

Diffusion on a rearranging lattice

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1998 J. Phys.: Condens. Matter 10 10931

(<http://iopscience.iop.org/0953-8984/10/48/014>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.210

The article was downloaded on 14/05/2010 at 18:02

Please note that [terms and conditions apply](#).

Diffusion on a rearranging lattice

Aninda Jiban Bhattacharyya[†] and S Tarafdar

Condensed Matter Physics Research Centre, Department of Physics, Jadavpur University, Calcutta 700032, India

Received 8 July 1998, in final form 17 September 1998

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 highly conducting (type 1) and the other poorly conducting (type 2), distributed at random. The two types of site are assigned different waiting times (τ_1 for type 1 and τ_2 for type 2). We assume that at intervals of time τ_r the site distribution changes. The effect of this rearrangement on the diffusion coefficient is studied with varying τ_r . We study this effect for different ratios of dwell time of the two types of site (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 up to 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 poorly conducting sites, and R is the ratio of the dwell times for types of site. Further for $\tau_r > 250 \tau$ (τ 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.

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 reorganization 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 of calculating the diffusivity of a disordered lattice which is rearranged after a characteristic time interval τ_r . We consider here 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 τ_r though the limits for $\tau_r = 0$ and $\tau_r = \infty$ can be exactly calculated. We have varied τ_r from 1 to 250 τ , where τ is the time unit for the random walk. Our simulation results agree with the limiting

[†] E-mail address: aninda@juphys.ernet.in.

values and we show that variation in D with τ_r within the limits can be represented by a simple interpolation formula. We also find that the limit for large τ_r is approached very closely for $\tau_r = 250 \tau$.

We have considered random arrangements of two types of site with different conductivities represented by different dwell times. This work has been developed with the quasi-two-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 τ_r is of the same order as the hopping time τ . 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 τ_r curves varying two parameters—(a) the ratio of dwell times on the two different types of site

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

(τ_1 , τ_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 $D_r = D_{max}/D_{min}$. ΔD 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 τ_r is explicitly specified and varied. As mentioned in the earlier section, the random walk (RW) is performed on a two-dimensional square lattice containing two types of site. 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 (ξ) 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 τ_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. The steps of the RW are as follows.

(1) The walker starts on an initial lattice point (x_0, y_0) 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 τ_r time steps; after that there is a rearrangement. This is implemented as follows.

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

(3) Step (1) is repeated during the time interval τ_r , with the current site coordinates instead of (x_0, y_0) .

(4) At $t = (\tau_r + 1)$, the system forgets the previously stored τ_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 τ_r .

The above procedure is repeated K times, where

$$K = \frac{N_{total}}{\tau_r}. \quad (2)$$

N_{total} is the 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 obtain a meaningful value of $\langle r^2 \rangle$. In this work the walker executes a random walk of (15 000–75 000) steps and r^2 is averaged over (20 000–100 000) walks. This gives sufficiently good convergence up to three significant figures for the diffusion coefficient. We have calculated D for τ_r varying from 1 to 250. For still higher τ_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 the finite size effects is avoided. There is however a restriction to the walk size due to limited computer time.

3. Results

3.1. Variation of D with τ_r for constant R and X

Figure 1 shows a typical result for $\langle r^2 \rangle$ versus t . The linear nature shows that diffusion is normal. So the diffusion coefficient is obtained from the relation

$$\langle r^2 \rangle = 4Dt. \quad (3)$$

Using the above RW algorithm, the diffusion coefficient was obtained as a function of τ_r , X and R . We have kept τ_r constant at $\tau_r = 10$, and τ_1 has been varied from 10 to 1.01. We find D does not change on further decrease of τ_1 . The minimum value τ_1 can have is 1 corresponding to $p_1 = 1$. Figures 2 and 3 are plots of D versus τ_r for different values of R (9.9, 8, 6 and 1) at $X = 0.14$ and $X = 0.80$ respectively. Figure 4 is a 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

$$D_{max} = \frac{1}{4\tau_r} \left[(1 - X) + \frac{X}{R} \right] \quad (4)$$

and

$$D_{min} = \frac{1}{4\tau_1} [(1 - X) + XR]^{-1} \quad (5)$$

with lattice constant $=1$. These values agree with the simulation results. In figures 2 and 3 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.

