DIFFUSION ON A REARRANGING LATTICE
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Abstract

In this paper we present a computer simulation of a random walk (RW) for diffusion on a rearranging lattice. The lattice consists of two types of sites – one good conducting (type 1) and the other poor conducting (type 2), distributed at random. The two types of sites are assigned different waiting times ($\tau_1$ for type 1 and $\tau_2$ for type 2). We assume that at intervals of time $\tau_r$, the site distribution changes. The effect of this rearrangement on the diffusion coefficient is studied with varying $\tau_r$. We study this effect for different ratios of dwell times of the two types of sites (R) and also for different fractions (X) of the less conducting sites. An empirical relation for $D(\tau_1, \tau_2, \tau_r, X)$ is suggested. We have employed the well model and considered diffusion controlled by sites, rather than bonds. So our approach is different from the dynamic bond percolation model, which studies these aspects. Our results show that the diffusion coefficient D may change by a factor of upto 3 (approximately) for rapid rearrangement, and there is a considerable effect of varying X and R on the range of variation of D, where X is the fraction of low conducting sites, and R is the ratio of the dwell times for the two types of sites. Further for $\tau_r \leq 250\tau$ (\tau is the time unit for the random walk) the effect of rearrangement becomes negligible. The results may be useful for studying diffusion and conduction of ion conducting polymers.

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1 Introduction:

A convenient way to study diffusion and conduction is through the random walk formalism. Disordered media, which comprise many systems of practical interest have been analytically treated by this method [1-3]. However, an additional complication may be present in the system in the form of dynamic disorder. In this case the system undergoes some reorganisation with a characteristic timescale. This picture applies to polymers and also to glasses above their glass transition temperature. Exact analytical results for one version of this situation have been obtained in a series of works [4-6], where the dynamical bond percolation model (DBPM) has been proposed and treated in detail.

In the present communication we are interested in a different approach to the same problem. We consider a "well" model instead of the "barrier" model. In other words we are concerned with sites rather than bonds. We study diffusion in this system in two-dimensions through a computer simulation of the random walk including the rearrangement effect.

No exact results are available for this model with finite renewal time $\tau_r$ though the limits for $\tau_r = 0$ and $\tau_r = \infty$ can be exactly calculated. We have varied $\tau_r$ from $\tau$ to 250$\tau$, where $\tau$ is the time unit for the random walk. Our simulation results agree with the limiting values and we show that variation in $D$ with $\tau_r$ within the limits can be represented by a simple interpolation formula. We also find that the limit for large $\tau_r$ is approached very closely for $\tau_r = 250\tau$.

We have considered random arrangements of two types of sites with different conductivities represented by different dwell times. This work has been developed with the quasi 2-dimensional polymer thin films in mind; here the highly conducting sites represent the amorphous phase and the low conducting sites the crystalline phase. However the treatment is general and may be applied to any other situation where there are two different species with different conductivities and rearrangement. It is our aim to identify clearly the regime where this effect is most important and to assess how much it can affect the diffusion coefficient. We show that the diffusion coefficient may increase by a factor of about 3 for very rapid rearrangement, i.e. if the characteristic rearrangement time $\tau_r$ is of the same order as the hopping time $\tau$. But for $\tau_r > \tau_s \approx 250\tau$ there is no significant change in the diffusion coefficient ($D$) i.e. the diffusing
particle sees the lattice as a quenched disordered system.

We have studied $D$ versus $\tau_r$ curves varying two parameters – (a) the ratio of dwell times on the two different types of sites

$$R = \frac{\tau_2}{\tau_1} = \frac{p_1}{p_2} \quad (1)$$

$\tau_1$, $\tau_2$, $p_1$ and $p_2$ are the dwell times and jump probabilities of type 1 and 2 sites respectively, and (b) the fraction of low conducting sites $X$. We also measure the range of variation in $D$ for different $X$. This may be measured by $\Delta D = D_{max} - D_{min}$ or $D_r = D_{max}/D_{min}$. $\Delta D$ has a maximum at $X=0.2$, and $D_r$ is maximum at $X=0.5$.

In the next section our random walk algorithm is described and in section 3 the results are given. In the last section we discuss the implication of our results and compare them with earlier work on related problems.

