslant a'$,

$$\overline{D_x^{(N)}}(\rho) \geqslant [a^{-1}\rho + a'^{-1}(1-\rho)]^{-1} \tag{2.8}$$

$$\overline{D_x^{(N)}}(\rho) \leqslant \tfrac{1}{2} - [(\tfrac{1}{2}-a)^{-1}\rho + (\tfrac{1}{2}-a')^{-1}(1-\rho)]^{-1} \tag{2.9}$$

Clearly these inequalities will also hold for $D_x^{(\mathrm{R})}(\rho) := \lim_{N\to\infty} \overline{D_x^{(N)}}(\rho)$.

It is easy to see that it suffices to prove only one of the bounds (2.8), (2.9). Writing $\overline{D_x^{(N)}}(\rho) = \overline{D_x^{(N)}}(a, a'; \rho)$ to indicate the dependence on a and a', we see that the following symmetry relations are obvious (remember that $\overline{D_x^{(N)}}$ is an average over all realizations of the random distribution of scatterers).

$$\overline{D_x^{(N)}}(a, a'; \rho) = \overline{D_x^{(N)}}(a', a; 1-\rho) \tag{2.10}$$

$$\begin{aligned}\overline{D_x^{(N)}}(a, a'; \rho) &= \overline{D_y^{(N)}}(\tfrac{1}{2}-a, \tfrac{1}{2}-a'; \rho) \\ &= \tfrac{1}{2} - \overline{D_x^{(N)}}(\tfrac{1}{2}-a, \tfrac{1}{2}-a'; \rho)\end{aligned} \tag{2.11}$$

where we have used the relation (1.5). So after we have established (2.8), (2.9) follows from (2.11), and vice versa.

Fix N, and use $\langle \cdots \rangle$ to denote averages over the random arrangements. Then, since the Bernoulli distribution on arrangements is translation invariant, we get from (2.3)

$$\langle \lambda_S \rangle = \left\langle \sum_{\substack{\alpha \\ A_\alpha = S}} \pi_\alpha^A \right\rangle = N\rho \langle \pi_0^A | A_0 = S \rangle$$

$$\langle \lambda_R \rangle = \left\langle \sum_{\substack{\alpha \\ A_\alpha = R}} \pi_\alpha^A \right\rangle = N(1-\rho) \langle \pi_0^A | A_0 = R \rangle$$

If A is an arrangement with $A_0 = S$ and $\bar{A}$ is the arrangement which agrees with A everywhere except at 0, where $\bar{A}_0 = R$, then, by Lemma 6.1 of ref. 7,

$$c^{-1}\pi_0^A \leqslant \pi_0^{\bar{A}} \leqslant c\pi_0^A$$

where $c = \max\{a/a', (1/2-a')/(1/2-a)\}$. Therefore

$$\frac{\rho}{1-\rho} c^{-1} \langle \lambda_R \rangle \leqslant \langle \lambda_S \rangle \leqslant \frac{\rho}{1-\rho} c \langle \lambda_R \rangle$$

If we combine this with $\langle\lambda_R\rangle + \langle\lambda_S\rangle = 1$, we get

$$\frac{\rho}{\rho + c(1-\rho)} \leqslant \langle\lambda_S\rangle \leqslant \frac{\rho}{c\rho + (1-\rho)} \tag{2.12}$$

If $c = a/a'$, i.e., $a/a' \geqslant (1/2 - a')/(1/2 - a)$, then by (2.4) and (2.12),

$$\overline{D_x^{(N)}}(a, a; \rho) = \langle\lambda_S\rangle a + \langle\lambda_R\rangle a' = a' + (a - a')\langle\lambda_S\rangle$$
$$\geqslant a' + (a - a')\frac{\rho}{\rho + (a/a')(1-\rho)} = [\rho a^{-1} + (1-\rho)a'^{-1}]^{-1} \tag{2.13}$$

which gives (2.8), and therefore (2.9). If $c = (1/2 - a')/(1/2 - a)$, we can apply the bound (2.13) to $\overline{D_x^{(N)}}(1/2 - a', 1/2 - a, \rho)$ to find

$$\overline{D_x^{(N)}}(\tfrac{1}{2} - a', \tfrac{1}{2} - a, \rho) \geqslant [\rho(\tfrac{1}{2} - a')^{-1} + (1-\rho)(\tfrac{1}{2} - a)^{-1}]^{-1}$$

Since from (2.10) and (2.11),

$$\overline{D_x^{(N)}}(a, a'; \rho) = \tfrac{1}{2} - \overline{D_x^{(N)}}(\tfrac{1}{2} - a'; \tfrac{1}{2} - a; 1 - \rho)$$

we get

$$\overline{D_x^{(N)}}(a, a'; \rho) \leqslant \tfrac{1}{2} - [(1-\rho)(\tfrac{1}{2} - a')^{-1} + \rho(\tfrac{1}{2} - a)^{-1}]^{-1}$$

which proves (2.9), hence (2.8).

To illustrate the analytical results, we calculate the diffusion constants for periodic arrangements of scatterers numerically by the following *cell method.* First we choose an arbitrary configuration of N_S scatterers in a unit cell of N sites. The value of D_x for this configuration is then obtained by computing the eigenvector π of the corresponding transition matrix T and evaluating (2.2). Several configurations at the same density are generated, and then the process is repeated at all densities $\rho = 0, 1/N, 2/N, \ldots, 1$ (see Figs. 2a–2c), corresponding to varying size N of the unit cell. Each dot represents a particular configuration of scatterers. The solid lines are the bounds (2.6), (2.7). One sees that in each case the diffusion constant lies between the bounds, and as N increases, the spread of D_x values decreases, illustrating the fact that the diffusion constant in the infinite limit is the same for almost all realizations.

Going back to the case of the dielectric material, we note that the lower bound in (2.5) has the same form as (2.6), but the upper bound in (2.5) is different from (2.7). This is most likely a consequence of the nonreversibility of the walk, since bounds of the form (2.5) do apply to the conductivity of an electric network,[6] or, equivalently, to the diffusion constant of a reversible random walk. An example of the latter is a

symmetric random walk on a lattice with two types of bonds, where the diffusion constant is indeed found to obey the Wiener bounds.[9] Since analytic expressions for macroscopic properties (transport coefficients, dielectric constants, optical properties) of materials with random microscopic geometry of its components are in general unknown and since numerical calculations of such properties by Monte Carlo or cell methods involve extensive use of computers, the much simpler calculation of bounds based on periodic geometries can provide useful information. It would obviously be of importance to develop a *generic* proof of the existence of such periodic geometries for heterogeneous media with random arrangements of defects or components.

3. LOW-DENSITY EXPANSION

In this section we consider a 2D lattice with randomly distributed scatterers and construct the low-density expansion for the diffusion constant up to second order in the density.

