Effects of structure on transport coefficients in a random medium

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(Received 11 May 1994)

The transport coefficients for a system of classical particles moving in a random medium are shown to depend on the detailed structure of the medium even at strictly fixed scatterer concentration. An example is developed in which the diffusion coefficient can be expressed in terms of the distribution of distances between scatterers; this expression reduces considerably the maximum and average relative error when compared with previous results. Some statistical properties of the distribution of coefficients at fixed concentration are investigated.

PACS number(s): 05.20.Dd, 44.30.+v, 66.30.Dn

Transport coefficients in random media have been the subject of considerable study in recent years [1,2]; much of this work has addressed anomalous diffusion in fractal geometries and percolation clusters, both of which are relevant to a number of physical situations, or models with a random distribution of transition rates or bond conductivities [3]. In this paper the focus is on the effect of the *detailed structure* of a random medium in the case of normal diffusion — when the mean-squared displacement grows linearly with time. A familiar problem is considered: that of diffusion of classical particles in a random medium of fixed scatterers, known as the Lorentz [4] or wind-tree model. This model has been used extensively to study the transport of mass, heat, or electric charge in inhomogeneous media and binary gas mixtures with a large molecular weight ratio. A particular case is developed in which the diffusion coefficient of specific configurations can be related *directly* to the distribution of path lengths between scatterers. Evidence is presented for structure-induced variations, and some properties of the distribution of diffusion coefficients at constant concentration are studied.

The specific model under study is a stochastic Lorentz model in the square lattice. Scatterers are placed randomly at nodes of the lattice with concentration c. Mutually independent particles move with unit speed from lattice node to node at integer time steps, and conserve the direction of their motion until they encounter a scatterer; at that point they turn at right angles, either left or right with equal probability. Having the particles not interact with each other means that the only relevant transport mode is diffusion of any of the quantities mentioned above [5]. While the concentration dependence of the diffusion coefficient in this model is known (see, for example, [6]), its detailed dependence on medium structure has not been studied before.

The discrete Green-Kubo relation for the diffusion coefficient in two-dimensional (2D) lattices [7],

$$D = \left(\frac{1}{2} \sum_{t=0}^{\infty} \langle\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle\rangle \right) - \frac{1}{4}, \tag{1}$$

expresses the diffusion coefficient in terms of velocity correlations. The last term, known as the propagation term, is due to the discreteness of time. The double angular brackets denote an average over initial conditions, configurations, and possible histories of the system. Under the Boltzmann approximation of uncorrelated collisions, one has for the model considered here $\langle\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle\rangle = (1-c)^t$, as in this case all memory of initial velocity is lost after the first collision. Then, Eq. (1) reduces to $D_B = 1/2c - \frac{1}{4}$, a result well-tested numerically [6,8], which will be henceforth called the simple Boltzmann approximation.

To begin the study of structural effects, the diffusion coefficient for a specific configuration of M sites can be defined as follows:

$$D = \left(\frac{1}{2M} \sum_{t=0}^{\infty} \sum_{p=1}^{M} \langle \mathbf{v}_p(0) \cdot \mathbf{v}_p(t) \rangle \right) - \frac{1}{4}, \tag{2}$$

where the second summation is over particles, located initially one at each node with velocity $+x$. (A further summation over initial directions can be performed, but that does not change any of the subsequent results.) This is exactly equivalent to placing one particle at a random position and averaging over histories. In this case the single angular brackets denote an average over possible histories, and in the Boltzmann approximation $\langle \mathbf{v}_p(0) \cdot \mathbf{v}_p(t) \rangle = f_p$, the length of the initial flight of particle p until it encounters the scatterer to its immediate right. Equation (2) can be also expressed in terms of the distance d_s between scatterer s and its next neighbor to the right. Knowing that initially there are d_s particles between the two scatterers allows substitution of the well-known Euler identity, yielding finally

$$D_B = \left(\frac{1}{4M} \sum_{s=1}^{N} (1 + d_s) d_s \right) - \frac{1}{4}, \tag{3}$$

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where now the summation is over $N = cM$ scatterers.

