

# Diffusion in a two-component disordered medium

A. É. Arinshtein and A. P. Moroz

*N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences*

(Submitted 12 December 1991)

Zh. Eksp. Teor. Fiz. **102**, 221–234 (July 1992)

A scaling approach to the description of diffusion in a disordered medium is proposed. A two-dimensional lattice model of hopping diffusion is considered. A right square lattice is used, consisting of “bonds” of two types with different characteristic hopping times. A lattice scale transformation procedure is developed which permits deriving the renormalization group equations for the space and time scale transformations. Explicit solutions of these equations yield the effective diffusion coefficient of a two-dimensional heterogeneous medium and the time dependence of the mean-square displacement of a particle undergoing a random walk. This dependence turns out to be nonlinear at finite times, but at large times it asymptotically approaches the linear diffusion regime, with a coefficient of proportionality equal to the effective diffusion coefficient.

## INTRODUCTION

In spite of numerous studies<sup>1–8</sup> the problem of investigating diffusion processes in disordered media remains a vital and interesting topic. This seemingly simple problem meets with mathematical difficulties due to the non-Markovian nature of random walks in disordered media and in many cases cannot be solved exactly. At the same time, many physical phenomena in real condensed media are diffusive in nature or involve diffusion processes and may be diffusion limited. Examples include diffusion in amorphous systems and polymer solutions and polymer gels,<sup>2</sup> the kinetics of diffusion-controlled chemical reactions,<sup>3</sup> etc. Certain properties of polymer molecules can be described in the language of self-avoiding random walks.<sup>4</sup>

Random walks in disordered systems are ordinarily studied on simple lattice models both by mathematical modeling<sup>5</sup> and by various analytical methods. The most widely used method is expansion in the concentration of impurities<sup>6</sup> with the use of the averaged generating functional.<sup>7</sup>

For the special case of random walks on fractals, a scaling approach has been used successfully<sup>8</sup> and seems very promising. It should be noted that real systems have definite fractal dimensionalities only in a narrow range of scales, and real systems on the whole must be treated as fractals of variable dimensionality. Consequently, the power-law time dependences obtained for the mean-square displacement are valid only in a narrow time interval.

The use of scaling ideas, which have proven extremely fruitful for describing phase transitions and the properties of polymer molecules, is possible here because of the analogy with the Kadanoff<sup>9</sup> procedure of coarsening a spin lattice (i.e., increasing its block size) and with the renormalization group method of calculating the percolation threshold in percolation theory.<sup>10</sup>

## STATEMENT OF THE PROBLEM AND DESCRIPTION OF THE MODEL

Our problem is to describe a diffusion process in a two-dimensional medium consisting of two types of regions with different diffusion coefficients. We assume that these regions are randomly placed on the plane in a uniform and independent manner. The “volume” fraction of regions with “fast” diffusion ( $D^I$ ) is denoted  $p$ , and that of regions with slow

diffusion ( $D^{II}$ ) by  $1 - p$  ( $D^I \gg D^{II}$ ). One of the characteristics of interest to us will be the average diffusion coefficient of such a medium,  $D_{av}$ .

When two types of regions are present it must be taken into account that the interaction of the diffusing particles with different regions can be different. Because of this difference, the probability of transition of a particle from a region of type I to a region of type II will differ from the probability of the reverse transition. For simplicity we will neglect this difference in the present paper, although in principle it could be taken into account in the proposed approach.

We consider a model of hopping diffusion, in which we specify a certain scale  $L_0$  for the elementary hop over a characteristic time  $\tau_0$ , the diffusion coefficient in such a medium being defined as  $D = L_0^2/\tau_0$ . We note that this description is somewhat arbitrary in the choice of the elementary scale  $L_0$ : if we let  $\tilde{L}_0 \rightarrow \lambda L_0$  and the characteristic hopping time  $\tilde{\tau}_0 \rightarrow \lambda^2 \tau_0$ , the diffusion coefficient itself will remain unchanged.

It is natural to suppose that a two-component disordered medium also has a certain leeway in the choice of elementary scale. However, for a two-component medium, scale invariance implies the possibility of a new division of the space into two types of regions, whose diffusion coefficients are determined with the aid of the scale transformation functions:

$$\tilde{D}^I = F_1(p, D^I, D^{II}), \quad \tilde{D}^{II} = F_2(p, D^I, D^{II}),$$

and by analogy with percolation models, a scale transformation changes the fractions occupied by regions of the first and second types:  $\tilde{p} = f(p)$ .

The scale-invariance property of the investigated system consists in the fact that its average diffusion coefficient does not depend on the choice of initial scale, i.e.,  $D_{av}(p, D^I, D^{II}) = D_{av}(\tilde{p}, \tilde{D}^I, \tilde{D}^{II})$ . In particular, if the division into the two types of regions is done in such a way that  $\tilde{p} = 1$  (or 0), beginning with a certain scale, then the average diffusion coefficient is  $D_{av} = \tilde{D}^I$  (or  $\tilde{D}^{II}$ ).

To describe hopping diffusion in a two-component medium we introduce a plane square lattice  $S_0$  having a “bond” (unit) length  $L_0$  and consisting of two types of bonds, fast (I) and slow (II), placed randomly, uniformly, and independently over the lattice. A particle executes a random

walk over the lattice, moving in each jump to one of the adjacent lattice sites, the direction of the jump being equiprobable in all directions, independent of the type of bond that must be jumped across. The time for a jump along a type-I bond is  $\tau_0^I$ , and that for a type-II bond is  $\tau_0^{II}$  ( $\tau_0^I \leq \tau_0^{II}$ ). The quantitative fractions of type-I and type-II bonds are  $p_0^I \equiv p_0$  and  $p_0^{II} = 1 - p_0$ , respectively.