The scatterers are again of two types, to be referred to as "impurities" and "host sites," having horizontal transition probabilities a and a', respec-

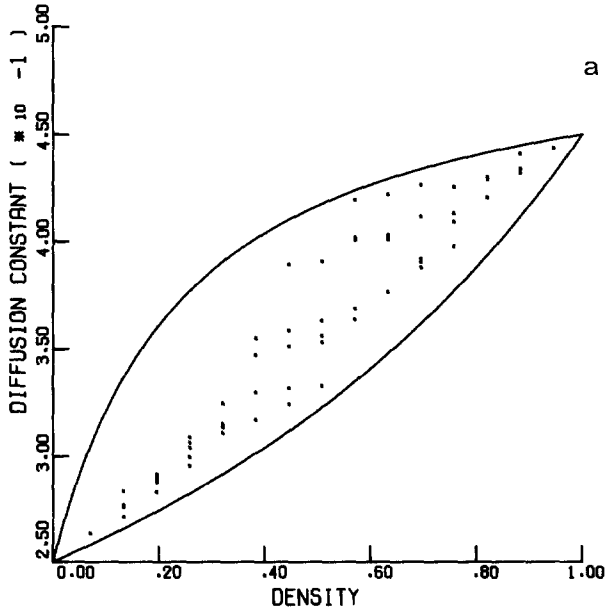
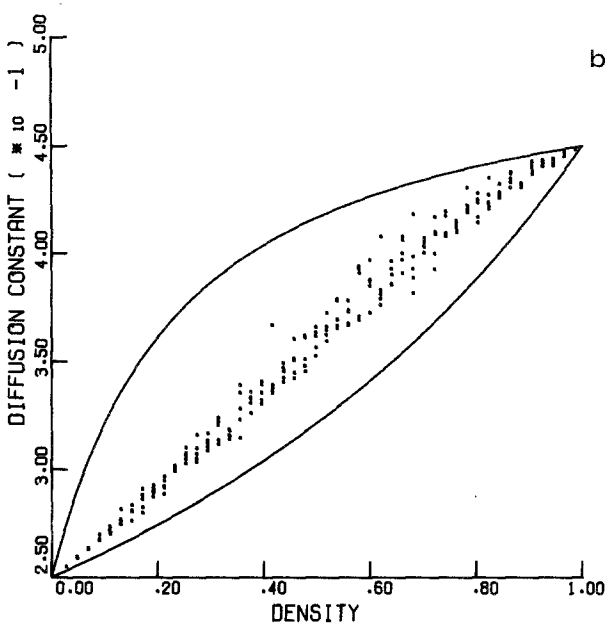


Fig. 2. The horizontal diffusion constant (dots) for different configurations of scatterers at various values of the density in a square unit cell of N sites, with $a = 0.45$, $a' = 0.25$. The curves are the lower and upper bounds (2.7) and (2.8). (a) $N = 16$, (b) $N = 49$, (c) $N = 100$.



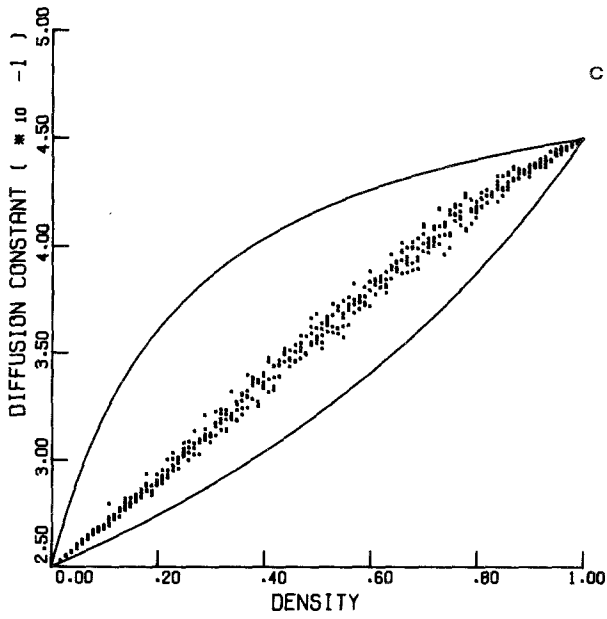


Fig. 2. (*Continued*)

tively (the corresponding vertical stepping probabilities are $b = 1/2 - a$ and $b' = 1/2 - a'$). Each site is independently chosen to be an impurity with probability ρ or a host site with probability $\rho' = 1 - \rho$. So with each site $r := (r_x, r_y)$, where the integers r_x and r_y run from $-m/2+1$ to $m/2$ (assume m even), we associate a random variable β_r, where

$$\beta_r = \begin{cases} 1 & \text{with probability } \rho \\ 0 & \text{with probability } 1-\rho \end{cases}$$

We again let $\overline{D_x^{(N)}}(\rho)$ and $D_x^{(\mathrm{R})}(\rho)$ denote the average diffusion constants over random-periodic or random configurations with density ρ, respectively. The unit cell in the random-periodic case will be a square with $N = m^2$ sites.

Each $\overline{D_x^{(N)}}(\rho)$ is a polynomial in ρ, so a well-defined density expansion in ρ exists. It is trickier to find an expansion for $D_x^{(\mathrm{R})}(\rho)$. Although it is known[3] that for each ρ,

$$D_x^{(\mathrm{R})} = \lim_{N \to \infty} \overline{D_x^{(N)}}(\rho)$$

it is not necessarily true that

$$\frac{\partial^k}{\partial \rho^k} D_x^{(\mathrm{R})}(\rho)|_{\rho=0} = \lim_{N \to \infty} \frac{\partial^k}{\partial \rho^k} \overline{D_x^{(N)}}(\rho)|_{\rho=0} \tag{3.1}$$

In ref. 2, the first term in the low-density expansion for $D_x^{(\mathrm{R})}(\rho)$ was computed by calculating the right-hand limit in (3.1) for $k = 1$ and asserting that this gives the correct value. This was proved in ref. 7, where it was also shown that (3.1) holds for $a' = 1/2$, $k = 1, 2$. The second-order expansion in this case was computed in terms of some probabilities for a simple random walk which could not be evaluated explicitly.[7] Here we compute the second-order term for the low-density expansion by evaluating the limit and asserting that (3.1) is true for $k = 2$, $a' \neq 1/2$ as well (actually, by asserting an equivalent relation). We do not prove that (3.1) holds; however, the result of ref. 7 leads us to believe that it is true. We will adapt the generating function method of ref. 2 to the case of a finite lattice as follows (see also ref. 9).

Start from a *finite* square lattice of m by m sites with periodic boundary conditions. Let $P_n(r, r_0)$ be the probability that the walker, starting from site r_0, is at site r after n steps. If T is the transition matrix of the walk, with matrix elements $T_{r,r'}$, then the generating function is

$$G(r, r_0; z) := \sum_{n=0}^{\infty} z^n P_n(r, r_0) = [\{1 - zT\}^{-1}]_{r,r_0} P(r_0) \tag{3.2}$$

where $P(r_0)$ is the initial distribution, which we will assume to be uniform, $P(r_0) = N^{-1}$. The moment generating function $\Gamma(\theta, z)$ is defined by

$$\Gamma(\theta, z) = \sum_{r,r'} \overline{G(r, r'; z)} e^{i\theta \cdot (r - r')} \tag{3.3}$$

where the bar denotes the average over the random variables $\{\beta_r\}$. Here $\theta = (\theta_x, \theta_y)$ is a vector of the reciprocal lattice, with $\theta_i = 2\pi r_i/m$, $i = x, y$. For later use we note the orthogonality relations

$$N^{-1} \sum_{r} e^{i(\theta - \theta') \cdot r} = \delta_{\theta,\theta'}; \qquad N^{-1} \sum_{\theta} e^{i\theta \cdot (r - r')} = \delta_{r,r'} \tag{3.4}$$

Defining

$$L_{xx}(z) := -\partial^2/\partial\theta_x^2 \, \Gamma(\theta, z)|_{\theta = 0} \tag{3.5}$$

one may obtain the horizontal diffusion constant as

$$2D_x = \lim_{z \uparrow 1} (1 - z^2) \, L_{xx}(z) \tag{3.6}$$

The limit $z \uparrow 1$ corresponds to the number of steps going to infinity.