2 The random walk algorithm :

Our random walk algorithm is an extension of the algorithm used earlier by Bhattacharyya et al [7], the new feature is that here $\tau_r$ is explicitly specified and varied. As mentioned in the earlier section, the random walk (RW) is performed on a 2-dimensional square lattice containing two types of sites. The distribution of the two different types in the lattice is random. The lattice sites actually represent small regions of the system which belong to a single phase only, and the lattice spacing ($\xi$) represents the distance between such sites. A site belonging to the $i^{th}$ phase is assigned a jump probability $p_i$ for jumping to a nearest neighbour site, at each time step. This implies an average waiting time $\tau_i$ at the $i^{th}$ site. A longer waiting time corresponds to a lower conductivity of the phase and hence of the site.

A distribution of energetically different sites on a lattice is usually represented in a simulation model by either of the following pictures :

1. Well model
2. Barrier model

In the well model each site is treated as a potential well. The well depth $w_i$ is a characteristic of the site type i and it determines how long the random walker will be trapped there.
In the barrier model a barrier \( b_{ij} \) is assumed to exist between sites \( i \) and \( j \). The probability for the particle to hop from \( i \) to \( j \) is determined by the nature of both the sites \( i \) and \( j \).

In the present work we have employed the considerably simpler well model, where the probability of jumping from a site is determined by the phase of that site only. The walker i.e. the diffusing particle is allowed to go to any of the four nearest neighbours with equal probability whether they belong to the highly or poorly conducting phase. We find normal diffusion as expected with the mean square distance travelled proportional to the time.

The steps of the RW are as follows.

1. The walker starts on an initial lattice point \( (x_o, y_o) \) on a two dimensional lattice. A random number is chosen to determine type of the site, and another to determine whether it jumps and its final position after the jump.

2. We assume that the host lattice retains the memory of a certain distribution of sites for \( \tau_r \) time steps, after that there is a rearrangement. This is implemented as follows.

   During the time interval \( \tau_r \) the walker stores the coordinates and the character (whether type 1 or type 2) of the sites visited. So if the walker visits the same site more than once within the interval \( \tau_r \), it finds there the same phase as was present earlier.

3. Step (1) is repeated during the time interval \( \tau_r \), with the current site coordinates instead of \( (x_o, y_o) \).

4. At \( t = (\tau_r + 1) \), the system forgets the previously stored \( \tau_r \) sites and their character and starts a fresh list for the next interval.

5. Steps (1-3) are repeated again for the next time interval \( \tau_r \).

The above procedure is repeated \( K \) times, where

\[
K = \frac{N_{total}}{\tau_r} \tag{2}
\]

\( N_{total} \) — total number of time steps for a particular walk.

Due to the stochastic nature of the process, one has to average over a large number of such
walks to get a meaningful value of $r^2_L$. In this work the walker executes a random walk of (15000-75000) steps and $r^2$ is averaged over (20000-100000) walks. This gives sufficiently good convergence up to 3 significant figures for the diffusion coefficient. We have calculated D for $\tau_r$ varying from (1-250). For still higher $\tau_r$ there is negligible change in D.

This random walk algorithm allows the walker to move on an effectively infinite sample. This is possible because here we do not take a quenched system with sites assigned specifically to a definite phase. So the problem of finite size effects is avoided. There is however a restriction to the walk size due to limited computer time.

### 3 Results :

#### 3.1 Variation in D with $\tau_r$ for constant R and X :

Using the above RW algorithm, the diffusion coefficient was obtained as a function of $\tau_r$, $X$ and $R$. We have kept $\tau_r$ constant at $\tau_2 = 10$, and $\tau_1$ has been varied from 10 to 1.01. We find that D does not change on further decrease of $\tau_1$. The minimum value $\tau_1$ can have is 1 corresponding to $p_1 = 1$. Figs. 1 and 2 are plots of D versus $\tau_r$ for different values of R (9.9, 8.6 and 1) at $X = 0.14$ and $X = 0.80$ respectively. Fig. 3 is plot of D versus $1/\tau_r$ for different R values at a constant $X (=0.14)$. The maximum and the minimum values for D corresponding to $\tau_r \rightarrow 0$ and $\tau_r \rightarrow \infty$ are given by

$$D_{max} = \frac{1}{4\tau_1} \left[ (1 - X) + \frac{X}{R} \right]$$  \hspace{1cm} (3)

and

$$D_{min} = \frac{1}{4\tau_1} \left[ (1 - X) + 1 \right]^{-1}$$  \hspace{1cm} (4)

with lattice constant = 1. These values agree with the simulation results. In figures 1 and 2 the simulation results for D are shown as discrete points, from the variation in D we suggest an empirical relation for $D = D(\tau_r, \tau_1, \tau_2, X)$. Calculated values from this relation are shown as continuous curves.