Equation (3) expresses the Boltzmann-level diffusion coefficient of this model in terms of structural properties of each configuration. Figure 1 shows a typical comparison of Eq. (3) with simulations done by the exact enumeration method [9] for the same set of 1000 systems of size 50×50 with $c = 0.5$ exactly. The choice of helical boundary conditions prevents occasional nondiffusing trajectories. The numerical method computes Eq. (2) directly over all trajectories consistent with the configuration; in this case the time summation is truncated after 600 time steps. The errors introduced by this truncation are very small. The correlation in Fig. 1 is not perfect, but the new result reduces the average relative error and maximum error between Eq. (3) and the numerical measurement when compared with the structure-indepedent approximation, $D_B = 3/4$ in this case. Table I shows such statistics for a range of concentrations; typical error reductions are between a third and a half.

The two limiting cases of highest and lowest D_B for $c = 1/2$ can be solved exactly starting with Eq. (3), and have been verified numerically. D is lowest when the scatterers are arranged in a checkerboard pattern; then the average initial flight is $\bar{f}_p = 3/2$, and $D_B = 1/2$ (0.5007 numerically). The maximum D corresponds to a configuration in which all scatterers are confined, for example, to either the top or the bottom half of the system. Then, Eq. (3) yields $D_B = (M/16) + (1/8) \sim 156.4$ for the 50×50 system, which compares well with the numerical measurement $D = 157.1$. In the last case the system was simulated for 8000 time steps, to take into account some very long initial flights. This example illustrates clearly the predictive power of Eq. (3), when the simple Boltzmann approximation is off by a factor of over 200.

Attempts to obtain further analytical results from Eq. (3), especially about the dependence of the standard deviation of D on c or system size M, have failed so far, largely because Eq. (3) has the implicit constraint $\sum d_s = M$, and therefore some basic results of sampling and probability theories could not be used.

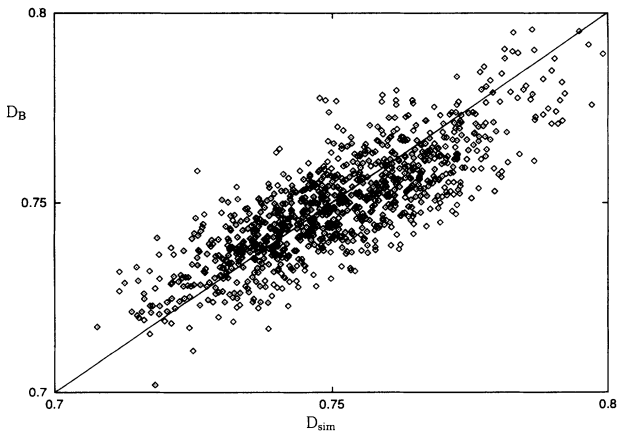

FIG. 1. Diffusion coefficient for 1000 configurations of size 50×50, concentration fixed at exactly $c = 0.5$. Horizontal axis: exact enumeration simulations D_{sim}; vertical axis: Eq. (3). Solid line: $D_B = D_{sim}$. The concentration-only prediction is $D_B = 0.75$.

TABLE I. Percent errors for 1000 configurations at several concentrations (column 1). Columns 2 and 3: average error relative to accurate simulations for the simple Boltzmann approximation $D_B = 1/2c - \frac{1}{4}$ and Eq. (3), respectively. Columns 4 and 5: maximum error relative to accurate simulations for simple Boltzmann approximation and Eq. (3), respectively.

c	$\bar{e}$	$\bar{e}$, Eq. (3)	e (max)	e (max), Eq. (3)
0.2	3.1	2.1	14.9	9.4
0.35	2.1	1.45	11.5	6.0
0.5	1.5	1.0	6.4	4.5
0.65	1.1	0.76	5.3	2.8
0.8	0.6	0.45	3.7	1.6
0.95	0.17	0.12	1.0	0.5