Performing the density expansion as in ref. 2, Appendix B, we find the following result for $D_x^{(R)}$, which, as before, denotes the diffusion constant for the *infinite* random lattice:

$$D_x^{(R)}(a, a'; \rho) = a' + (a - a') \, \overline{\pi^*(\rho)} \tag{3.7}$$

where

$$\overline{\pi^*(\rho)} = \lim_{z \uparrow 1} \lim_{N \to \infty} \overline{\pi^*(N, z, \rho)} \tag{3.8}$$

with

$$\overline{\pi^*(N, z, \rho)} = \rho + N^{-1} \sum_{n=1}^{\infty} \left[\sum_{r_0} \sum_{r_1} \cdots \sum_{r_n} \Delta(r_0 - r_1) \, \Delta(r_1 - r_2) \cdots \right.$$
$$\left. \times \Delta(r_{n-1} - r_n) \, \overline{\beta_{r_0} \beta_{r_1} \cdots \beta_{r_n}} \right] \tag{3.9}$$

$$\Delta(r) = 2(a - a') N^{-1} \sum_{\theta} g(\theta) \exp(-i\theta \cdot r) \tag{3.10}$$

$$g(\theta) = \frac{z(\cos\theta_x - \cos\theta_y)}{1 - z\alpha_1 \cos\theta_x - z\alpha_2 \cos\theta_y} \tag{3.11}$$

$$\alpha_1 = 2a', \qquad \alpha_2 = 1 - \alpha_1 \tag{3.12}$$

The quantity (3.8) is the average stationary occupation probability of the walker to be on an impurity in the infinite lattice. It is easy to verify that the formulas given above reproduce the results of ref. 2.

The following symmetry relations are obvious [compare (2.10), (2.11)]:

$$D_x^{(\mathrm{R})}(a, a'; \rho) = D_x^{(\mathrm{R})}(a', a; 1-\rho) \tag{3.13}$$

$$\begin{aligned} D_x^{(\mathrm{R})}(a, a'; \rho) &= D_y^{(\mathrm{R})}(1/2-a, 1/2-a'; \rho) \\ &= 1/2 - D_x^{(\mathrm{R})}(1/2-a, 1/2-a'; \rho) \end{aligned} \tag{3.14}$$

where we have used the relation $2D_x^{(\mathrm{R})} + 2D_y^{(\mathrm{R})} = 1$. Thus, the low-density expansion can be used to obtain a high-density expansion as well. In the case $a' = 1/2 - a$, we write $D_x^{(\mathrm{R})}(a; \rho) := D_x^{(\mathrm{R})}(a, 1/2-a; \rho)$, which satisfies the additional symmetry relation

$$D_x^{(\mathrm{R})}(a; \rho) = 1/2 - D_x^{(\mathrm{R})}(a; 1-\rho) \tag{3.15}$$

In particular, $D_x^{(\mathrm{R})}(a, 1/2-a; 1/2) = 1/4$. This exact value for density $\rho = 1/2$ will allow for an easy check on the accuracy of the density expansion.

Now we want to obtain explicit expressions for the coefficients in the expansion of (3.8) and (3.9) in powers of the density,

$$\overline{\pi^*(N, z, \rho)} = c_1(N, z)\rho + c_2(N, z)\rho^2 + \cdots \tag{3.16a}$$

$$\overline{\pi^*(\rho)} = c_1\rho + c_2\rho^2 + \cdots \tag{3.16b}$$

$$c_i = \lim_{z \uparrow 1} \lim_{N \to \infty} c_i(N, z) \tag{3.16c}$$

Here we assert without proof that

$$\frac{\partial^i}{\partial \rho^i} \overline{\pi^*(\rho)}|_{\rho=0} = \lim_{z \uparrow 1} \lim_{N \to \infty} \frac{\partial^i}{\partial \rho^i} \overline{\pi^*(N, z, \rho)}|_{\rho=0}$$

The coefficients b_i in (1.1) are then obtained as

$$b_0 = a', \qquad b_i = (a - a')c_i, \qquad i = 1, 2, \ldots \tag{3.17}$$

Of course, the validity of such an expansion is not *a priori* clear. For the case $a' = 1/4$, it has been rigorously proven[7] that, for some $\varepsilon > 0$,

$$\overline{\pi^*(\rho)} = d_1\rho + d_2\rho^2 + \mathcal{O}(\rho^{2+\varepsilon}) \tag{3.18}$$

All terms of first order in the density correspond to $r_0 = r_1 = \cdots = r_n$ in (3.9), so the first-order coefficient $c_1(N, z)$ in (3.16) is given by

$$c_1(N, z) = [1 - \Delta(0)]^{-1} \tag{3.19}$$

In the limit $N \to \infty$ the summation in (3.10) can be replaced by an integration. The integral occurring in $\Delta(0)$ is elementary and we find, as $z \uparrow 1$,

$$c_1 = (1 - \Delta_1)^{-1} \tag{3.20}$$

where

$$\Delta_1 = 2(a - a')G_1 \tag{3.21}$$

and

$$G_1 = (2/\pi)[\alpha_1^{-1} \arctan (\alpha_1/\alpha_2)^{1/2} - \alpha_2^{-1} \arctan (\alpha_2/\alpha_1)^{1/2}] \tag{3.22}$$

The parameters α_1 and α_2 are defined in (3.12). In the case $a' = 1/4$, Δ_1 is identically zero.