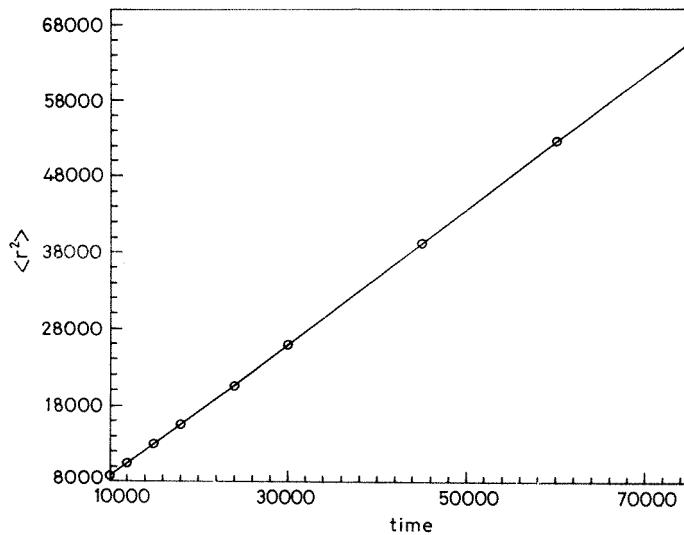


Figure 1. Plot of $\langle r^2(t) \rangle$ versus time for $X = 0.14$ and $R = 9.90$.

We now give the proposed formula for D . D may be written in terms of an effective time τ_{eff} which is some sort of average over the characteristic times for the two types of site. Casting equations (4) and (5) in this form, we have

$$\tau_{eff}(\tau_r \rightarrow \infty) = \tau_{max} = \tau_1(1 - X) + \tau_2 X \quad (6)$$

and

$$\frac{1}{\tau_{eff}(\tau_r \rightarrow 0)} = \frac{1}{\tau_{min}} = \frac{1 - X}{\tau_1} + \frac{X}{\tau_2} \quad (7)$$

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 τ_r we propose the following relation

$$\frac{1}{\tau_{eff}(X, \tau_1, \tau_2, \tau_r)} = \frac{1}{\tau_{max}} \frac{\alpha_2}{\alpha_1 + \alpha_2} + \frac{1}{\tau_{min}} \frac{\alpha_1}{\alpha_1 + \alpha_2} \quad (8)$$

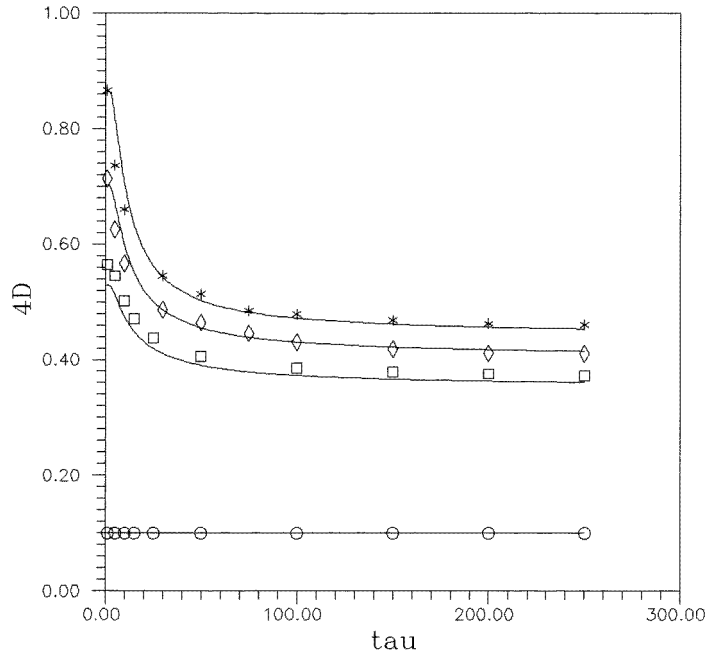


Figure 2. Plot of diffusion coefficient (D) versus renewal time τ_r at $X = 0.14$ for $R = 9.9$ (\star), $R = 8$ (\diamond), $R = 6$ (\square) and $R = 1$ (\circ). The calculated values using equation (7) are shown by continuous lines.

where

$$\alpha_1 = 1 - \exp\left(-\frac{\tau_1}{X\tau_r}\right) \quad (9)$$

$$\alpha_2 = \exp\left(-\frac{\tau_2}{(1-X)\tau_r}\right). \quad (10)$$

This relation reduces to the correct limits for $X = 0$ and $X = 1$, as well as $\tau_r \rightarrow 0$ and $\tau_r \rightarrow \infty$. 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 2 and 3. The form of equation (8) is not symmetric with respect to interchange of phases 1 and 2; the D versus τ_r curve has sharp gradient at $\tau_r \rightarrow 0$ for small X , whereas for large X the slope $(dD/d\tau_r)|_{\tau_r \rightarrow 0}$ is almost zero. The simulation results have a steep gradient at $\tau_r \rightarrow 0$ for high as well as for low X . So our formula (8) works better in the dilute limit of the traps, i.e. low conducting sites. Interchanging the factor X and $(1 - X)$ in equations (9) and (10) we obtain a formula more appropriate for the dilute limit of the highly conducting sites (i.e. large X). Using this formula we find a better fit for $X = 0.80$ and worse fit for $X = 0.14$. However since our two X values are not chosen symmetrically about $X = 0.50$, the overall results are better for equation (8). The simulation was performed only for those X values where experimental results are available [9]. The whole range of X values will be explored and compared with an analytical calculation which is in progress.