We now give the proposed formula for D. D may be written in terms of an effective time $\tau_{eff}$ which is some sort of average over the characteristic times for the two types of sites. So
\[ D = 1/4\tau_{\text{eff}}. \] Casting equations (3) and (4) in this form, we have

\[ \tau_{\text{eff}}(\tau_r \to \infty) = \tau_{\text{max}} = \tau_1(1-X) + \tau_2X \] (5)

and

\[ \frac{1}{\tau_{\text{eff}}(\tau_r \to 0)} = \frac{1}{\tau_{\text{min}}} = \frac{1-X}{\tau_1} + \frac{X}{\tau_2} \] (6)

i.e. in the first case the walker sees an average waiting time, whereas in the second case it sees an average jump frequency. In other words in the first case we have a Voigt average of waiting times and in the second case a Reuss average [8]. For finite \( \tau_r \) we propose the following relation

\[ \frac{1}{\tau_{\text{eff}}(X, \tau_1, \tau_2, \tau_r)} = \frac{1}{\tau_{\text{max}}} \cdot \frac{\alpha_2}{\alpha_1 + \alpha_2} + \frac{1}{\tau_{\text{min}}} \cdot \frac{\alpha_1}{\alpha_1 + \alpha_2} \] (7)

where

\[ \alpha_1 = 1 - \exp\left(-\frac{\tau_1}{X\tau_r}\right) \] (8)

\[ \alpha_2 = \exp\left(-\frac{\tau_2}{(1-X)\tau_r}\right) \] (9)

This relation reduces to the correct limits for \( X=0 \) and \( X=1 \), as well as \( \tau_r \to 0 \) and \( \tau_r \to \infty \). It reproduces quite well the strong nonlinearity in \( D \) between the limiting values. The calculated values are slightly higher than the simulation results, as shown in figures 1 and 2. The agreement between the empirical formula and simulation results is better for low \( X \). For higher \( X \) the calculated \( D \) does not fall as sharply with \( \tau_r \), as the simulation results.

Salient features of our results are as follows. The change in \( D \) with \( \tau_r \) is significant for \( \tau_r < \tau_s \approx 250\tau \). The hopping time \( \tau \) is the smallest time scale for our system. For \( \tau_r > \tau_s \) the system is effectively quenched. This is seen more clearly in fig.3. We find that the limiting value of \( D \) for \( \tau_r \to \infty \) is hardly different from the last calculated data point corresponding to \( \tau_r = 250\tau \). So we take \( \tau_s = 250\tau \). For small \( X \) and large \( R \), i.e. the residence probability of the type 1 phase being negligibly small, the average time elapsed between jumps \( \tau_i \) may be approximated as \( \tau \). In this case we can get an estimate of \( \tau_s \) in real units. For a polymer system, \( \tau_i \approx 10^{-6} \text{ sec} \) according to nuclear magnetic resonance (NMR) linewidth narrowing experiments [9,10]. so from \( \tau_s = 250\tau \), we find that \( \tau_s \sim 10^{-4} \text{ sec} \).
3.2 Range of variation of D for different X:

It is obvious that for any value of R, $\Delta D = 0$ and $D_r=1$ for both $X=1$ and $X=0$, i.e. if there is only one type of site on the lattice. We find that $D_r$ has a maximum for $X = 0.50$, whereas $\Delta D$ has a maximum at $X = 0.20$. This is because $D$ itself is larger at lower $X$. The $X$ values of peaks obtained for $D$ may not correspond to those obtained while studying conductivity. This is due to the fact that the charge carrier concentration comes into play when conductivity is calculated.

Again if $R = 1$, i.e. all sites are equivalent, $\Delta D=0$ and $D_r=1$. The effect of increasing $R$ towards $R \to \infty$ is seen in figs 1 and 2.

4 Discussion:

4.1 Comparison with DBPM Model:

We discuss briefly the DBPM model which is concerned with the barrier model i.e. the bond picture of the same problem.