Next we turn to the calculation of the second-order coefficient c_2. Since

$$\overline{\beta_{r_1}^k \beta_{r_2}^l} = \overline{\beta_{r_1} \beta_{r_2}} = \rho^2; \qquad k \geqslant 1, \quad l \geqslant 1, \quad r_1 \neq r_2 \tag{3.23}$$

the terms in (3.9) of second order in the density are those where in the average precisely *two distinct scatterers*, say μ and ν, are involved. Without loss of generality we assume that $r_0 = \mu$, so that each of the other sites $r_1, \ldots, r_n$ occurring in the summand of (3.9) can be chosen independently from the set $\{\mu, \nu\}$ in such a way that site ν occurs at least once. In this way we generate a sequence of sites,

$$\mu, \mu, \ldots, \mu, \nu, r_{k+1}, r_{k+2}, r_{k+3}, \ldots, r_n \tag{3.24}$$

where the first k positions ($1 \leqslant k \leqslant n$) contain site μ, then the first ν at position $k+1$, followed by $(n-k)$ sites independently chosen from $\{\mu, \nu\}$. With each "transition" from σ to σ' ($\sigma, \sigma' \in \{\mu, \nu\}$) is associated a contribution $\Delta(\sigma - \sigma')$. Thus, we get the following contribution associated with the complete sequence (3.24):

$$\text{first } k-1 \text{ transitions:} \quad [\Delta(0)]^{k-1} \tag{3.25a}$$

$$k\text{th transition:} \quad \Delta(\mu - \nu) \tag{3.25b}$$

$$\text{last } n-k \text{ transitions:} \quad \sum_{\sigma = \mu, \nu} \langle \nu | T_\Delta^{n-k} | \sigma \rangle \tag{3.25c}$$

where T_Δ, with matrix elements denoted by $\langle \sigma | T_\Delta | \sigma' \rangle$, is the "transition matrix"

$$T_\Delta = \begin{bmatrix} \Delta(0) & \Delta(\mu - \nu) \\ \Delta(\nu - \mu) & \Delta(0) \end{bmatrix} \tag{3.26}$$

We obtain the following expression after collecting all contributions of order ρ^2 in (3.9):

$$c_2(N, z) = N^{-1} \sum_{\mu,\nu}{}' \sum_{n=1}^{\infty} \sum_{k=1}^{n} \Delta(0)^{k-1} \Delta(\mu - \nu) \sum_{\sigma} \langle \nu | T_\Delta^{n-k} | \sigma \rangle \tag{3.27}$$

where the prime on the first summation sign indicates that the terms with $\mu = \nu$ should be omitted. Carrying out the summations over n and k, this becomes

$$c_2(N, z) = N^{-1} \sum_{\mu,\nu}{}' [1 - \Delta(0)]^{-1} \Delta(\mu - \nu) \sum_{\sigma} \langle \nu | G | \sigma \rangle \tag{3.28}$$

where G is the matrix

$$G = [1 - T_\Delta]^{-1} \tag{3.29}$$

The derivation of the second-order term c_2 presented here can easily be extended to higher orders using the "transition matrix" language introduced above.

Using that $\Delta(\sigma - \sigma') = \Delta(\sigma' - \sigma)$, we find from (3.28),

$$c_2(N, z) = N^{-1} \sum_{\mu,\nu}{}' [1 - \Delta(0)]^{-1} \Delta(\mu - \nu)[1 - \Delta(0) - \Delta(\mu - \nu)]^{-1} \tag{3.30}$$

Now we can carry out the summation over one of the indices because of the translation invariance of Δ, so

$$c_2(N, z) = \sum_{r \neq 0} [1 - \Delta(0)]^{-1} \Delta(r)[1 - \Delta(0) - \Delta(r)]^{-1} \tag{3.31}$$

In the limit of an infinite lattice we can express $\Delta(r)$ as an integral,

$$\Delta(r) = 2(a - a')(2\pi)^{-2} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} g(\theta) e^{-i\theta \cdot r} \, d\theta \tag{3.32}$$

and we list the following symmetry properties:

$$\Delta(r_x, r_y) = \Delta(-r_x, r_y) = \Delta(r_x, -r_y) = \Delta(-r_x, -r_y) \tag{3.33}$$

An extensive analysis of the lattice sums occurring in (3.31) has been given by Ernst and van Velthoven[9] for the case $a' = 1/4$. Following their approach, we separate out the single and double "crossings" between two impurities:

$$c_2(N, z) = \sum_{r \neq 0} \frac{\Delta(r)}{[1-\Delta(0)]^2} + \sum_{r \neq 0} \frac{\Delta^2(r)}{[1-\Delta(0)]^3} + \sum_{r \neq 0} \frac{\Delta^3(r)}{[1-\Delta(0)]^3 [1-\Delta(0)-\Delta(r)]} \tag{3.34}$$

Using the orthogonality relation (3.4), we have

$$\sum_r \Delta(r) = 0 \tag{3.35}$$

and

$$\Delta_2 := \sum_r \Delta^2(r) = \{2(a-a')\}^2 G_2 \tag{3.36}$$

where

$$G_2 = N^{-1} \sum_\theta g^2(\theta) \tag{3.37}$$

3.1. The Case $0 < a < 1/2$, $0 < a' < 1/2$

In the limit $N \to \infty$ the sum (3.37) becomes an integral. Assuming that $a' > 0$, one can evaluate this integral for $z \uparrow 1$ as

$$\begin{aligned} G_2 = (2/\pi)[&\alpha_1^{-2} \arctan(\alpha_1/\alpha_2)^{1/2} \\ &+ \alpha_2^{-2} \arctan(\alpha_2/\alpha_1)^{1/2} - (1/2\alpha_1)(\alpha_2/\alpha_1)^{1/2} \\ &- (1/2\alpha_2)(\alpha_1/\alpha_2)^{1/2} - 1/(\alpha_1\alpha_2)^{1/2}] \end{aligned} \tag{3.38}$$

So we have the following expression for the second-order coefficient c_2 as defined in (3.16c):

$$c_2 = -\frac{\Delta_1}{[1-\Delta_1]^3} + \frac{\Delta_2}{[1-\Delta_1]^3} + \frac{1}{[1-\Delta_1]^3} \sum_{r \neq 0} \frac{\Delta^3(r)}{1-\Delta_1-\Delta(r)} \tag{3.39}$$

We have checked numerically that the third term in (3.39) contributes less than 1% for $|a' - 1/4| \leqslant 0.1$. For the case $a' = 1/4$, even more accurate approximations to c_2 can be obtained by adding higher powers of a few low-order lattice integrals to the first two terms in (3.39) (see ref. 9). We

will not pursue this further here, since, as a' approaches 0 or 1, these refined approximations become inaccurate as well. This limiting case will be treated separately below.

Combining the results obtained so far, we get the following expression for $D_x^{(R)}(a;\rho)$ to second order in the density, where the coefficient of ρ^2 has an accuracy of 1% for $|a'-1/4| \leqslant 0.1$:

$$D_x^{(R)}(a;\rho) = a' + (a-a')\left\{\frac{1}{1-\Delta_1}\rho + \frac{-\Delta_1+\Delta_2}{(1-\Delta_1)^3}\rho^2\right\} \tag{3.40}$$

Here

$$\Delta_1 = 2(a-a')G_1, \qquad \Delta_2 = 2(a-a')^2 G_2 \tag{3.41}$$

with G_1 and G_2 given by (3.22) and (3.38).

