PARTICLE MOTION THROUGH A DYNAMICALLY DISORDERED MEDIUM: THE EFFECTS OF BOND CORRELATION AND APPLICATION TO POLYMER SOLID ELECTROLYTES

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To study the diffusion of small particles through a dynamically disordered medium, a dynamic bond percolation model has been developed. This differs from the standard percolation theory, in that the lattice is no longer static but undergoes rearrangements which reassign the open and closed bonds. Physically, these rearrangements correspond to orientational motions of the (polymer) host lattice.

An interesting feature of this model is that, even below the percolation threshold, diffusive behavior can occur, as long as the renewal time τ_{ren}, the time characteristic of the rearrangement of bonds, is short compared to the observation time.

Ionic conductivity in polymeric electrolytes is one of the systems for which this model is useful. In these materials, carrier ions diffuse through a medium (the polymer) which is undergoing dynamic motion caused by configurational motions of the polymer. Since polymer chain motions will affect several ion binding sites simultaneously or serially, the model is further elaborated to account for correlations in the segmental motions of the polymer host. The renewal of the bonds is changed from occurring randomly to include simple correlation effects.

Of principal concern in this study is the effect that correlated renewals have on the transport behavior of the model. Simulations were done on a 1-D lattice and a diffusion coefficient calculated. The values of the diffusion coefficients from the two systems (with and without correlated renewal) are studied and their behavior as a function of the fraction of available bonds, f, and the renewal time is compared.

For both correlated and uncorrelated renewals, the systems were diffusive. The diffusion coefficients, in both cases, increased with increasing f and decreasing τ_{ren}, corresponding to an increase in the free volume, the configurational entropy, and the temperature of the polymer systems. The diffusion coefficient from the correlated systems were always smaller than those from the uncorrelated systems, except for the limit f = 100% and $\tau_{ren} \ll \tau_{hop}$. The ratio of the diffusion coefficients for the correlated and uncorrelated systems was studied as a function of τ_{ren} and f. This ratio falls off to a constant value as τ_{ren} is increased and reaches minimum value at f = 50%. This behavior of the ratio as a function of f can be explained by considering the diffusion of the bonds in the lattice for the correlated case.

1. INTRODUCTION

Percolation models are often used to study transport properties in rigid media.[1] In bond percolation schemes, a particle is allowed to hop from site to site on a lattice in which a given fraction of intersite bonds is randomly blocked. This model has been applied to the study of transport in framework solid electrolytes.[2] The development of solvent free polymer-salt complexes as solid electrolytes[3,4] has stimulated interest in the transport properties of these non-framework ionic conductors. The importance of polymer backbone fluctuations to the transport of the ions has been demonstrated in a variety of systems.[5,6,7] Theories based on free volume and configurational entropy have been used to describe the temperature dependent conductivity of polymeric solid electrolytes.[4,8] Amorphous regions of the polymer host, above its glass transition temperature, have a substantial amount of free volume or configurational

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entropy which increases with temperature and facilitates ion transport.

The application of the bond percolation model to polymer solid electrolytes is possible if the model is modified to account for the segmental motions of the polymer host. In the Dynamic Bond Percolation (DBP) model, the dynamics of the polymer host are taken into account by considering lattice rearrangements which reassign the blocked and unblocked bonds. The application of DBP to polymer electrolytes, including both its relationship to the free volume model,[9] and formal properties of the model itself[10,11,12] have been studied previously. A slightly different model has been recently investigated by Harrison and Zwanzig.[12]

The objective of the present study is to alter the DBP model to include correlations among the lattice bonds undergoing rearrangement, and to make a qualitative investigation of how correlation affects the diffusion coefficients obtained from numerical simulations. Work by Kutner and Kehr[13] has considered a model which formally resembles DBP with correlated renewal. This work looks at diffusion with two kinds of particles where one kind may, in our case, take the part of the migrating bonds. Here we consider a model in which the lattice motion is far more strongly correlated than in refs. 9–11 or 12. It involves permitting open, or available, bonds to move only between one bond site to the next bond site, and may correspond to a polymer electrolyte in which backbone motions indeed move the available ion motion pathways down the lattice. It also characterizes well the one-dimensional case of light particles (the ions) moving in concert with heavy particles (the lattice). and should be useful in describing the coupled rotation and hopping processes which occur in protonic electrolytes.[14]