We define the "intrinsic" diffusion coefficients of the bonds (regions) as follows:

$$D_{c_0}^I = L_0^2 / \tau_0^I, \quad D_{c_0}^{II} = L_0^2 / \tau_0^{II} = h_0 D_{c_0}^I, \quad (1)$$

$$h_0 = \tau_0^I / \tau_0^{II}, \quad 0 \leq h_0 \leq 1.$$

### SCALE TRANSFORMATION OF THE LATTICE

The supposed leeway in the choice of scale of the investigated system means that we can choose a lattice with a different elementary unit. We choose the new lattice not in an arbitrary way but in relation to the old lattice, through the following "diagonal" transformation:

$$\{S_0 \rightarrow S_1: L_0 \rightarrow L_1, \quad L_1 = 2^h L_0\}, \quad (2)$$

as a result of which the diagonal of the unit cell of the initial lattice  $S_0$  becomes the "bond" (edge) of the new lattice  $S_1$  (see Fig. 1).

For an  $n$ -fold diagonal transformation we have

$$\{S_{n-1} \rightarrow S_n: L_{n-1} \rightarrow L_n, \quad L_n = 2^h L_{n-1}\}, \quad (2a)$$

where  $L_n$ , the bond length of the lattice  $S_n$ , is given by  $L_n = 2^{n/2} L_0$ .

We denote by  $\{\Omega_{n,m}\}$  the set of all possible random-walk trajectories of a particle on the lattice  $S_n$  (including self-crossing) with a length of  $2^m$  units of this lattice (i.e.,  $2^m L_n$ );  $R_{n,m,\omega}$  is the distance between the start and end of some trajectory of the set  $\{\Omega_{n,m}\}$ , and  $t_{n,m,\omega}$  is the time required to travel this trajectory.

Then we define the average diffusion coefficient  $D_{n,m}$  on the lattice  $S_n$  as

$$D_{n,m} = \langle R_{n,m,\omega}^2 / t_{n,m,\omega} \rangle_{\Omega_{n,m}}, \quad (3)$$

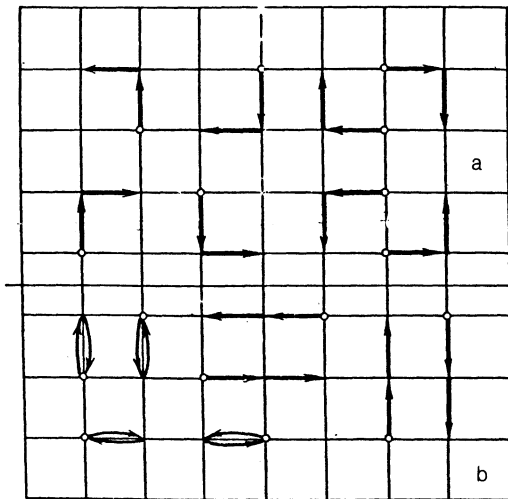


FIG. 1. Possible forms of two-unit trajectories: a—those taken into account; b—those discarded.

where the angle brackets denote averaging over the set of trajectories  $\Omega_{n,m}$  (we note that  $\langle R_{n,m,\omega}^2 \rangle_{\Omega_{n,m}} = 2^m L_n^2 = 2^{n+m} L_0^2$ ).

We define the notation

$$D_{n,\infty} = \lim_{m \rightarrow \infty} D_{n,m}, \quad D_{\infty,m} = \lim_{n \rightarrow \infty} D_{n,m},$$

$$D_{c,p} = \lim_{m \rightarrow \infty} D_{0,m} = D_{0,\infty}.$$

Although direct calculation of  $D_{0,\infty}$  is impossible, this quantity can be related to another quantity that can be determined, viz.,  $D_{\infty,0}$ . Indeed, if the hypothesis that the system is self-similar is correct, i.e., if there exist transformation laws for the observable quantities on going from one lattice to the next ( $S_{n-1} \rightarrow S_n$ ) and if a complete averaging occurs at large scales, then  $D_{n,\infty}$  does not depend on  $n$ ; in precisely the same way,  $D_{\infty,m}$  does not depend on  $m$ . Since  $D_{n,\infty} \equiv D_{\infty,m}$  for  $n, m \rightarrow \infty$ , it follows that

$$D_{av} = \lim_{n \rightarrow \infty} D_{n,0} = D_{\infty,0}.$$

### CONSTRUCTION OF LATTICE-COARSENING ALGORITHM (SCALE TRANSFORMATION)

Let us first calculate the average diffusion coefficient for trajectories consisting of one unit (and then of two units) of the original lattice  $S_0$ . For one-unit trajectories we have

$$D_{0,0} = p_0 D_{c_0}^I + (1-p_0) D_{c_0}^{II} = D_{c_0}^I + D_{c_0}^{II} = [p_0 + (1-p_0)h_0] D_{c_0}^I, \quad (4)$$

where  $D_{c_0}^I \equiv p_0 D_{c_0}^I$  and  $D_{c_0}^{II} \equiv (1-p_0) D_{c_0}^{II}$  are the effective diffusion coefficients for bonds of types I and II, and  $h_0 = \tau_0^I / \tau_0^{II} = D_{c_0}^{II} / D_{c_0}^I$ .

For two-unit trajectories on the lattice  $S_0$  we have

$$D_{0,1} = [p_0^2 + 4p_0(1-p_0)h_0 / (1+h_0) + (1-p_0)^2 h_0] D_{c_0}^I. \quad (5)$$

Here the first and third terms correspond to trajectories consisting of two bonds of the same type (type I or II, respectively). The time required for a particle to travel such a trajectory is equal to  $2\tau_0^I$  or  $2\tau_0^{II}$ , respectively (for the fast or slow trajectory). The second term corresponds to "mixed" trajectories consisting of two bonds of different types. The time required for a particle to travel such a trajectory is  $\tau_0^I + \tau_0^{II}$ .