In Fig. 3 we present the result of the density expansions (3.40) for $a=0.4$, $a'=0.25$. In this case $\Delta_1 = 0$, since G_1 vanishes; see (3.22). The data points (open circles), representing the exact value of the diffusion constant, were calculated by the cell method with a unit cell of 40 by 40 sites. We use an iterative method to solve the linear system of equations which

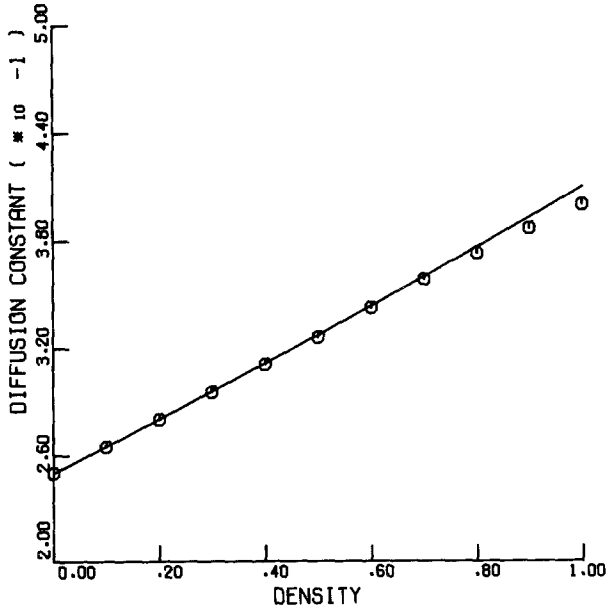


Fig. 3. Horizontal diffusion constant versus the density for randomly distributed scatterers. Circles: exact result calculated numerically for a unit cell of 40 by 40 sites. Line: approximation to second order in the density, $a=0.4$, $a'=0.25$.

determines the eigenvector π of the transition matrix (see Section 2). Each data point takes about 5 CPU sec of computation time on a CDC Cyber 170-750.

It is seen that the density expansion to second order is remarkably accurate even for moderately high densities. Also note that the exact diffusion constant does not deviate much from the contribution to first order in the density.

3.2. The Case $a = 1/2$, $a' = 0$

We consider the limiting case where from a type-a scatterer (impurity) only horizontal jumps are possible and from type-b scatterers (host sites) only vertical jumps: $a = 1/2$, $a' = 0$, and calculate the first- and second-order coefficients c_1 and c_2 in (3.16b). This case is different from the general situation treated before in that the walk is no longer necessarily irreducible: there may be isolated horizontal or vertical strips from which the walker cannot escape, as well as sites which are not reachable from other sites, i.e., which are transient. The latter however, do not contribute to the diffusion constant. Examples are given in Fig. 4. For any ρ strictly between zero and one, the probability of "isolated strips" goes to zero as the unit cell becomes arbitrarily large.

It turns out that in this case the density expansion up to second order fails to produce a good approximation to the exact diffusion constant. Therefore this example, apart from its intrinsic interest, may serve as a demonstration that the accuracy of the density expansion up to second order critically depends on the values of the parameters a and a'.

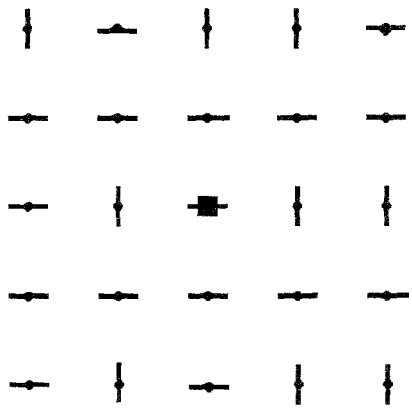


Fig. 4. Unit cell of 5 by 5 sites. —●— Type-a scatterer; ● type-a' scatterer. From row 2 or 4 the walker cannot escape. The site marked ■ is not reachable from any other site.

Since the calculation of the expansion coefficients for the diffusion constant $D_x^{(R)}(\rho)$ is quite lengthy in this case, we refer the reader to the Appendix for the details. The result of the expansion (1.1) to second order in the density reads

$$D_x^{(R)}(\rho) = (\ln 2)\rho^2 + \mathcal{O}(\rho^3) \tag{3.42a}$$

Notice that the diffusion constant is zero to first order in the density.

The second-order approximation gives $D_x^{(R)}(1/2) = 0.173$, which is 31% below the exact value 0.25. The approximation (3.42a) is to be used for $\rho < 0.5$. For $\rho > 0.5$ we have [see (3.15)],

$$D_x^{(R)}(\rho) = 0.5 - (\ln 2)(1-\rho)^2 + \mathcal{O}((1-\rho)^3) \tag{3.42b}$$

The result of the second-order approximation (3.42) is plotted in Fig. 5 as the solid curves. The circles are the values computed by the cell method, with a unit cell of 40 by 40 sites. Since the system of linear equations to be solved is much more ill-conditioned than in the previous case, the computation requires now about 50 CPU sec per data point.

One may wonder about the effect of the finite size of the unit cell. We know from symmetry considerations that at density $\rho = 0.5$ the exact value

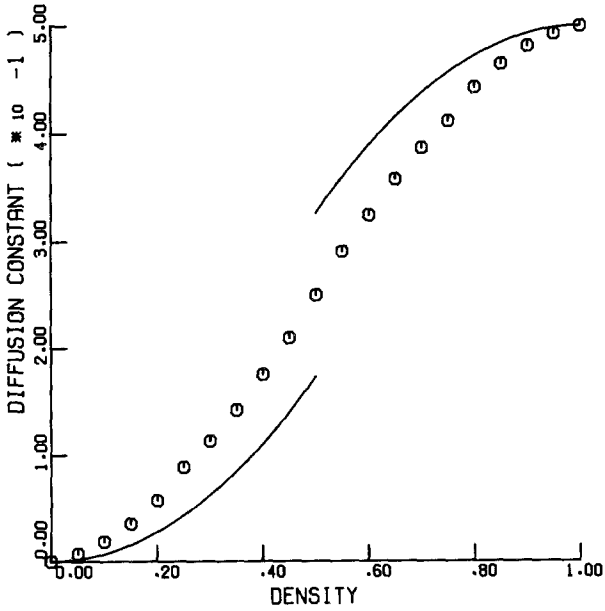


Fig. 5. Horizontal diffusion constant versus the density for randomly distributed scatterers. Circles: exact result calculated numerically for a unit cell of 40 by 40 sites. Line: approximation to second order in the density. $a = 0.5$, $a' = 0.0$.

of the occupation probability is 0.5, whereas the numerical value for the 40-by-40 unit cell was 0.497. Therefore we seem to be close enough to "infinity" to qualify the data points as the exact values for the infinite lattice.

In this case we find very poor agreement between the exact results and those of the density expansion.

4. MONOTONICITY LAW

In this section we discuss an analogue of the monotonicity law for reversible random walks[8] in the case of anisotropic scatterers, an example of a nonreversible walk.

First we consider the following simple example. Take a periodic lattice generated by the 2-by-2 unit cell depicted in Fig. 6. Each of the four sites has different stepping probabilities p_β and $q_\beta = 1/2 - p_\beta$ in the horizontal and vertical directions, respectively, where $0 \leqslant p_\beta \leqslant 1/2$. We always assume in this section that the random walk on this periodic lattice is irreducible. The corresponding transition matrix T between the internal states is

$$T = \begin{bmatrix} 0 & 2p_2 & 0 & 2q_4 \\ 2p_1 & 0 & 2q_3 & 0 \\ 0 & 2q_2 & 0 & 2p_4 \\ 2q_1 & 0 & 2p_3 & 0 \end{bmatrix} \tag{4.1}$$

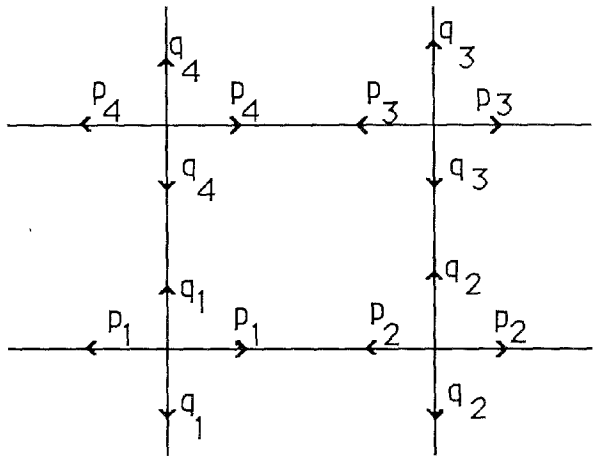


Fig. 6. Two-by-two unit cell with four distinct scatterers.