Salient features of our results are as follows. The change in D with τ_r is significant for $\tau_r < \tau_s \approx 50 \tau$. The major fall however occurs within $\tau_r = 50$. The hopping time τ is the smallest time scale for our system. For $\tau_r > \tau_s$ the system is effectively quenched. This is seen more clearly in figure 4. We find that the limiting value of D for $\tau_r \rightarrow \infty$ is

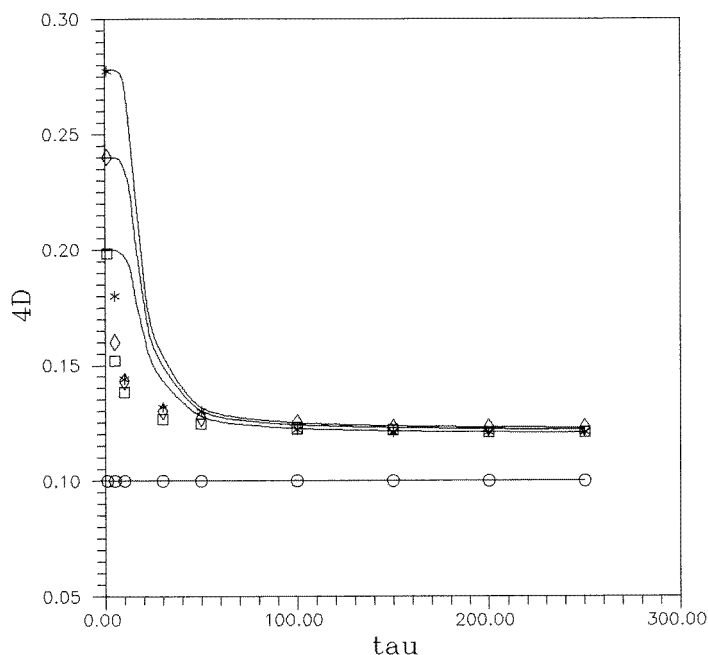


Figure 3. Plot of diffusion coefficient (D) versus renewal time τ_r at $X = 0.80$ for $R = 9.90$ (\star), $R = 8$ (\diamond), $R = 6$ (\square) and $R = 1$ (\circ). The calculated values using equation (7) are shown by continuous lines.

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 τ_i may be approximated as τ . In this case we can obtain an estimate of τ_s in real units. For a polymer system, $\tau_i \approx 10^{-6}$ s according to nuclear magnetic resonance (NMR) linewidth narrowing experiments [10, 11]. So from $\tau_s = 250 \tau$, we find that $\tau_s \sim 10^{-4}$ s.

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 ΔD 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 $R \rightarrow \infty$ is seen in figures 1 and 2.

4. Discussion

4.1. Comparison with DBPM model

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

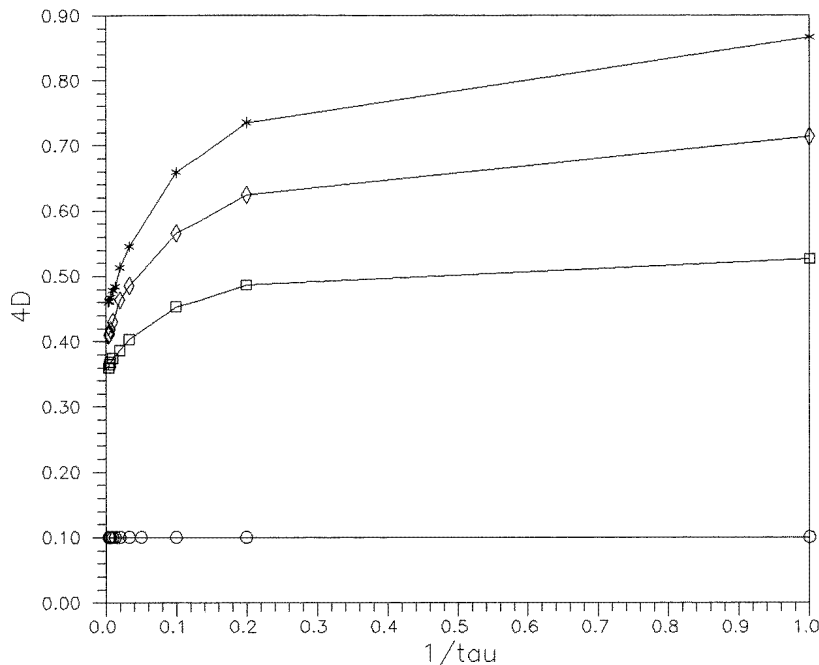


Figure 4. Plot of diffusion coefficient (D) versus $1/\tau_r$ at $X = 0.14$ for $R = 9.9$ (\star), $R = 8$ (\diamond), $R = 6$ (\square) and $R = 1$ (\circ). The continuous lines are simply lines joining the points.