2. MODEL AND DISCUSSION

In the dynamic bond percolation models[1] a hopper is propagated from site to site within a lattice. The probability of the hopper moving from one site to another across a bond, w_{ij}, is assigned either the value 0 (bond blocked) or the value w. A given fraction, f, of the bonds are unblocked. These unblocked bonds are randomly distributed throughout the lattice. Thus the probability P_i for the hopping ion to be located on site i is given by

$$\frac{dP_i}{dt} = \sum_j \left(w_{ji}P_j - w_{ij}P_i \right),\qquad (1)$$

where the sum runs only over nearest neighbors, and

$$w_{ij} = \begin{cases} 0 & \text{probability } (1-f) \\ w & \text{probability } f \end{cases}\qquad (2)$$

Equation (1) is the kinetic equation, or master equation, for the system. In static bond percolation theory, the bond w_{ij} for any given pair of sites i and j is fixed once and forever to be either available ($w_{ij} = w$) or closed ($w_{ij} = 0$). In dynamic percolation models, the assignment of w_{ij} to either zero or w varies with time. Thus, to add dynamics to the system the assignment of blocked bonds is randomly redistributed, keeping the overall fraction f constant, on a time scale, τ_{ren}. The other relevant parameters of the model are the observation and hopping times, τ_{obs} and τ_{hop}, respectively. Numerical simulations and a closed-form evaluation[10,11] for a one-dimensional model show that diffusion occurs in the limit of $\tau_{obs} > \tau_{ren}, \tau_{hop}$. When no fluctuations of the lattice are allowed to occur, $\tau_{ren} > \tau_{obs}$, diffusion is prohibited below the percolation threshold.[10] This second limit, $\tau_{ren} > \tau_{obs}$, corresponds to a polymer electrolyte that is either highly crystalline or is below its glass transition temperature with a resulting low conductivity.
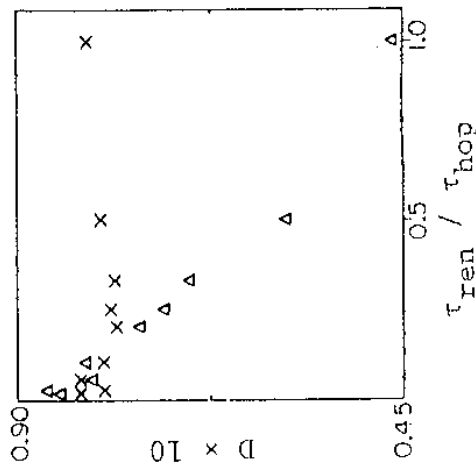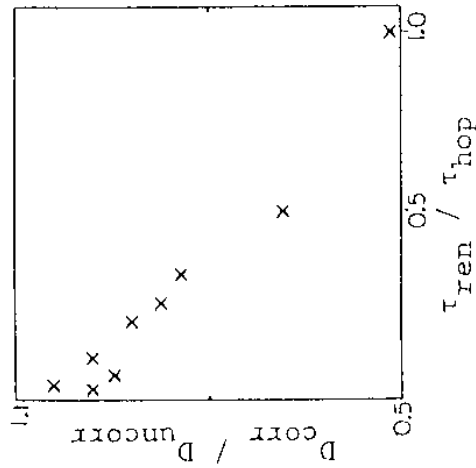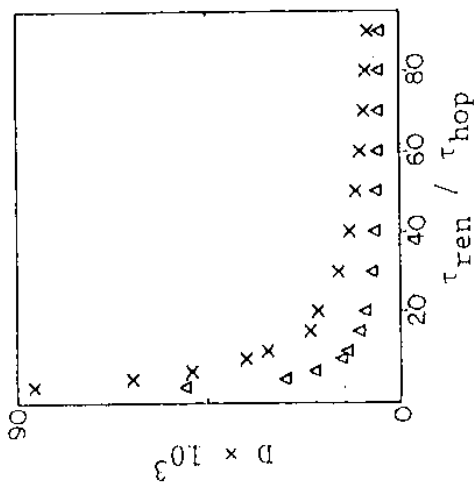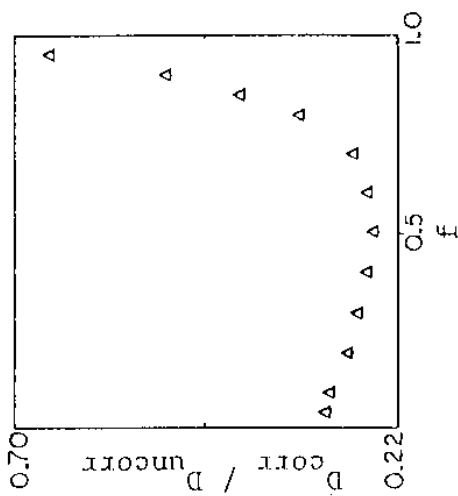
FIGURE 1