We now perform lattice transformation (2):  $S_0 \rightarrow S_1$ . We construct the diagonal lattice  $S_1$  out of three types of bonds—fast, slow, and mixed—in such a way that the fraction and position in  $S_1$  of the bonds of each of these types corresponds to the fractions and positions in  $S_0$  of the two-unit configurations (trajectories) of the corresponding type (see the explanation of formula (5) above). Then the fractions comprised of fast, slow, and mixed bonds are, respectively

$$p_1^{(1)} = p_0^2, \quad p_1^{(2)} = (1-p_0)^2, \quad p_1^{(3)} = 2p_0(1-p_0). \quad (6)$$

The hopping time along a bond of each of the three types is also specified in such a way that it corresponds to the time of travel of the two-unit trajectory of the corresponding type on the lattice  $S_0$ . Then for the fast, slow, and mixed bonds of the lattice  $S_1$  we have, respectively

$$\tau_1^{(1)} = 2\tau_0^I, \quad \tau_1^{(2)} = 2\tau_0^{II},$$

$$\tau_1^{(3)} = \tau_0^I + \tau_0^{II} = [(1+h_0)/h_0] \tau_0^I. \quad (7)$$

It can be easily verified that for the lattice  $S_1$  specified in this way the average diffusion coefficient on the one-unit trajectories is equal to the diffusion coefficient on the two-unit trajectories of lattice  $S_0$ :

$$D_{10} = D_{01}. \quad (8)$$

We make the following conjecture: the lattice  $S_1$  constructed in the manner described above is approximately diffusion-equivalent (i.e., equivalent from the standpoint of the diffusion characteristics) to the original lattice  $S_0$ , i.e.,

$$D_{11} \approx D_{02}, \quad D_{03} \approx D_{12}, \dots, D_{1, m-1} \approx D_{0, m}, \dots, D_{1, \infty} \approx D_{0, \infty}. \quad (9)$$

The approximation consists in the fact that we have taken into account the  $\Gamma$ -shaped two-unit trajectories on  $S_0$  and discarded the rest (see Fig. 1); for a lattice consisting of bonds of the same type our approximation is exact.

This conjecture means that a random walk of  $2^m$  steps on the lattice  $S_0$  (i.e., on the set of trajectories  $\{\Omega_{0, m}\}$ ) is equivalent on the average to a random walk of  $2^{m-1}$  steps on  $S_1$  (i.e., on the set of trajectories  $\{\Omega_{1, m-1}\}$ ). We note that for any  $m$  we have

$$\langle R_{0, m, \omega}^2 \rangle_{\Omega_{0, m}} = \langle R_{1, m-1, \omega}^2 \rangle_{\Omega_{1, m-1}} = L_m^2 = 2^m L_0^2. \quad (10)$$

Let us now turn to construction of the coarsened lattice  $\tilde{S}_1$ , which, like  $S_0$ , consists of two types of bonds. We divide the total number of mixed bonds of lattice  $S_1$ , which comprise a fraction  $p_1^{(3)}$ , into two parts:

$$p_1^{(3)} = \alpha_0 p_1^{(3)} + (1 - \alpha_0) p_1^{(3)}, \quad 0 \leq \alpha_0 \leq 1. \quad (11)$$

We combine (formally, for now) the first part into one group with fast bonds and the second into a group with slow bonds. As a result, instead of three types of bonds we have only two, the fractions of each being [see Eq. (6)]

$$p_1^I = p_1 = p_1^{(1)} + \alpha_0 p_1^{(3)}, \quad (12)$$

$$p_1^{II} = 1 - p_1 = p_1^{(2)} + (1 - \alpha_0) p_1^{(3)}.$$

In accordance with such a division the contribution to the diffusion coefficient  $D_{01}$  corresponding to the mixed bonds (the second term in formula (5)) is also divided into two parts. The first of these, which is proportional to  $\alpha_0$ , is combined with the first term, and the second, proportional to  $1 - \alpha_0$ , with the third. As a result we obtain from (5) an expression analogous in structure to (4):

$$D_{10} = D_1^I + D_1^{II}, \quad (13)$$

where

$$D_1^I = p_0 [p_0 + 4\alpha_0(1 - p_0)h_0 / (1 + h_0)] D_{c_0}^I = [p_0 + 4\alpha_0(1 - p_0)h_0 / (1 + h_0)] D_{c_0}^I, \quad (13a)$$

$$D_1^{II} = (1 - p_0) [(1 - p_0) + 4(1 - \alpha_0)p_0 / (1 + h_0)] h_0 D_{c_0}^I = [(1 - p_0) + 4(1 - \alpha_0)p_0 / (1 + h_0)] D_{c_0}^{II}. \quad (13b)$$

The average intrinsic diffusion coefficients of the bonds of the first and second groups are given by

$$D_{c_1}^I = D_1^I / p_1, \quad D_{c_1}^{II} = D_1^{II} / (1 - p_1). \quad (14)$$

We replace all the bonds in the first group with identical bonds corresponding to a diffusion coefficient  $D_{c_1}^I$  and those of the second group, with bonds corresponding to  $D_{c_1}^{II}$ . As a result, we obtain a lattice  $\tilde{S}_1$  consisting of bonds with only

two intrinsic diffusion coefficients, i.e., two types of bonds. The average diffusion coefficient  $\tilde{D}_{10}$  for one-unit trajectories on the lattice  $\tilde{S}_1$  is calculated from formulas (13).

We make another conjecture: For a suitable choice of  $\alpha_0$  ( $0 \leq \alpha_0 \leq 1$ ), which according to (11) and (12) determines the division of the bonds of lattice  $S_1$  into two types, the lattice  $\tilde{S}_1$  obtained will be approximately diffusion-equivalent to the lattice  $S_1$ :

$$\tilde{D}_{11} \approx D_{11}, \quad \tilde{D}_{12} \approx D_{12}, \dots, \tilde{D}_{1, m} \approx D_{1, m}, \dots, \tilde{D}_{1, \infty} \approx D_{1, \infty}. \quad (9a)$$