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.

$$D(\omega, \tau_r) = D_0 \left(\omega - \frac{i}{\tau_r} \right).$$

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

The present model for $R \rightarrow \infty$ 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 i.e. 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 is confined to a finite cluster after some characteristic time which is a function of X . If τ_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 $\langle r^2 \rangle$ starts to increase again. This continues in steps as shown in figure 5 of [5].

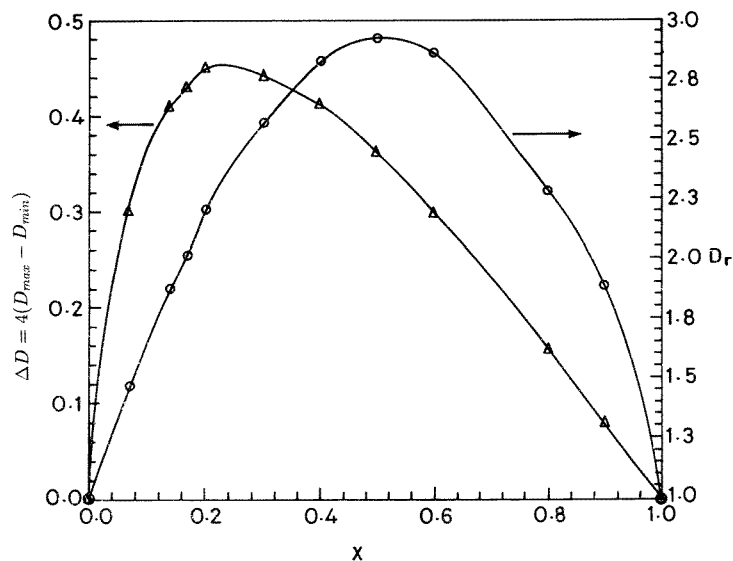


Figure 5. Plot of ΔD (Δ) and D_r (O) versus X for a fixed $R = 9.9$.

Let us now consider a similar situation in our model. Here the walker is 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 $\langle r^2 \rangle$ increases in steps just as in the DBPM. This shows that the overall diffusion behaviour is similar, though the microscope 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 against $1/\tau_r$ in [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 $\tau \sim 7 \times 10^{-7}$ s [10, 11]; τ_s is of the order of milliseconds. For larger τ_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 τ_r refers to the time for interchange of crystalline and amorphous sites. This is similar to the original definition of renewal time (τ_{ren}) by Druger *et al* [5], but in other works different renewal times for crystalline and amorphous regions have been considered [12]. Chang and Xu have considered rotation of polymer chain sections in their work [13].

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 τ_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.

Acknowledgments

AJB is grateful to the UGC for the award of Senior Research Fellowship. The authors are also grateful to K P N Murthy, S M Bhattacharjee, T K Ballabh and T R Middy for stimulating discussions.

References

- [1] Bouchaud J P and Georges A 1990 *Phys. Rep.* **195** 127
- [2] Havlin S and Ben-Avraham D 1987 *Adv. Phys.* **36** 695
- [3] Haus J W and Kehr K W 1987 *Phys. Rep.* **150** 263
- [4] Nitzan A and Ratner M A 1994 *J. Phys. Chem.* **P98** 1765
- [5] Druger S D, Nitzan A and Ratner M A 1983 *J. Phys. Chem.* **79** 3133
- [6] Druger S D, Ratner M A and Nitzan A 1985 *Phys. Rev. B* **31** 3939
- [7] Bhattacharyya A J, Middy T R and Tarafdar S 1998 *Pramana J. Phys.* **50** 205
- [8] Voigt W 1889 *Ann. Phys.* **38** 573
Reuss A 1929 *Z. Angew. Math. Mech.* **9** 49
- [9] Maurya K K, Srivastava N, Hashmi S A and Chandra S 1992 *J. Mater. Sci.* **27** 6357
- [10] Chung S H, Jeffrey K R and Stevens J R 1991 *J. Chem. Phys.* **93** 1803
- [11] Wang C, Liu Q, Cao Q, Meng Q and Yang L 1992 *Solid State Ion.* **53-56** 1106
- [12] Ratner M A and Shriver D F 1988 *Chem. Rev.* **88** 109 and references therein
- [13] Chang W and Xu G 1993 *J. Chem. Phys.* **99** 2001