The ratio of the diffusion coefficients obtained from the DBP models in one dimension with correlated and uncorrelated renewals, D_{corr}/D_{uncorr}, as a function of relative renewal and hopping times, τ_{ren}/τ_{hop}. (a) D_{corr}/D_{uncorr} decreases to a constant value as the τ_{ren}/τ_{hop} increases from 1 to 90. (b) D_{corr}/D_{uncorr} approaches 1.0 as τ_{ren}/τ_{hop} decreases from 1 to 0.01 (f = 0.20).

FIGURE 2

The diffusion coefficients obtained from the DBP model in one dimension as a function of the relative renewing and hopping times, τ_{ren}/τ_{hop}. $\triangle$, correlated renewals; X, uncorrelated renewals. (a) As τ_{ren}/τ_{hop} increases from 1 to 90 both diffusion coefficients decrease. (b) As τ_{ren}/τ_{hop} decreases from 1.0 to 0.01 D_{corr}, $\triangle$, increases while D_{uncorr}, X, remains constant (f = 0.20).

FIGURE 3

(a) The ratio of the diffusion coefficients obtained from the DBP model in one dimension with correlated and uncorrelated renewals, D_{corr}/D_{uncorr}, as a function of the fraction of unblocked bonds, f. (b) The individual diffusion coefficients both increase as f increases from 0.05 to 0.95; $\triangle$, D_{corr}; X, D_{uncorr} (τ_{ren}/τ_{hop} = 20).
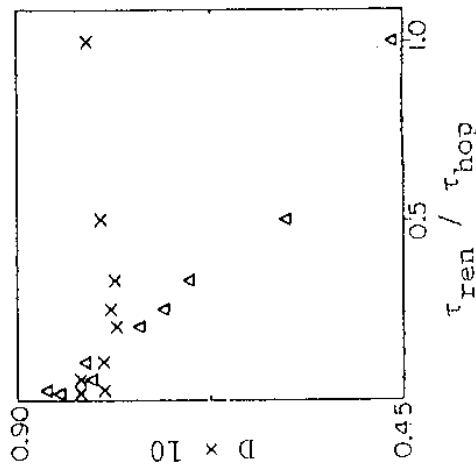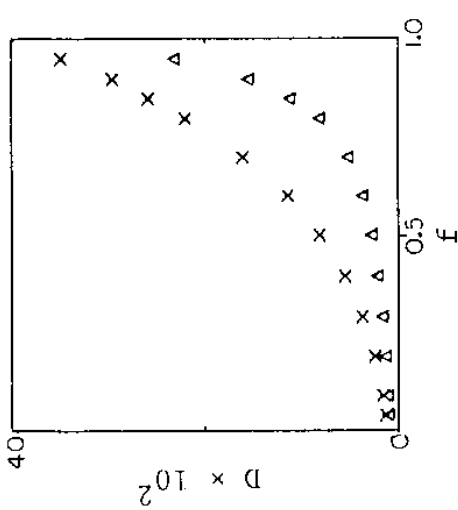
To make the model more physically reason-
able, correlated instead of random[9-11] bond
renewals are used. This better represents the
important segmental fluctuations of the polymer
host in polymer electrolytes. To render bond
renewal a strongly correlated process a
restriction is added such that a bond can renew
only by exchanging blocked/unblocked status
($w_{ij} = 0$ or $w_{ij} = w$) with one of its nearest
neighbors. This exchange occurs with a charac-
teristic timescale, τ_{ren}. The results of
numerical simulations on a one-dimensional lat-
tice give the mean-squared displacement of the
hopper as a linear function of time, the slope
being the diffusion coefficient. The effect of
the added limitation of correlated renewal is
determined by examining the relative diffusion
coefficients of the correlated and uncorrelated
systems, D_c/D_u, as a function of the para-
meters, f, τ_{ren}, τ_{hop}.

