Diffusion in a random medium: A Monte Carlo study

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(Received 10 February 1992; revised manuscript received 15 October 1992)

We use lattices with randomly distributed site-barrier energies to study diffusion properties as a function of disorder and temperature. We study the case of "dynamic" disorder whereby the random environment is renewed at each successive jump of the hopping particle, and also the case of "static" disorder with frozen randomly distributed barriers. The transition characteristics are governed by Boltzmann statistics. We employ standard Monte Carlo techniques to monitor properties such as the mean-square displacement. The trends of the motion are shown to include local trapping at early times, allowing for the search of a crossover time to the conventional diffusive regime, $\langle R^2 \rangle \sim t$, as a function of temperature. We find that the crossover time versus temperature dependence is of the Arrhenius type determined by an effective activation energy barrier for percolation in the case of static disorder. For a uniform distribution of the barriers, this activation barrier is shown to coincide with the threshold concentration for bond percolation, as simple arguments suggest. We also demonstrate that an increase in the degree of dynamic disorder leads to an increase in the particle mobility. Some relationships of the present model to several experimental systems are discussed.

PACS number(s): 05.40.+j, 05.60.+w

I. INTRODUCTION

Random environments offer the prototype of disorder. It is well known that transport properties behave irregularly in such cases, leading to anomalous diffusion, as, for example, for Brownian particles [1]. This topic has been treated from several different points of view, utilizing a variety of different techniques. A detailed presentation of most classic and recent studies and results in the field may be found, e.g., in the review articles of Weiss and Rubin [2], Haus and Kehr [3], Havlin and Ben Avraham [4], and Bouchaud and Georges [5]. Analytical methods include models for the transition probabilities [2–8] leading to known but highly complicated differential equations, which can be solved under certain assumptions, e.g., the effective-medium approximation (EMA) [9,10], renormalization-group analysis [11], etc. Additionally, computer simulation models for disordered systems also abound, as, for example, the percolation model [4,12] (a binary system of open and closed sites), and other fractal structures. Of particular interest is the addition of a local drift force (bias of motion), see, e.g., the one-dimensional treatment of Lehr, Machta, and Nelson [13], as there is a large number of related applications.

A naive but common method to introduce randomness is to build up a random environment of site (or bond) energies. One can view this either as a lattice of random barriers or random wells [3,4]. The two models, even though at first sight may seem identical, are amenable to different treatments. Moreover, randomness may be viewed as being imposed by either "dynamic" or "static" disorder. In the first case the renewal of the barriers

occurs upon each jump of the tracer because the local environment is formed by particles that are identical with the hopping one and performing the same kind of motion. Evidently, this case is more appropriate for describing self-diffusion. In the static case one deals with a frozen lattice of random barriers and a tracer atom moves without changing them. This model has been treated extensively in the literature, see [3], and it is believed to describe diffusion of foreign particles, conductivity, etc. In both cases the fundamental questions concern the influence of disorder on the onset of typical diffusive behavior of the mean-square displacement (MSD) $\langle R^2 \rangle \sim Dt$, as well as the determination of the diffusion constant D for varying degree of disorder. In a previous work [15], we determined analytically the impact of dynamic disorder on D under the tacit assumption that $\langle R^2 \rangle \sim Dt$ holds for the long-time limit and an effective diffusion coefficient D_{eff} may be derived, provided a probability distribution of the barrier heights is adopted explicitly. In the case of static disorder we treated the D_{eff} in terms of a percolation problem [15] whereby a tracer was considered as effectively avoiding any barrier which is higher than some critical one E_p, and we related E_p to the dispersity σ of the probability distribution. The purpose of the present investigation is to assess the validity of the analytical treatments [15] by means of computer simulation. Experimental studies of diffusion and self-diffusion in disordered systems derive as a rule some effective activation energy of the process E_{eff}. Our numeric investigations demonstrate the dependence of E_{eff} on temperature T and degree of disorder σ. Our results show that for dynamic disorder one indeed observes a non-Arrhenius behavior of D_{eff} with T. For static dis-

order we demonstrate that E_{eff} is determined by some effective percolation barrier E_p.

The effective activation energy of the process E_{eff} should be determined on the ground of some averaging procedure and reflect either the mean jump frequency $\langle v \rangle$ [15] or the mean stay time $\langle \tau \rangle$ [8,9,14] of the moving particle. In general, $\langle v \rangle$ is determined by the jump probability p_i distribution function that the moving particle will overcome barrier E_i, $\langle v \rangle = \sum_i v_i p_i$, while $\langle \tau \rangle = \sum_i \tau_i p_i$. Evidently, in view of $v = \tau^{-1}$, one has $\langle v \rangle \neq \langle \tau \rangle^{-1}$, except for the case when p_i is given by a δ function. The decision which type of averaging is the proper one must be made with respect to the nature of the processes involved. Thus it is well known, that in parallel chemical reactions the overall rate is determined by the fastest process, whereas for chain reactions proceeding successively the slowest is the governing one. In the case of tracer diffusion a different mechanism may hold at different lattice dimensionalities. Since random walks in one-dimensional (1D) lattices (as well as in systems with hierarchy constraints) may be considered as a process of successive events whereby barriers cannot be surrounded or bypassed, it is to be expected that $\langle \tau \rangle$ is the relevant quantity. However, in lattices with dimension $d \geq 2$, $\langle v \rangle$ controls the effective rate, as higher barriers are usually avoided. In a Monte Carlo simulation one obtains averaged quantities without a priori assumption on the relevance of $\langle v \rangle$ or $\langle \tau \rangle$. