Diffusion with rearranging traps

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A model for diffusion on a cubic lattice with a random distribution of traps is developed. The traps are redistributed at certain time intervals. Such models are useful for describing systems showing dynamic disorder, such as ion-conducting polymers. In the present model the traps are infinite, unlike an earlier version with finite traps. For the infinite trap version a simple analytical calculation is possible and the results agree qualitatively with simulations.

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I. INTRODUCTION

Diffusion in a disordered system is a well-studied problem [1,2]. Different approaches have been taken—such as models that consider intersite barriers of varying heights, or models that picture sites for diffusing particles as wells with varying depths, and also combinations of barrier and well models [3]. Problems where the diffusing particle may encounter randomly distributed traps have also been studied [4–6]. However, one class of problem involves *dynamic disorder*, i.e., wells, barriers, or traps whose distribution in space changes with time. In other words the locations of the traps get redistributed at certain time intervals. Such models describe systems like ion-conducting polymers or glasses above the glass transition temperature [7,8].

Models with dynamic disorder have also been studied for some time. The dynamic bond percolation model (DBPM) [7,9] of Ratner and co-workers and its many variations study one aspect of the problem quite extensively. Effective medium approaches have also been used [10,11].

A different formulation of the dynamic disorder problem, considering a well model rather than a barrier model, was suggested by Bhattacharyya and Tarafdar [12]. Mandal *et al.* [8] applied the model [12] to explain experimental results on the PEO-NH_4ClO_4 system [13]. The model [12] considers a random distribution of two types of site on a square lattice, both having finite dwell times, i.e., nonzero jump rates. It is not a ''percolation'' model in the sense that it never has zero diffusivity. The diffusion coefficient for different ratios of the two types of site and for different rearrangement times was calculated by computer simulation.

In the present work we take the rearranging lattice model with finite traps [12] to the limit where one type of site is an infinite trap. In this limit the diffusion coefficient as a function of the trap concentration c and rearrangement time τ_r are calculated in three dimensions. The results are compared with the finite trap model as well as the DBPM, and are supported by computer simulations.

II. THE REARRANGING TRAP MODEL

We consider a cubic lattice with a fraction c of sites occupied by traps. A particular configuration of traps remains constant from $t=0$ to a time $t=\tau_r$. After that, the traps get rearranged, although the trap concentration c is constant. If N_0 walkers start a random walk on the lattice from different sites at $t=0$, during time τ_r a certain number get trapped. The well-known diffusion law for the mean square distance covered in time t gives

$$\langle r^2 \rangle = 2dD_0 t. \tag{1}$$

The total square distance that would have been traveled by the N_0 walkers in the absence of traps is

$$(r_0^2)_{tot} = 2dN_0 D_0 \tau_r . \tag{2}$$

If there are traps this value is reduced to, say, $(r_{tr}^2)_{tot}$, since some of the walkers get trapped at different times. Here D_0 is the diffusion coefficient with no traps, and d is the dimension of the system.

After the interval τ_r, since traps are rearranged, previously trapped walkers may be set free and resume their walk. In the next interval from $t=\tau_r$ to $t=2\tau_r$ they again cover a total distance$(r_{tr}^2)_{tot}$. Figure 1 shows how the square distance covered increases with time in our simulation described in Sec. III. So for a time interval much greater than τ_r the diffusion coefficient on a rearranging lattice is given by

$$D(c,\tau_r) = (r_{tr}^2)_{tot}/2dN_0\tau_r . \tag{3}$$

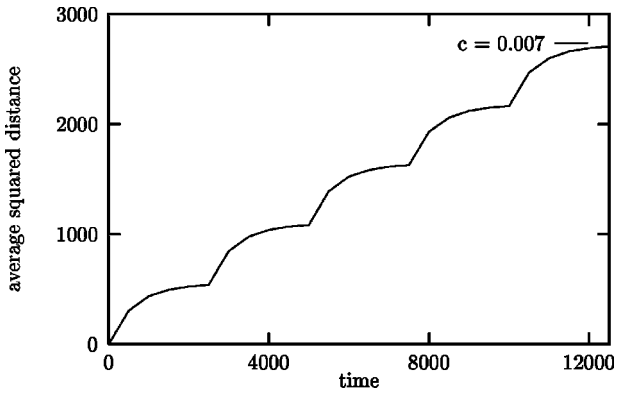

FIG. 1. Plot of average squared distance versus time t for $c=0.007$ and $\tau_r=2500$ from computer simulation. Units are arbitrary.