We choose the parameter  $\alpha_0$  from the following considerations. The lattice-coarsening procedure under study reduces to analysis of a certain effective trajectory joining sites of the new coarsened lattice. This procedure can also be used to frame the solution of the percolation problem. It turns out that for correct determination of the percolation threshold in the given algorithm the trajectories consisting of two types of bonds must also be divided in some proportion between the two types of new coarsened bonds. Since the percolation problem (the problem of connectedness) in our algorithm (unlike the case of a diffusion process) corresponds to the sequential traversal of a trajectory, an averaging of the transit time of a particle on the specified trajectory occurs. Consequently, if we first replace the mixed bonds by bonds of two types in the proportion corresponding to the percolation problem (a fast fraction  $\mu$  and a slow fraction  $1 - \mu$ , the answer for which in the percolation problem is well known:  $\mu = p$ ) and compare with the diffusion-equivalent division (fractions  $\alpha_0$  and  $1 - \alpha_0$ , respectively), then the following relation must hold:

$$\frac{\Delta^2}{\mu \tau_1 + (1 - \mu) \tau_2} = \alpha_0 \frac{\Delta^2}{\tau_1} + (1 - \alpha_0) \frac{\Delta^2}{\tau_2}, \quad (15)$$

from which we immediately find the desired form of  $\alpha_0$ :

$$\alpha_0 = p_0 h_0 / (1 - p_0 + p_0 h_0). \quad (16)$$

Thus the fraction of mixed bonds put into the first (fast) group is proportional to the fraction of fast bonds  $p_0$  in the original lattice (as in the connectedness problem) and also (and this is a peculiarity of the diffusion process) to the hopping time  $\tau_0^I$  for this bond:  $\alpha_0 \propto p_0 \tau_0^I$  (and, accordingly,  $1 - \alpha_0 \propto (1 - p_0) \tau_0^{II}$ ).

We have thus described the procedure for going from a random walk of a particle over an original lattice  $S_0$  consisting of two types of bonds to a random walk on a coarsened lattice  $\tilde{S}_1$  which is similar to it.

To obtain the diffusion coefficient averaged over a large scale it is necessary to apply the described procedure many times, replacing in formulas (5), (6), (12), (13), (13a,b), (14), and (16) for each quantity the first subscript 0 by  $n$  and the subscript 1 by  $n + 1$ . Here it is understood that after each step of the scale transformation  $S_{n-1} \rightarrow \tilde{S}_n$  the constructed two-component lattice  $\tilde{S}_n$  is used as the initial  $S_n$  and the transformation procedure is repeated anew:  $S_n \rightarrow \tilde{S}_{n+1}$ .

A direct check shows, however, that the relative position of bonds of the same type is independent only on the original lattice  $S_0$ . As the lattice is coarsened by the procedure described, a correlation between the properties of adjacent bonds arises, and the probability that two bonds of the

same type will be adjacent becomes larger than that for bonds of different types.

This correlation can be taken into account as follows: let the probability of realization of a trajectory consisting of two type-I bonds be

$$\bar{P}_1^{(1)} = p_0 Q_0(p_0).$$

[ $Q_0(p_0) = p_0$  in the absence of a correlation.] Since the correlation for type-II bonds is the same as for type-I bonds, the probability of realization of a trajectory consisting of two type-II bonds is

$$\bar{P}_1^{(2)} = (1-p_0) Q_0(1-p_0).$$

Then the probability of realizing a mixed trajectory will be

$$\bar{P}_1^{(3)} = 1 - [p_0 Q_0(p_0) + (1-p_0) Q_0(1-p_0)].$$

As a result, in place of expression (5) we obtain

$$D_{0,1} = [\bar{P}_1^{(1)} + 2h_0 \bar{P}_1^{(3)} / (1+h_0) + \bar{P}_1^{(2)} h_0] D_{c_0}^{-1}. \quad (17)$$

The other quantities transform in an analogous way. Then, since the conditional probability  $Q$  also depends on the number of the coarsening step  $n$  [i.e.,  $Q(p_n) \equiv Q_n(p_n)$ ], the coarsening procedure must be applied the necessary number of times.

Since  $Q_n(p)$  must satisfy the requirement  $p_n \leq Q_n(p_n) \leq 1$ , we choose  $Q_n(p)$  in an extremely simple form that does not depend explicitly on  $n$ :

$$Q_n(p_n) \equiv Q(p_n) = 1/2(p_n + 1), \quad (18a)$$

$$Q_n(1-p_n) \equiv Q(1-p_n) = 1/2(2-p_n). \quad (18b)$$

As a result, we arrive at the following relations specifying the transition from the lattice  $S_n$  to the lattice  $\tilde{S}_{n+1}$ :

$$p_{n+1} = p_n [1/2(p_n + 1) + \alpha_n(1-p_n)]. \quad (19)$$

$$D_{n+1}^I = [1/2(p_n + 1) + 2\alpha_n(1-p_n)h_n / (1+h_n)] D_n^I. \quad (20)$$

$$D_{n+1}^{II} = [1/2(2-p_n) + 2(1-\alpha_n)p_n / (1+h_n)] D_n^{II}, \quad (21)$$

$$D_{c_{n+1}}^I = D_n^I / p_n, \quad D_{c_{n+1}}^{II} = D_n^{II} / (1-p_n), \quad (22)$$

$$h_n = D_{c_n}^{II} / D_{c_n}^I = [D_n^{II} / (1-p_n)] [p_n / D_n^I], \quad (23)$$

$$\alpha_n = p_n h_n / (p_n h_n + 1 - p_n), \quad (24)$$

$$D_{n_0} = D_n^I + D_n^{II}. \quad (25)$$

For an  $n$ -fold transformation  $S_0 \rightarrow \tilde{S}_n$  we have

$$D_n^I = p_0 D_{c_0}^I \prod_{k=0}^{n-1} [1/2(p_k + 1) + 2\alpha_k(1-p_k)h_k / (1+h_k)], \quad (26)$$

$$D_n^{II} = (1-p_0) D_{c_0}^{II} \prod_{k=0}^{n-1} [1/2(2-p_k) + 2(1-\alpha_k)p_k / (1+h_k)], \quad (27)$$

$$h_n = h_0 \frac{p_n(1-p_0)}{p_0(1-p_n)} \prod_{k=0}^{n-1} \frac{[1/2(2-p_k) + 2(1-\alpha_k)p_k / (1+h_k)]}{[1/2(p_k + 1) + 2\alpha_k(1-p_k)h_k / (1+h_k)]}. \quad (28)$$