Correlations in the renewal process reduce
the diffusion coefficient such that $D_c/D_u < 1$,
Figures 1-3. At two extreme limits, $f \to 1.00$
τ_{ren}, the value of D_c/D_u approaches unity,
Figures 1b and 3a. For the case of $f \to 1.00$,
the renewal process becomes unimportant since
there are essentially no blocking bonds. For
the case of $\tau_{hop} \gg \tau_{ren}$ the lattice fluctuates
rapidly relative to the hopper motion. In the
time between one hop and the next the lattice
passes through such a large number of config-
urations that all correlations are lost and the
correlated renewals become effecitvely random.
The value of the ratio D_c/D_u decreases as
τ_{ren}/τ_{hop} increases, illustrated in Figure 1.
For $\tau_{ren} > \tau_{hop}$ the hopper samples a cluster of
connected sites in the time between consecutive
renewals. During this time the hopper encoun-
ters blocked bonds which bar its movement.
Uncorrelated renewals can open up new areas of
available sites while correlated renewals only
free one site per renewal, limiting diffusion.

As τ_{ren} becomes large the hopper samples all
sites available to it before the next renewal
occurs and the effects of correlation reach a
limit. This limit is observed as D_c/D_u reaches
a constant value, Figure 1a.

The dependence of D_c/D_u on the bond fraction
f reflects the dynamics of the bond diffusion
itself. Like any system of diffusing entities
with short range (e.g., excluded volume) inter-
actions this diffusion process is slowest at
$f = 0.5$, and roughly proportional to $f(1-f)$.
Accordingly the factor D_c/D_u goes through a
similar minimum as shown in Figure 3a. The
lack of symmetry of the D_c/D_u vs. f curve
results from the fact that D_c is related to the
diffusion of the ions which obviously increases
strongly with f.

The independent behavior of the diffusion
coefficients for the cases of correlated and
uncorrelated bond renewal as a function of f
and τ_{ren}/τ_{hop} are plotted in Figures 2 and 3b.
Relating the system to polymer electrolytes, an
increase in f and decrease in τ_{ren}/τ_{hop} corre-
sponds to an increase in free volume and con-
figurational entropy and a decrease in percent
crystallinity of the polymer host, resulting in
an improvement of ionic conductivity. These
factors are true of both correlated and
uncorrelated[9-11] bond renewals.

An important feature of the DBP model is
that diffusion can still occur when the frac-
tion of unblocked bonds is below that which
defines the percolation threshold in static
percolation models[1] (f < 1.0 for one dimen-
sion). Extending the simulations to two dimen-
sions, it will be of considerable interest to
see if there are any sudden changes in the
behavior of the diffusion coefficient at the
percolation thresholds found in the static
models. Our work as well as that of Harrison
and Zwanzig[12] in models with independent
(uncorrelated) renewals shows that although

there is substantial change in the quantitative behavior of D(f) as f passes through the threshold value f_c, the abrupt change of the static model is very much smoothed by renewal. We expect this general behavior to occur also for strongly correlated renewal and beyond the effective medium approximation. Experimentally, this means that independent of carrier concentration or of polymer chain length, diffusion of mobile ions will be expected above the glass transition temperature.

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