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This argument is the same as in [9]. The problem is thus reduced to calculating $(r_{tr}^2)_{tot}$. With traps having infinite depth (i.e., infinite dwell time), this is estimated as follows, without involving any complicated mathematics.

A. Calculating the diffusion coefficient $D(c,\tau_r)$

Suppose N_0 particles start a random walk at $t=0$ on a cubic lattice occupied randomly by fraction c of traps. The remaining $(1-c)$ sites are ''allowed'' sites. If a particle encounters a trap it gets stuck until the next rearrangement time; $\langle r_{tr}^2 \rangle$ is calculated as the mean distance traveled by each of the N_0 particles $(r^2{}_{tot})/N_0$. If there were no traps $(r_0^2)_{tot}$ would be given by Eq. (2). This is the total distance traveled by all the particles in time τ_r. In the presence of traps more and more particles get stuck and the total square distance traveled does not reach the value in Eq. (1), but falls short by an amount Δr^2:

$$\Delta r^2 = 2dN_0 D_0 \tau_r - (r_{tr}^2)_{tot}. \tag{4}$$

Knowing Δr^2 one can calculate $D(c,\tau_r)$ from the relation

$$D(c,\tau_r) = (r_{tr})_{tot}^2 / 2dN_0 \tau_r. \tag{5}$$

B. Calculation of Δr^2: the trapping law

To calculate Δr^2 we assume a simple law for trapping. We assume that the number of particles dN trapped in the time interval t to $t+dt$ is proportional to N, the number of particles at time t, c, the trap concentration, and dt. So

$$dN = -acNdt. \tag{6}$$

$a \sim dS(t)/dt$, where $S(t)$ is the number of distinct sites visited in time t [14]. For three or higher dimensions

$$S(t) \propto t$$

[15], so a is a constant depending on the dimension of the system but independent of t. We have thus the simple trapping rule

$$N = N_0 \exp(-act). \tag{7}$$

It may be mentioned here that the problem of absorption by traps is well studied, and exact analytical results have been worked out for the asymptotic limit $t \to \infty$ [16,17]. In the asymptotic limit the number of surviving particles at time t is given by

$$N(t \to \infty) \to \ N_0 \exp(-ac^{2/(d+2)} t^{d/(d+2)}), \tag{8}$$

where the exponents of c and t as well as a are dimension dependent. However, this result is valid only when the probability of survival becomes very small $\sim 10^{-13}$ [18]. In the regime we are interested in the simple expression Eq. (7) agrees much better with simulation results than Eq. (8) as we show in Fig. 2 for trapping in three dimensions. We may

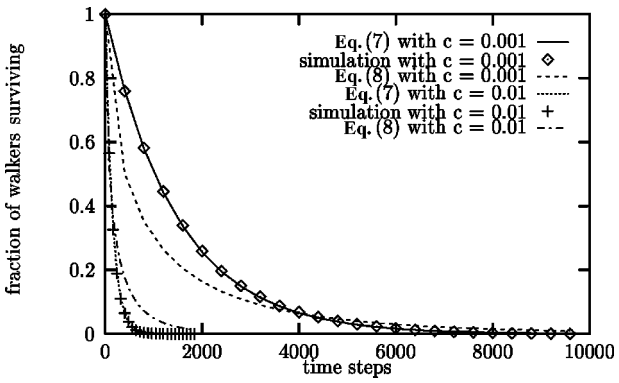

FIG. 2. Plot of fraction of walkers surviving versus time steps from simulation, Eq. (7) and Eq. (8) for $c=0.001$ and $c=0.01$.

now proceed to calculate D. The particles trapped at time t to $t=t+dt$ contribute an amount δr^2 less to $(r_{tr}^2)_{tot}$ than they would if not trapped:

$$\delta r^2 = 2dD_0(\tau_r - t). \tag{9}$$

Henceforth we consider the case $d=3$ only.