To calculate the diffusion constants, we need the eigenvector π of T corresponding to the eigenvalue one. The components $\{\pi_\beta\}$ have a convenient representation in terms of the determinant

$$A(\lambda) = |\lambda I - T| \tag{4.2}$$

where T is the transition matrix of the Markov chain and I the unit matrix. When the minor obtained from $A(\lambda)$ by deleting row β and column β is denoted by $A_\beta(\lambda)$, then[10]

$$\pi_\beta = A_\beta(1)/A'(1), \qquad A'(1) = \sum_{\gamma=1}^{4} A_\gamma(1) \tag{4.3}$$

Explicit calculation yields (suppressing the argument of the A_β's)

$$\begin{aligned} A_1 &= 4(p_2q_3 + p_3q_4); \qquad A_2 = 4(p_1q_4 + p_4q_3) \\ A_3 &= 4(p_4q_1 + p_1q_2); \qquad A_4 = 4(p_3q_2 + p_2q_1) \end{aligned} \tag{4.4}$$

Now we look at the derivative of $D_x = \sum p_\beta \pi_\beta$ with respect to one of the horizontal transition probabilities, say p_1. We find

$$\frac{\partial D_x}{\partial p_1} = \frac{4A_1^2}{\{\sum_\gamma A_\gamma\}^2} = 4\pi_1^2 \tag{4.5}$$

and similarly,

$$\frac{\partial D_x}{\partial p_\alpha} = 4\pi_\alpha^2, \qquad \alpha = 1,..., 4 \tag{4.6}$$

The derivative of D_x is strictly positive, since we have assumed the walk to be irreducible, which implies that the minors $A_\beta(1)$ and the probabilities π_β are strictly positive.

The result (4.6) leads us to conjecture that for a unit cell of N sites with arbitrary stepping probabilities p_β and $q_\beta = 1/2 - p_\beta$ at site β,

$$\partial D_x/\partial p_\alpha = N\pi_\alpha^2, \qquad \alpha = 1,..., N \tag{4.7}$$

It turns out that (4.7) is indeed correct, and can be generalized to walks with non-nearest-neighbor transitions, higher-dimensional lattices, etc. (see ref. 14). It can also be shown that the monotonicity law (4.7) still holds if the transition probabilities are $a + bp_i$ to jump horizontally from site i, $c + dp_i$ to jump vertically, and $1 - 2(a + c) - 2(b + d)p_i$ to stay at site i. Note that in this case all transitions from site i are described by a *single* parameter p_i.

From (4.7) it is easily shown that all derivatives of D_x of odd order are nonnegative. To show this, first note that the minor $A_\alpha(1)$ does not depend on p_α, so

$$\frac{\partial \pi_\alpha}{\partial p_\alpha} = -\frac{A_\alpha}{[A'(1)]^2}\frac{\partial A'(1)}{\partial p_\alpha} \tag{4.8}$$

and, since $A'(1)$ is linear in p_α,

$$\frac{\partial^n \pi_\alpha}{\partial p_\alpha^n} = n!\left(\frac{\partial \pi_\alpha}{\partial p_\alpha}\right)^n \pi_\alpha^{-(n-1)} \tag{4.9}$$

Using (4.7) and (4.9), we find for the nth derivative of D_x with respect to p_α,

$$\frac{\partial^n D_x}{\partial p_\alpha^n} = Nn!\left(\frac{\partial \pi_\alpha}{\partial p_\alpha}\right)^{n-1} \pi_\alpha^{-(n-3)} \tag{4.10}$$

which is nonnegative for odd n.

To demonstrate that the result (4.7), although it may be regarded as self-evident, is not trivial, we construct a counterexample for which, *a priori*, the monotonicity law might be regarded as equally self-evident. Consider again the 2-by-2 unit cell of Fig. 6, the only difference now being that there is a waiting probability $r_\beta = 1 - 2(p_\beta + q_\beta)$ at each site β, with $q_\beta \leqslant 1/2 - p_\beta$. The transition matrix is the same as in (4.1) except for the diagonal elements $T_{\beta\beta} = r_\beta$. This example violates the condition, as formulated above, under which the monotonicity law with waiting times holds, since in this case we have *two* independent parameters p_β, q_β at each site β, instead of a single one.

To simplify the calculations, we set $p_2 = q_3 = 0$, which still leaves the walk irreducible. Again we differentiate D_x with respect to p_1, *but now keeping* q_1 *constant*. The result is

$$\partial D_x/\partial p_1 = 2[q_2(p_4 + q_4) + q_1(q_2 - p_4)]\, 64p_3^2 q_2 q_4/[A'(1)]^2 \tag{4.11}$$

which may become negative. For example, if $p_4 = q_4 = 1/4$, this is the case when $q_2 < 2q_1(1/4 - q_2)$. This is somewhat unexpected, since increasing p_1 while keeping q_1 constant (therefore decreasing r_1) means that the probabilities of stepping horizontally, vertically, or pausing at site 1 are larger, unchanged, and smaller, respectively. So one would think that D_x should increase. The counterexample shows that this is not the case.

We end this section by showing how the monotonicity law can be used to show that the average diffusion constants $D_x^{(N)}(\rho)$ and $D_x^{(R)}(\rho)$ are

(strictly) monotone functions of ρ. Consider a lattice with two possible values for the transition probability p_k. We assign the p_k at random such that $p_k = a$ with probability ρ and $p_k = a'$ with probability $1-\rho$, where $a > a'$. As before, we let $c = \max\{a/a', (\frac{1}{2}-a')/(\frac{1}{2}-a)\}$. We will show for each $\rho > 0$,

$$\frac{\partial}{\partial \rho} \overline{D_x^{(N)}}(\rho) \geqslant c^{-4}(a-a') \left(\frac{N}{N+1}\right)^2 \tag{4.12}$$

This implies for all ρ, $\Delta\rho > 0$,

$$\liminf_{N \to \infty} \overline{D_x^{(N)}}(\rho + \Delta\rho) - \overline{D_x^{(N)}}(\rho) \geqslant c^{-4}(\Delta\rho)(a-a') \tag{4.13}$$

where the convergence is uniform for $\rho \geqslant \rho_0 > 0$. Hence

$$D_x^{(R)}(\rho + \Delta\rho) - D_x^{(R)}(\rho) \geqslant c^{-4}(\Delta\rho)(a-a') \tag{4.14}$$