We have been unable to find a rigorous justification of the possibility of replacing the three types of bonds by effective bonds of two types at each step. However, we can give physical arguments analogous to those given by Kadanoff.<sup>9</sup> Between bonds of the same type there exists a certain correlation which increases with increasing coarsening scale, and the mixed-bond fraction, decreasing with each coarsening

step, goes asymptotically to zero; as a result, the error introduced will be insignificant. In addition, as was shown above, our proposed lattice-coarsening procedure corresponds to the analogous procedure in the connectedness problem, for which the scaling approach is well founded. To check our assumptions we compared the values of the average diffusion coefficient  $D_{av}$ , calculated at the second step of the recursive procedure, with the results of a modeling ( $D_{mod}$ ) of the random walk of a particle over four-unit trajectories on the original two-component lattice. For  $h_0 = 0.1$  the disagreement did not exceed 5.1% (see below), and for larger  $h_0$  it was even smaller. Thus the assumptions made can be regarded as quite correct.

|           |       |       |       |       |       |       |       |       |       |
|-----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| $p_0$     | 0,1   | 0,2   | 0,3   | 0,4   | 0,5   | 0,6   | 0,7   | 0,8   | 0,9   |
| $D_{av}$  | 0,013 | 0,020 | 0,034 | 0,060 | 0,105 | 0,179 | 0,293 | 0,460 | 0,696 |
| $D_{mod}$ | 0,013 | 0,019 | 0,033 | 0,061 | 0,110 | 0,187 | 0,301 | 0,464 | 0,696 |

## INFINITESIMAL SCALE TRANSFORMATION (RENORMALIZATION GROUP EQUATION)

Formulas (19)–(25) correspond to a discrete transformation of the lattice  $S_n \rightarrow \tilde{S}_{n+1}$ , which corresponds to a coarsening of the scale  $L_n \rightarrow L_{n+1} = 2^{1/2} L_n$  by a factor of  $2^{1/2}$ . Let us now find the lattice transformation  $S_n \rightarrow S_{n+\delta n}$  corresponding to an infinitesimal scale transformation  $L_n \rightarrow 2^{\delta n/2} L_n = L_{n+\delta n}$  by a factor of  $2^{\delta n/2}$ , where  $\delta n \rightarrow 0$ . For this purpose we rewrite formulas (19)–(21) and (23) in the following form:

$$p_{n+\delta n} = p_n [1 + 1/2(1-p_n)(2\alpha_n - 1)\delta n]. \quad (29)$$

$$D_{n+\delta n}^I = \{1 - 1/2(1-p_n)[1 - 4\alpha_n h_n / (1+h_n)]\delta n\} D_n^I. \quad (30)$$

$$D_{n+\delta n}^{II} = \{1 - 1/2 p_n [1 - 4(1-\alpha_n) / (1+h_n)]\delta n\} D_n^{II}. \quad (31)$$

$h_{n+\delta n}$

$$= \frac{p_{n+\delta n}(1-p_n) \{1 - 1/2 p_n [1 - 4(1-\alpha_n) / (1+h_n)]\delta n\}}{p_n(1-p_{n+\delta n}) \{1 - 1/2(1-p_n)[1 - 4\alpha_n h_n / (1+h_n)]\delta n\}} h_n. \quad (32)$$

Expressions (29)–(32) correspond to (19)–(21) and (23) for  $\delta n = 1$  and go over to identities for  $\delta n = 0$ , which corresponds to the identity transformation of the lattice  $S_n$  into itself. We assume that expressions (29)–(32) are valid even at nonzero  $\delta n \rightarrow 0$ . Then, using the fact that for small  $\delta n$  we have  $1 + x\delta n \approx \exp(x\delta n)$ , and going over from a sum to an integral in the argument of the exponential function which then appears in the correspondingly transformed expressions (26)–(28), we obtain formulas for the effective diffusion coefficient and the quantity  $h(n)$  in the form

$$D_n^I \equiv D^I(n) = p_0 D_{c_0}^I \exp \left\{ - \frac{1}{2} \int_0^n [1 - p(k)] \times \left[ 1 - \frac{4\alpha(k)h(k)}{1+h(k)} \right] dk \right\}, \quad (33)$$

$$D_n^{II} \equiv D^{II}(n) = (1-p_0) D_{c_0}^{II} \exp \left\{ - \frac{1}{2} \int_0^n p(k) \times \left[ 1 - \frac{4[1-\alpha(k)]}{1+h(k)} \right] dk \right\}. \quad (34)$$

$$h_n = h_0 \frac{p(n)(1-p_0)}{p_0[1-p(n)]} \exp \left\{ -\frac{1}{2} \int_0^n [p(1+h-4(1-\alpha))] \frac{dk}{1+h} \right\}. \quad (35)$$

We note that Eq. (35) is obtained by dividing expression (34) by (33), multiplying by the ratio  $p(n)/[1-p(n)]$ , and using the definition (23) of  $h(n)$ .

From Eq. (29) with (24) we obtain an equation for the fast-bond fraction  $p(n)$ :

$$\frac{dp(n)}{dn} = \frac{p(1-p)[ph-(1-p)]}{2[ph+(1-p)]}. \quad (36)$$

By differentiating (35) with respect to  $n$  and using (24) and (36), we can convert the integral equation to a differential equation:

$$\frac{dh(n)}{dn} = \frac{h(1-h)p(1-p)}{ph+(1-p)}. \quad (37)$$

The initial conditions for Eqs. (36) and (37) are

$$h(0) = h_0, \quad p(0) = p_0 \quad (0 \leq h_0, \quad p_0 \leq 1).$$

The system of equations (36), (37), and expressions (33) and (34) specify the scale transformation  $S_0 \rightarrow S_n$ .

#### CALCULATION OF AVERAGE DIFFUSION COEFFICIENT

Figure 2 shows a phase portrait of the system of equations (36), (37) in the square  $0 \leq h, p \leq 1$ . The point  $(p=1, h=0)$  is an unstable node, the point  $(p=1/2, h=1)$  is a saddle, and the lines  $p=0$  and  $p=1$  are lines of stable equilibrium.