Integrating Eq. (9) over the interval τ_r for all particles trapped during this time, we have

$$\Delta r^2 = \int_{t=0}^{\tau_r} \delta r^2 dN = 6 \int_0^{\tau_r} acN_0 \exp(-act) dt (\tau_r - t) D_0 \tag{10}$$

or

$$\Delta r^2 = 6D_0 N_0 [\tau_r + \exp(-ac\tau_r)/ac - 1/ac]. \tag{11}$$

Since

$$(r_{tr}^2)_{tot} = 6N_0 D_0 \tau_r - \Delta r^2, \tag{12}$$

the diffusion coefficient in the presence of traps with a rearrangement time τ_r is

$$D = (D_0/ac\tau_r)(1 - e^{-ac\tau_r})(1-c). \tag{13}$$

The factor $(1-c)$ accounts for the particles that are trapped at the outset, i.e., at $t=0$.

We have assumed in Eq. (9) that each particle contributes $\langle r^2 \rangle_{\tau_r} t/\tau_r$ to the total squared distance in time t. Here $\langle r^2 \rangle_{\tau_r}$ is the square distance covered in time τ_r. We have not considered the joint probability of a particle covering distance r in time t and getting trapped between t and $t+dt$. This assumption makes the calculation very simple and the results obtained reproduce the simulation qualitatively. Instead of taking the difference Δr^2 in Eq. (4), the same result can be obtained by calculating directly the mean square distance traveled by the trapped walkers. In that case the contribution due to the walkers that have not been trapped at all during τ_r has to be added separately. Equation (13) shows that $D/(1-c)$ plotted against the scaling variable $c\tau_r$ should give a single curve for different c and τ_r.

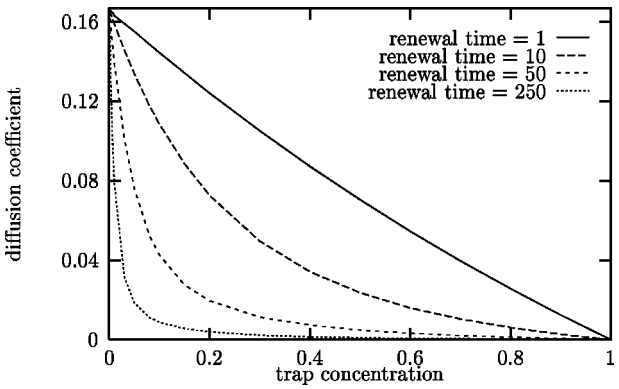

FIG. 3. Plot of calculated diffusion coefficient versus trap concentration for renewal times 1, 10, 50, and 250 in arbitrary units.

C. The limiting cases

For $\tau_r \to 0$, that is, for very rapid rearrangement,

$$D/D_0 = 1 - c \tag{14}$$

as expected. For $\tau_r \to \infty$, that is, when the system is effectively quenched, with no rearrangement

$$D/D_0 = 1 \tag{15}$$

for $c = 0$ and

$$D/D_0 = 0 \tag{16}$$

for $c > 0$. A nonzero trap concentration, however small, gives $D = 0$ in the limit $\tau_r \to \infty$. Figure 3 shows D vs c for different τ_r. The value of a is taken as $a = 0.68$, as given by our simulation results for the survival of random walkers in a three-dimensional lattice with traps.

III. SIMULATING DIFFUSION IN THE REARRANGING TRAP MODEL

We have simulated the random walk on a three-dimensional rearranging lattice, and calculated the diffusion coefficient for different c and τ_r. The algorithm is somewhat similar to the finite trap model in [12].

We work on an effectively infinite lattice, thus avoiding finite size effects. A random walker starts to walk on a cubic lattice of unit spacing with a concentration c of traps. The location of the traps is not preassigned; the walker decides whether the current site is a trap from a random number as it goes along. However, once assigned, the trap location remains fixed for time τ_r until the next rearrangement. Each trap is of infinite depth, so the walker encountering a trap has to remain there until the next rearrangement. To incorporate this in the algorithm, as soon as the walker falls into a trap, we freeze that walker up to the next rearrangement. To ensure that a site once assigned as allowed is not seen as a trap on a subsequent visit, we maintain a list of all allowed sites visited during τ_r, so that if these are revisited they are still assigned as allowed.

We average over 10^5 walks to get $\langle r^2 \rangle$ for different time intervals $t \gg \tau_r$. $\langle r^2 \rangle$ vs t is shown in Fig. 1; the curve is exactly like the results shown in [9]. $D(c, \tau_r)$ calculated from the average slope of $\langle r^2 \rangle$ vs t is plotted against τ_r for different c and shown in Fig. 4. According to Eq. (13) simulated results for different c and τ_r when scaled as $D(c, \tau_r)/(1-c)$ and plotted against $c\tau_r$ should collapse to a single curve. We find that results for $\tau_r = 250$ and 2000 do almost coincide and compare favorably with Eq. (13), as shown in Fig. 5.