Starting with a one-dimensional model, a series of works have been published [4-6] which develop the dynamic bond percolation (DBPM) model, including different features and extending it to higher dimensions. These works develop an analytical approach to the problem of diffusion in a rearranging lattice with bond renewal. Here one type of site is conducting and the other is completely insulating. The review by Nitzan and Ratner [4] gives a complete overview of the model.

The most significant result of this work is the demonstration that, the diffusion coefficient $D(\tau_r)$ with renewal is identical to a frequency dependent diffusion coefficient $D(\omega)$ on a static lattice through an analytical continuation rule.

$$D(\omega, \tau_r) = D_o(\omega - \frac{i}{\tau_r})$$

Their work is also compared with effective medium models [4].

The present model for $R \to \infty$ may be compared with the DBPM. A basic difference is to be
noted in the two cases. In DBPM or any standard bond percolation model the insulating sites are blocked, that is inaccessible to the walker. In the present model, however, the insulating sites are infinite traps, from which the walker cannot escape. The diffusion behaviour of the two models is quite similar, in spite of this difference. Let us consider the situation below the percolation threshold. In DBPM the walker gets confined to a finite cluster after some characteristic time which is a function of X. If \( \tau_r \) is larger than this time, the mean square distance travelled saturates to a constant value. On renewal, the sites rearrange and the walker is released from the previous cluster it occupied. Now \( < r^2 > \) starts to increase again. This continues in steps as shown in fig(5) of ref [5].

Let us now consider a similar situation in our model. Here the walker gets trapped in one of the insulating sites after a certain time depending on X. But after renewal the site may change to a conducting site and release the walker, so \( < r^2 > \) increases in steps just as in the DBPM. This shows that the overall diffusion behaviour is similar, though the microscopic pictures are quite different. Of course the percolation threshold in this case, is expected to be the site percolation rather than the bond percolation threshold appropriate for the DBPM. We have not yet attempted simulation of this limiting situation.

The qualitative appearance of the curves for D vs \( 1/\tau_r \) in ref[5] is very similar to our figure 3, which illustrates the underlying similarity of the two approaches.

### 4.2 Conclusion :

The effect of rearrangement of the lattice due to liquid-like behaviour at short length scales is considered to be very important for studying conduction in polymers. We have assessed how important it can be and when particularly it must be taken into account.

This effect becomes unimportant after \( \tau_r > \tau_s \). Assuming \( \tau \approx 7 \times 10^{-7} \) sec [9,10], \( \tau_s \) is of the order milliseconds. For larger \( \tau_r \) it suffices to take the quenched lattice limit.

Our system is an infinite lattice, so finite size effects which may distort the results considerably are absent. It is to be noted that our definition of \( \tau_r \) refers to the time for interchange of crystalline and amorphous sites. This is similar to the original definition of renewal time (\( \tau_{ren} \))
by Druger et al [5], but in other works different renewal times for crystalline and amorphous regions have been considered [11]. Chang and Xu have considered rotation of polymer chain sections in their work [12].

We plan to incorporate our findings reported here, in an ongoing calculation on a detailed study of temperature and salt fraction dependence of conductivity of polymer-salt complexes. In this study the variation of $\tau_r$ with temperature or other factors may be important. However, as we have shown the rearrangement effect itself cannot be responsible for a change in $D$ by as much as several orders of magnitude and the effect is most pronounced at low crystallinities.

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Figure Captions:

1. Fig.1 : Plot of diffusion coefficient (D) versus renewal time $\tau_r$ at $X=0.14$ for $R=9.9$ ($\ast$), $R=8$ ($\diamond$), $R=6$ ($\bigtriangleup$) and $R=1$ (o). The Calculated values using eqn.(7) are shown by continuous lines.

2. Fig.2 : Plot of diffusion coefficient (D) versus renewal time $\tau_r$ at $X=0.80$ for $R=9.9$ ($\ast$), $R=8$ ($\diamond$), $R=6$ ($\bigtriangleup$) and $R=1$ (o). Calculated values using eqn. (7) are shown by continuous lines.

3. Fig.3 : Plot of diffusion coefficient (D) versus $1/\tau_r$ at $X=0.14$ for $R=9.9$ ($\ast$), $R=8$ ($\diamond$), $R=6$ ($\bigtriangleup$) and $R=1$ (o). The continuous lines are simply lines joining the points.

4. Fig.4 : Plot of $\Delta D$ ($\triangle$) and $D_r$ (o) versus $X$ for a fixed $R = 9.9$. 