Dividing Eq. (36) by (37), we obtain the ordinary differential equation

$$\frac{dp}{dh} = \frac{p(1+h)}{2h(1-h)} - \frac{1}{2h(1-h)}, \quad (38)$$

the solution of which with the specified initial conditions  $p(h_0) = p_0$  has the form

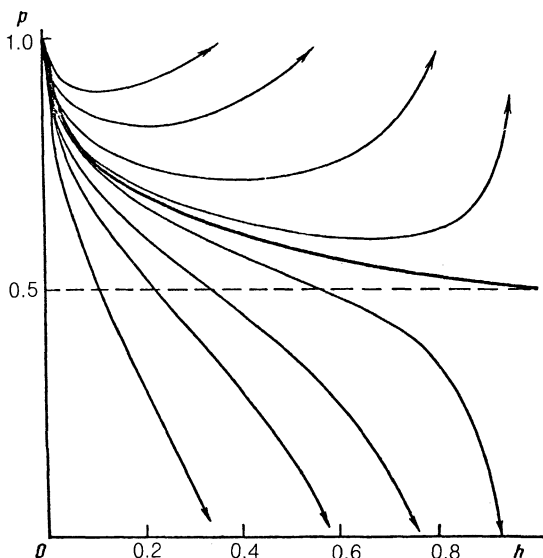


FIG. 2. Phase portrait of the system of Eqs. (36), (37); the solid curve is the separatrix.

$$p(h) = \frac{1 - [p_0 h_0 + (1-p_0)] (h/h_0)^{1/2}}{1-h}. \quad (39)$$

We now return to the system of master equations (36) and (37). We are interested in the behavior of  $p(n)$  and  $h(n)$  as  $n \rightarrow \infty$ . If the initial point  $(p_0, h_0)$  lies to the left of the separatrix

$$p_c(h) = 1/(1+h^{1/2}), \quad (40)$$

then as  $n \rightarrow \infty$

$$p(n) \rightarrow 0, \quad h(n) \rightarrow h_0/[p_0 h_0 + (1-p_0)]^2 \equiv h_\infty^{(0)}. \quad (41)$$

If the initial point  $(p_0, h_0)$  lies to the right of the separatrix (40), then as  $n \rightarrow \infty$

$$p(n) \rightarrow 1, \quad h(n) \rightarrow [p_0 h_0 + (1-p_0)]^2/h_0 \equiv h_\infty^{(1)}. \quad (42)$$

In the first case only type-II regions (slow bonds) remain in the system on a large scale, whereas in the second case only fast bonds remain. If the initial point lies on the separatrix (40), then the number of fast and slow bonds becomes equal, but their diffusion coefficients are the same.

Let us now take up the problem of directly calculating the limiting values of the effective diffusion coefficients for  $n \rightarrow \infty$ . Going over in expressions (33) and (34) to an integral over  $h$  with the use of relation (37) and then using Eqs. (24) and (39), we obtain for  $n \rightarrow \infty$

$$D_\infty^{(0)} = D_{c0} p_\infty (1+h_0)/(1+h_\infty), \quad (43)$$

$$D_\infty^{(1)} = D_{c0} (1-p_\infty) [h_\infty (1+h_0)/h_0 (1+h_\infty)], \quad (44)$$

where we have introduced the quantities  $p_\infty$  and  $h_\infty$  which, depending on the initial conditions, are equal to (respectively):

$(0, h_\infty^{(0)})$  if the initial point lies to the left of the separatrix;

$(1, h_\infty^{(1)})$  if the initial point lies to the right of the separatrix;

$(1/2, 1)$  if the initial point lies on the separatrix.

As a result, we obtain for the average diffusion coefficient

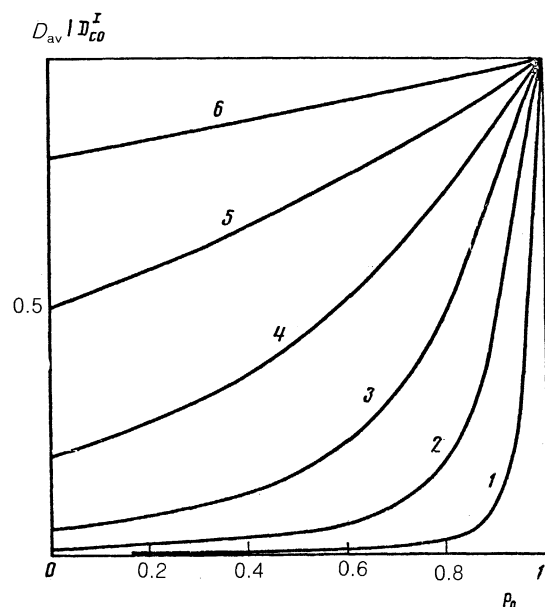


FIG. 3. Concentration dependence  $D_{av}(p_0)$  for different values of  $h_0$ : 1—0.001; 2—0.01; 3—0.05; 4—0.2; 5—0.5; 6—0.8.

cient  $D_{av} = D_{\infty}^I + D_{\infty}^{II}$

$$D_{av} = D_{c_0}^I \frac{h_0(1+h_0)}{h_0 + [p_0 h_0 + (1-p_0)]^2}. \quad (45)$$

We note that the final expression is universal for all locations of the initial point  $(p_0, h_0)$  relative to the separatrix (40).

The  $D_{av}(p_0)$  concentration dependences are shown in Fig. 3 for various values of  $h_0$ . The curves are monotonic but with an inflection point, and for a given  $h_0$  the value of the concentration  $p_{0II}$  at the inflection point is such that the point  $(p_{0II}, h_0)$  lies on the separatrix (40).

#### DEPENDENCE OF THE MEAN-SQUARE DISPLACEMENT ON TIME

The value of  $D_{av}$  obtained above is asymptotic, when the scale of the random walk of the particle is large and a complete averaging has been done in the system (if averaging is possible at all). At finite scales or for a finite time of the random walk the motion of the particle will be substantially influenced by fluctuations in the position of the regions, and the time dependence of the observable quantities will therefore be nontrivial. In principle the time dependence of the quantity  $D_{av}(n)$  introduced above can be determined for finite values of  $n$ , but it is of greater interest to construct the time dependence of the average mean-square displacement  $R_{av}^2(t)$ .