In addition, some properties of distributions of D at strictly constant c were explored numerically. D was measured directly with the exact enumeration method. Coefficients for 1000 independent configurations of size 50×50 were generated for a number of concentrations, as shown in Table II. Histograms of the diffusion coefficients revealed a bell-shaped curve, and the hypothesis of a Gaussian distribution was tested by the Kolmogorov-Smirnov method [10]. Cumulative distributions were generated with the best estimates of μ, σ for the Gaussian, and compared with the actual cumulative distribution of the diffusion coefficients. The two parameters (mean, standard deviation) are shown in columns 2 and 3; the number in parenthesis in column 2 is the simple Boltzmann-level diffusion coefficient [see paragraph below Eq. (1)]. Column 4 shows the largest distance (the Kolmogorov-Smirnov distance d_{KS}) between both cumulative distributions, and column 5 shows the probability P that d_{KS} is greater than what was observed. The Gaussian hypothesis is most likely when $1/4 \leq P \leq 3/4$.

TABLE II. Statistics for 1000 systems of size 50×50. Column 1: scatterer concentration. Column 2: average diffusion coefficient; simple Boltzmann-level result in parentheses. Column 3: standard deviation of the diffusion coefficients. Column 4: largest distance between actual cumulative distribution function of diffusion coefficients and Gaussian hypothesis. Column 5: probability that the Gaussian hypothesis is valid (see text for interpretation).

c	μ (D_B)	σ	d_{KS}	P
0.05	9.725 (9.750)	0.9942	0.066	0.026
0.2	2.254 (2.250)	0.1074	0.054	0.108
0.35	1.179 (1.178)	0.0370	0.054	0.108
0.5	0.751 (0.750)	0.0165	0.043	0.313
0.65	0.520 (0.519)	0.0079	0.036	0.536
0.8	0.375 (0.375)	0.0031	0.049	0.181
0.95	0.276 (0.276)	0.00062	0.043	0.313

The concentration dependence of σ and σ/D on c at constant M was investigated with the data of Table II. It was found that the two quantities vary with c faster than an algebraic power law and slower than exponentially. Hypotheses of fits of the forms σ, $\sigma/D \sim c^a e^{-c}$, e^{c^a} were not successful. The dependence of σ on system size appears to be more straightforward. This was explored for $c = 0.5$, and system sizes between 25 and 200. The standard deviation seems to increase linearly with $1/L$, $L = \sqrt{M}$, with $\sigma L \sim 0.8$ roughly constant.

In this paper the effects of structure on the diffusive transport coefficients of classical particles in a random medium of fixed scatterers have been studied. Equation (3), which is exact in the Boltzmann approximation, gives the diffusion coefficient for particular configurations in terms of distances between scatterers, and is a significant improvement over the predictions based on the concentration of scatterers alone (see Fig. 1 and Table I). The average relative errors, compared with very accurate simulations, are below 2.1% for a wide range of concentrations.

The properties of diffusion coefficient distributions at constant scatterer concentration were explored; the standard deviation scales with system size, but no simple relations were found for concentration dependence. Comparing the difference between the quantities in column 2 and the quantity in column 3 (the standard deviation) in Table II indicates that ascertaining the effects of correlated trajectories (ring contributions) may not be possible in this model. Statistical tests show that it is possible, but not likely, that the distributions are Gaussian. These findings seem to indicate that further analytical results might be obtainable for this model.

The results in this paper can be seen as a step towards the detailed understanding of transport phenomena in inhomogeneous media. The effects of "nonthermodynamic" (structural) quantities on fluctuations of transport coefficients have been postulated by Ernst *et al.* as a possible cause of the lack of a good understanding of long-time tails in the Lorentz gas [11]. It is hoped that this paper will encourage further work on the explanation of diffusive phenomena in random media; the effects on other transport coefficients (e.g., viscosity) are likely to be less noticeable because of self-averaging.

The author would like to thank M. H. Ernst, D. Frenkel, and H. van Beijeren for useful discussions. The work at Los Alamos was performed under the auspices of the U. S. Department of Energy. The work at the Santa Fe Institute was supported in part by grants from the John D. and Catherine T. MacArthur Foundation, the National Science Foundation, and the U. S. Department of Energy.

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