Consider an $m \times m$ unit cell with $N = m^2$ sites and let Λ_j be the set of arrangements A of scatterers with exactly j impurities. There are N translations τ of the unit cell with periodic boundary conditions and we let τA denote the appropriately translated arrangement. Then

$$\lambda_S^A = \sum_{\substack{\tau \\ (\tau A)_0 = S}} \pi_0^{\tau A}, \qquad \lambda_R^A = \sum_{\substack{\tau \\ (\tau A)_0 = R}} \pi_0^{\tau A}$$

For notational convenience we write

$$\sum^S = \sum_{\substack{\tau \\ (\tau A)_0 = S}} ; \qquad \sum^R = \sum_{\substack{\tau \\ (\tau A)_0 = R}}$$

Let $r(j)$ be the average fraction of time spent on impurities, averaged over all arrangements with j impurities, i.e.,

$$r(j) = \binom{N}{j}^{-1} \sum_{A \in \Lambda_j} \sum^S \pi_0^{\tau A}$$

Then $1 - r(j)$ is the average fraction of time spent on host sites,

$$1 - r(j) = \binom{N}{j}^{-1} \sum_{A \in \Lambda_j} \sum^R \pi_0^{\tau A}$$

If $A \in \Lambda_j$ with $A_0 = S$ and $\bar{A}$ is the arrangement that agrees everywhere with A except at 0, where $\bar{A}_0 = R$, then by Lemma 6.1 of ref. 7,

$$c^{-1}\pi_0^A \leqslant \pi_0^{\bar{A}} \leqslant c\pi_0^A$$

Therefore

$$r(j)=\binom{N}{j}^{-1}\sum_{A\in\Lambda_j}\sum^{S}\pi_0^{\tau A}\leqslant c\binom{N}{j}^{-1}\sum_{A\in\Lambda_j}\sum^{S}\pi_0^{\overline{\tau A}}=c\binom{N}{j}^{-1}\sum_{A\in\Lambda_{j-1}}\sum^{R}\pi_0^{\tau A}$$

This gives

$$r(j)\leqslant c\frac{j}{N-j+1}[1-r(j-1)]$$

and similarly

$$r(j)\geqslant c^{-1}\frac{j}{N-j+1}[1-r(j-1)]$$

It follows immediately from above, using the monotonicity of $r(j)$, which is a consequence of (4.7), that

$$r(j)\geqslant\frac{j}{c(N+1)}$$

$$1-r(j)\geqslant\frac{N-j}{c(N+1)}$$

We now differentiate $\overline{D_x^{(N)}}(\rho)$,

$$\overline{D_x^{(N)}}(\rho)=\sum_{j=0}^{N}\rho^j(1-\rho)^{N-j}\sum_{A\in\Lambda_j}D_x^A$$

$$\frac{\partial}{\partial\rho}\overline{D_x^{(N)}}(\rho)=\sum_{j=1}^{N}\rho^{j-1}(1-\rho)^{N-j}\left\{j\sum_{A\in\Lambda_j}D_x^A-(N-j+1)\sum_{A\in\Lambda_{j-1}}D_x^A\right\}$$

Consider the term in the brackets. Note that $D_x^A=D_x^{\tau A}$ for any translation τ. We have

$$j\sum_{A\in\Lambda_j}D_x^A-(N-j+1)\sum_{A\in\Lambda_{j-1}}D_x^A=\sum_{A\in\Lambda_j}\sum^{S}D_x^{\tau A}-\sum_{A\in\Lambda_{j-1}}\sum^{R}D_x^{\tau A}$$

$$=\sum_{A\in\Lambda_j}\sum^{S}(D_x^{\tau A}-D_x^{\overline{\tau A}})$$

If $\bar{A}$ is any arrangement with $\bar{A}_0=R$ and B is any assignment of horizontal probabilities which agrees with $\bar{A}$ everywhere except at 0, where p_0 lies between a' and a, then by another application of Lemma 6.1 of ref. 7

$$\pi_0^B\geqslant c^{-1}\pi_0^{\bar{A}}$$

Therefore, by (4.7),

$$D_x^A - D_x^{\bar{A}} \geqslant c^{-2} N(a-a')(\pi_0^{\bar{A}})^2$$

So,

$$\begin{aligned}
& j \sum_{A \in \Lambda_j} D_x^A - (N-j+1) \sum_{A \in \Lambda_{j-1}} D_x^A \\
& \quad \geqslant \sum_{A \in \Lambda_j} \sum^{S} c^{-2} N(a-a')(\pi_0^{\overline{\tau A}})^2 \\
& \quad = c^{-2} N \sum_{A \in \Lambda_{j-1}} \sum^{R} (a-a')(\pi_0^{\tau A})^2 \\
& \quad \geqslant c^{-2} N(a-a') \left[\binom{N}{j-1} (N-j+1) \right]^{-1} \left[\sum_{A \in \Lambda_{j-1}} \sum^{R} \pi_0^{\tau A} \right]^2 \\
& \quad = c^{-2} N(a-a') \left[\binom{N}{j-1} (N-j+1) \right]^{-1} \left\{ \binom{N}{j-1} [1 - r(j-1)] \right\}^2 \\
& \quad \geqslant c^{-2} N(a-a') \left[\binom{N}{j-1} (N-j+1) \right]^{-1} \left[\binom{N}{j-1} \frac{N-j+1}{c(N+1)} \right]^2 \\
& \quad = c^{-4} (a-a') \left(\frac{N}{N+1} \right)^2 \binom{N-1}{j-1}
\end{aligned}$$

Therefore,

$$\begin{aligned}
\frac{\partial}{\partial \rho} \overline{D_x^{(N)}}(\rho) & \geqslant c^{-4} (a-a') \left(\frac{N}{N+1} \right)^2 \sum_{j=1}^{N} \rho^{j-1} (1-\rho)^{N-j} \binom{N-1}{j-1} \\
& = c^{-4} (a-a') \left(\frac{N}{N+1} \right)^2
\end{aligned}$$

which proves (4.12). Hence

$$\liminf_{N \to \infty} \frac{\partial}{\partial \rho} \overline{D_x^{(N)}}(\rho) \geqslant c^{-4} (a-a')$$

which yields (4.13). It is easy to check that the convergence is uniform for $\rho \geqslant \rho_0 > 0$.