To determine the desired time dependence we will use the scale transformation algorithm given above. However, for calculating the time dependence we will consider the change of the time scale rather than of the spatial scale as before.

Let us modify the discrete scale transformation algorithm as follows. Each step of the scale transformation corresponds to a doubling of the time:

$$t_{n+1} = 2t_n. \quad (46)$$

For motion along bonds of type I the mean-square displacement in the time  $t_n$  is equal to the square of the bond length  $L_n^2$  times the corresponding scale  $S_n$ , while the mean-square displacement in the doubled time  $2t_n$  is  $2L_n^2$  times that factor. For motion along the slow bonds the squares of the displacement in times  $t_n$  and  $2t_n$  are  $h_n L_n^2$  and  $2h_n L_n^2$ , respectively [for the original lattice  $S_0$  the mean-square displacement along type-II bonds is  $(\tau_0^I/\tau_0^{II})L_0^2$ ]. If over a time  $2t_n$  a particle has passed through bonds of both types (the analog of the mixed bond of the coarsened lattice), then the mean-square displacement will be  $4h_n L_n^2/(1+h_n)$ . As a result, instead of the discrete relations (20) and (21) we obtain for the squares of the displacement through regions I and II

$$R_{I,n+1}^2 = 2[1/2(p_n - 1) + 2\alpha_n(1-p_n)h_n/(1+h_n)]R_{I,n}^2, \quad (47)$$

$$R_{II,n+1}^2 = 2[1/2(2-p_n) + 2(1-\alpha_n)p_n/(1+h_n)]R_{II,n}^2, \quad (48)$$

and on going to an infinitesimal transformation we will have in place of (30) and (31)

$$R_{I,n+\delta n}^2 = (1+\delta n) \{1 - 1/2(1-p_n) [1 - 4\alpha_n h_n / (1+h_n)] \delta n\} R_{I,n}^2, \quad (49)$$

$$R_{II,n+\delta n}^2 = (1+\delta n) \{1 - 1/2 p_n [1 - 4(1-\alpha_n)/(1+h_n)] \delta n\} R_{II,n}^2. \quad (50)$$

Ultimately we get

$$R_I^2(n) = p_0 L_0^2 \exp \left\{ n - \frac{1}{2} \int_0^n [1 - p(k)] \times \left[ 1 - \frac{4\alpha(k)h(k)}{1+h(k)} \right] dk \right\}, \quad (51)$$

$$R_{II}^2(n) = (1-p_0) h_0 L_0^2 \exp \left\{ n - \frac{1}{2} \int_0^n p(k) \times \left[ 1 - \frac{4[1-\alpha(k)]}{1+h(k)} \right] dk \right\}. \quad (52)$$

In addition to equations for the functions  $p$  and  $h$ , which retain the form in (36)–(38), Eq. (46) yields an equation for  $t(n)$ :

$$dt(n)/dn = t(n),$$

which relates the scale transformation parameter  $n$  with the time  $t$ :

$$t(n) = \tau_0^I e^n. \quad (53)$$

Substituting (39)—the solution of Eq. (38)—into (37), we obtain an ordinary differential equation for the function  $h(n)$ , the solution of which, with allowance for (53), gives the time dependence  $h(t)$ :

$$\dot{h}(t) \frac{[p_0(1-p_0)(1-h_0^2)]^2}{[p_0 h_0 + (1-p_0)]^2} = h_0 \left[ h(t) - \left( c_0 + \frac{1}{c_0} \right) h^{1/2}(t) + 1 \right]^2 \frac{t}{\tau_0^I}, \quad (54)$$

where

$$c_0 = [p_0 h_0 + (1-p_0)] h_0^{-1/2}.$$

Passing in (51) and (52) to integration over  $h$  with allowance for (54), in the case of a finite number of steps of the scale transformation; i.e., in a finite time, we obtain the

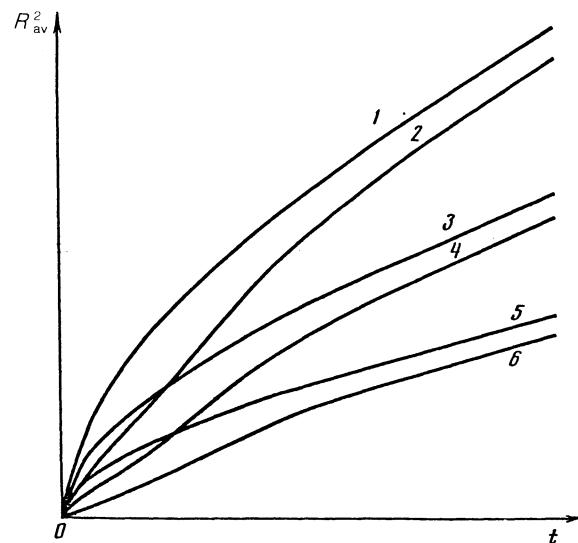


FIG. 4. Dependence of the mean-square displacement on time for uniform (1,3,5) and nonuniform (2,4,6) initial distributions of particles, with  $p_0 = 0.4$  (1,2), 0.3 (3,4), 0.2 (5,6);  $h_0 = 0.001$ .

following expression for  $R_{av}^2(t)$ :

$$R_{av}^2(t) = \frac{D_{c0}^1 t (1+h_0) [p_0(1-p_0)(1-h_0^2) + h_0(t/\tau_0^1)^{1/2}]}{p_0(1-p_0)(1-h_0^2) + \{h_0 + [p_0 h_0 + (1-p_0)]^2\} (t/\tau_0^1)^{1/2}} \quad (55)$$

To sum up, we have found that at short times the dependence  $R_{av}^2(t)$  is nonlinear, but for  $h_0 \neq 0$  its asymptotic behavior for  $t \gg \tau_0^1 [p_0(1-p_0)(1-h_0^2)/h_0]^2$  becomes linear:

$$R_{av}^2(t) \approx \frac{h_0(1+h_0)}{h_0 + [p_0 h_0 + (1-p_0)]^2} D_{c0}^1 t = D_{av} t, \quad (56)$$

where  $D_{av}$  agrees exactly with expression (45) (see Fig. 4).