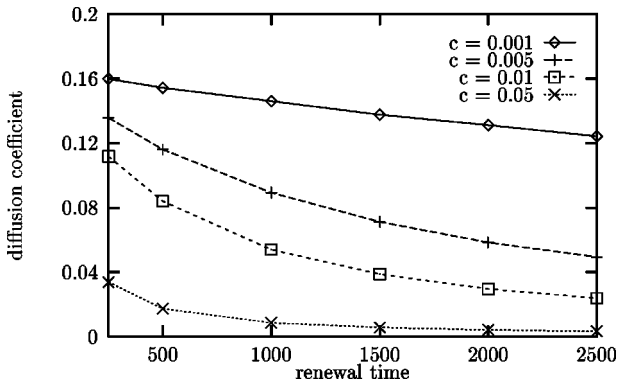

FIG. 4. Plot of diffusion coefficient versus renewal time for $c = 0.001, 0.005, 0.01$, and 0.05 from simulation, in arbitrary units.

IV. DISCUSSION

Figure 5 shows that the calculated results do not agree exactly with the value obtained from our simulations. The reason is probably that our simplified calculation ignores the distribution of distances traveled by different walkers and assumes an equal average distance covered by all the walkers. However, the agreement is quite satisfactory in spite of this.

The present model, although closely related to the DBPM [9] and the finite trap model [12], shows features distinct from either of them. We discuss here the points of similarity and dissimilarity between the models.

Physically the difference between the finite trap model [12] and the present one is only that here the traps are infinite. At this limit, however, a qualitative difference enters, the appearance of the percolation threshold. Now, in the quenched limit $\tau_r \to \infty$, when the trap positions are frozen,

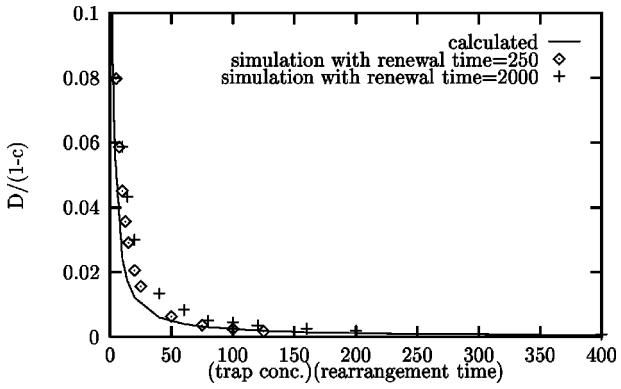

FIG. 5. Comparison of $D/(1-c)$ versus $c\tau_r$ from simulation and theory [Eq. (13)] for renewal times 250 and 2000.

the diffusion coefficient is zero for nonzero c, so the threshold is at $c=0$. The position of the threshold is at $c=0$ whatever the dimension of the system. So the difference from the model [12] is that there is a threshold. On the other hand, the DBPM does have a percolation threshold p_c at the appropriate bond percolation threshold for the dimension of the system.

Our simulation results shown in Fig. 1 resemble the DBPM results for $p<p_c$. So the trapping effect is stronger here than in the DBPM. This is expected since, with sites as infinite traps, a random walker must fall in a trap given sufficient time, even if the trap concentration is very small. In the bond model ''forbidden'' sites are inaccessible for the walker and may be avoided for $c<p_c$.

The finite trap model was shown to account successfully for the dynamic disorder in the polymer electrolyte PEO-NH_4ClO_4 [8]. There the crystalline regions in the polymer are assumed to be the sites with longer dwell time, and the amorphous regions the highly conducting sites with smaller dwell time. The infinite trap model is suited for systems with stronger trapping, and also systems where reacting species are diffusing in a viscous medium, for example, formation of excimers in fluorescence experiments, where fluorescing monomers combine with each other to form an ''excited dimer'' or excimer [19]. The excimer has a certain lifetime after which it may dissociate, i.e., the walker is released from the trap. However, in this case $dN \propto c^2$ rather than c as in Eq. (6) if c is the monomer concentration.

The primary interest of this model is that it is possible to calculate the dynamic disorder effect in a very simple way compared to the DBPM, which requires very involved mathematics, and the results are qualitatively very similar.

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