APPENDIX

In this Appendix a derivation of the result (3.42a) is presented. We start from the formulas (3.7)–(3.12), taking first the limit $N \to \infty$ and then

the limit $z \uparrow 1$. The first quantity we have to consider is $\Delta(r)$, as defined in (3.32):

$$\Delta(r) = \frac{2(a-a')}{(2\pi)^2} \int_{-\pi}^{\pi} d\theta_x \int_{-\pi}^{\pi} d\theta_y \times \left(\frac{z(\cos\theta_x - \cos\theta_y)}{1 - z\alpha_1 \cos\theta_x - z\alpha_2 \cos\theta_y} \right) e^{-ir_x\theta_x} e^{-ir_y\theta_y} \tag{A.1}$$

where $\alpha_1 = 2a'$, $\alpha_2 = 1 - 2\alpha_1$. It is convenient to express $\Delta(r)$ in terms of integrals of Bessel functions. For that purpose, introduce the function

$$U(z; r_x, r_y) = \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} d\theta_x \int_{-\pi}^{\pi} d\theta_y \frac{e^{-i(r_x\theta_x + r_y\theta_y)}}{1 - z\alpha_1 \cos\theta_x - z\alpha_2 \cos\theta_y}$$

$$= \int_0^\infty dx\, e^{-x} I_{r_x}(z\alpha_1 x)\, I_{r_y}(z\alpha_2 x) \tag{A.2}$$

where $I_k(x)$ is the kth Bessel function of purely imaginary argument.[12] Then $\Delta(r) = \Delta(k, m)$, k and m integer, can be written as

$$\Delta(k, m) = (a - a')\, z[U(z; k+1, m) + U(z; k-1, m) - U(z; k, m+1) - U(z; k, m-1)] \tag{A.3}$$

For the case $a' = 0$ we have $\alpha_1 = 0$, $\alpha_2 = 1$. Using that $I_k(0) = \delta_{k,0}$ and

$$\int_0^\infty dx\, e^{-x} I_k(zx) = z^{|k|}(1 - z^2)^{-1/2}[1 + (1 - z^2)^{1/2}]^{-|k|} \tag{A.4}$$

we find

$$U(z; k, m) = U(z; -k, m) = U(z; k, -m) = U(z; -k, -m) = \delta_{k,0} U(z; m) \tag{A.5a}$$

where

$$U(z; m) = z^{|m|}(1 - z^2)^{-1/2}[1 + (1 - z^2)^{1/2}]^{-|m|} \tag{A.5b}$$

It follows that

$$\Delta(0, 0) = -zU(z; 1) \tag{A.6a}$$

$$\Delta(k, 0) = \tfrac{1}{2} z \delta_{k,1} U(z; 0), \qquad k \geqslant 1 \tag{A.6b}$$

$$\Delta(0, m) = -\tfrac{1}{2} z[U(z; m+1) + U(z; m-1)] = -U(z; m), \qquad m \geqslant 1 \tag{A.6c}$$

$$\Delta(k, m) = \tfrac{1}{2} z \delta_{k,1} U(z; m), \qquad k \geqslant 1, \quad m \geqslant 1 \tag{A.6d}$$

The coefficients c_i in (3.16b) are given by

$$c_i = \lim_{z \uparrow 1} c_i(z) \tag{A.7}$$

From

$$c_1(z) = [1 - \Delta(0,0)]^{-1} \tag{A.8a}$$

we find, using (A.6a) and (A.5b),

$$c_1 = \lim_{z \uparrow 1} \{1 + z(1-z^2)^{-1/2}[1 + (1-z^2)^{1/2}]\}^{-1} = 0 \tag{A.8b}$$

Since $b_0 = a' = 0$ and $b_1 = (a - a')c_1 = 0$, the horizontal diffusion constant (1.1) is zero to first order in the density.

Next we consider the second-order coefficient $b_2 = \frac{1}{2}\lim_{z \uparrow 1} c_2(z)$, where

$$c_2(z) = \sum_{r \neq 0} [1 - \Delta(0)]^{-1} \Delta(r)[1 - \Delta(0) - \Delta(r)]^{-1} \tag{A.9}$$

We split up the summation over $r = (k, m) \neq (0, 0)$ in three parts, making use of the symmetry of $\Delta(k, m)$:

$$\sum_{r \neq 0} S(k,m) = 2 \sum_{m=1}^{\infty} S(0,m) + 2 \sum_{k=1}^{\infty} S(k,0) + 4 \sum_{k=1}^{\infty} \sum_{m=1}^{\infty} S(k,m) \tag{A.10}$$

where $S(k, m)$ denotes the summand of (A.9). Using (A.6), one finds

$$\begin{aligned} c_2(z) = {} & 2 \sum_{m=1}^{\infty} [1 - \Delta(0,0)]^{-1} \Delta(0,m)[1 - \Delta(0,0) - \Delta(0,m)]^{-1} \\ & + 2[1 - \Delta(0,0)]^{-1} \Delta(1,0)[1 - \Delta(0,0) - \Delta(1,0)]^{-1} \\ & + 4 \sum_{m=1}^{\infty} [1 - \Delta(0,0)]^{-1} \Delta(1,m)[1 - \Delta(0,0) - \Delta(1,m)]^{-1} \end{aligned} \tag{A.11}$$

The second term in (A.11) is easily shown to go to zero as $z \uparrow 1$, and is omitted in the following. In the other two terms we expand the last factor in a geometrical series. Using (A.6), we arrive at

$$c_2(z) = \sum_{m=1}^{\infty} \sum_{j=1}^{\infty} a_j^{(m)} \tag{A.12a}$$

with

$$a_j^{(m)} = \left[2(-)^j + 4\left(\frac{1}{2}z\right)^j \right] (1-z^2)^{1/2} \left(\frac{z}{1 + (1-z^2)^{1/2}} \right)^{mj} \tag{A.12b}$$

For $|z|<1$ the series $\sum_j a_j^{(m)}$ is absolutely convergent for all m and the double series $\sum_m \sum_j |a_j^{(m)}|$ is convergent. Therefore we may interchange the order of summation (ref. 13, p. 241). Carrying out the summation over m, we find

$$c_2(z)=2\sum_{j=1}^{\infty}(-)^j f_j(z)+4\sum_{j=1}^{\infty}\left(\frac{1}{2}z\right)^j f_j(z) \tag{A.13a}$$

where

$$f_j(z)=(1-z^2)^{1/2}\frac{z^j}{[1+(1-z^2)^{1/2}]^j-z^j} \tag{A.13b}$$

We cannot evaluate the series (A.13a) exactly. But we only need the limiting value as $z\uparrow 1$. It is immediate that

$$0\leqslant f_j(z)\leqslant j^{-1} \tag{A.14}$$

So the second series in (A.13a) is bounded by the convergent series $\sum (1/2)^j j^{-1}$ and therefore, by Weierstrass' test, uniformly convergent (ref. 13, p. 345). The first series needs a little more consideration, since it is not absolutely convergent for $z=1$. But since $f_j\geqslant 0$, $f_{j+1}/f_j\leqslant 1$ (easy to prove), and $f_j\to 0$ as $j\to\infty$, we have that the absolute value of the remainder after m terms is smaller than that of the first neglected term (ref. 13, p. 250), so

$$|S-S_m|\leqslant f_{m+1}(z)\leqslant (m+1)^{-1} \tag{A.15}$$

where S and S_m are the sum and partial sum after m terms of the first series in (A.13a), respectively. So the remainder is bounded by $(m+1)^{-1}$, uniformly in z; hence (ref. 13, p. 332), the first series is also uniformly convergent. Therefore we may take the limit $z\uparrow 1$ first to get

$$c_2=\sum_{j=1}^{\infty}\left[2(-)^j+4\left(\frac{1}{2}\right)^j\right]\frac{1}{j}=-2\ln 2+4\ln 2=2\ln 2 \tag{A.16}$$

and $b_2=(a-a')c_2=(1/2-0)c_2=\ln 2$. Inserting the results for b_0, b_1, and b_2 found above in (1.1), we arrive at (3.42a).

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