For  $h_0 \equiv 0$  the dependence  $R_{av}^2(t)$  does not become linear anywhere:

$$R_{av}^2(t) = p_0 D_{c0}^1 (t/\tau_0^1)^{1/2} = p_0 L_0^2 (t/\tau_0^1)^{1/2}. \quad (57)$$

## CONCLUSION

As we have said, the diffusion problem is easy to state, and the solution, if it can be found, is easily interpreted. The model considered here can describe a number of real physical situations, such as the diffusion of small molecules in dilute polymer solutions. In this case the type-I regions correspond to diffusion in the pure solvent, and the type-II regions to diffusion through the polymer balls. It can be assumed that the type-II regions correspond to reversible traps with a lifetime  $\tau_2^{II} - \tau_1^I$ , and for  $\tau_2^{II} \rightarrow \infty$  (or  $h_0 \rightarrow 0$ ) they correspond to trapping centers.

The case  $h_0 = 0$  also describes the kinetics of a monomolecular chemical reaction with randomly located initiating centers. This problem was considered in Refs. 6, where it was shown that at long times one has  $R_{av}^2(t) \propto t^{1/2}$ , which corresponds to our result (57). If, however, the disorder in the position of the initiating centers is not taken into account, then  $R_{av}^2(t) \rightarrow \text{const.}$  This difference can be attributed to the influence of fluctuations in the distribution of initiating centers on the character of the diffusive motion of the particles.

Similarly, in the case  $h_0 \neq 0$  at short times, fluctuations in the position of the type-II regions have a substantial effect on the character of the diffusive motion, and, as a result, the dependence  $R_{av}^2(t)$  at short times is nonlinear [see Eq. (56)].

Expression (56) describes the diffusion of particles which initially are distributed uniformly in space. However, in our case a uniform distribution of particles in space is not an equilibrium situation, since over time a larger number of particles will accumulate in the type-II (slow) regions than in the type-I (fast) regions. In view of this circumstance we can take the nonequilibrium character of the initial distribu-

tion into account as follows: a fraction  $p_0 + (1-p_0)h_0$  of the particles participates in the diffusive motion immediately, while the remaining fraction  $(1-p_0)h_0$  is initially in a bound state (i.e., does not participate in the diffusive motion), but over a time  $\tau_2^{II} - \tau_1^I$  these particles join in the motion. The time corresponding to the onset of motion of the bound particles is uniformly distributed over the interval  $\tau_2^{II} - \tau_1^I$ . As a result, the time dependence of the mean-square displacement will be described by the expression

$$\tilde{R}_{av}^2(t) = [p_0 + h_0(1-p_0)] R_{av}^2(t) + \frac{(1-h_0)(1-p_0)}{\tau_2^{II} - \tau_1^I} \int_0^{\tilde{t}} R_{av}^2(t-\tau) d\tau, \quad (58)$$

where  $\tilde{t} = t$  if  $t \leq \tau_2^{II} - \tau_1^I$ , and  $\tilde{t} = \tau_2^{II} - \tau_1^I$  if  $t \geq \tau_2^{II} - \tau_1^I$ , and the function  $R_{av}^2(t)$  is defined in expression (56).

We will not write out here the awkward expressions that result from an elementary calculation of the integral in (58). We will merely note that the dependence in (58) is nonlinear at short times, while for  $t \rightarrow \infty$  it has the same asymptotic behavior as the function  $R_{av}^2(t)$  given in Eq. (56):  $\tilde{R}_{av}^2(t) \approx D_{av} t$  (see Fig. 4).

While the nonlinear character of  $R_{av}^2(t)$  is due both to fluctuations in the distribution of impurities and to the nonequilibrium nature of the initial distribution, the time dependence in (58) is nonlinear exclusively by virtue of the presence of fluctuations, the influence of which becomes unimportant at long times (unless  $h_0 = 0$ ). In principle any initial conditions can be taken into account in an analogous way.

In conclusion we note that the proposed approach can be used to study even more general situations. For example, the difference in the interaction of diffusing particles with different types of regions can be taken into account by a change in the relationships among the selection probabilities for the direction of motion from a site surrounded by bonds of different types or by the introduction of a probability for the particle to remain in place (sojourn probability).

<sup>1</sup>J. W. Haus and K. W. Kehr, Phys. Rep. **150**, 265 (1987).

<sup>2</sup>A. I. Maklakov, V. D. Skrida, and N. F. Fatkullin, *Self-Diffusion in Polymer Solutions and Melts*, [in Russian], Izd. KGU, Kazan' (1987).

<sup>3</sup>M. V. Smoluchovsky, Z. Phys. Chem. **28**, 113 (1924).

<sup>4</sup>J. M. Ziman, *Models of Disorder*, Cambridge University (1978).

<sup>5</sup>K. W. Kehr, P. Kutner, and J. K. Binder, Phys. Rev. B **23**, 4941 (1981).

<sup>6</sup>V. Ya. Balagurov and V. T. Vaks, Zh. Eksp. Teor. Fiz. **65**, 1939 (1973) [Sov. Phys. JETP **38**, 968 (1974)].

<sup>7</sup>I. M. Lifshitz, S. A. Gradeskul, and L. A. Pastur, *Introduction To the Theory of Disordered Systems*, [in Russian], Moscow (1982), Ch. 1.

<sup>8</sup>S. Alexander and R. Orbach, J. Phys. Lett. (Paris) **43**, L625 (1982).

<sup>9</sup>L. P. Kadanoff, Physics (N.Y.) **2**, 263 (1966) [see R. C. Balescu, *Equilibrium and Nonequilibrium Statistical Mechanics*, Wiley, New York (1975) [Russian translation: Mir, Moscow (1978), Vol. 1, p. 371]].

<sup>10</sup>S. Kirkpatrick, Rev. Mod. Phys. **45**, 574 (1973).

Translated by Steve Torstveit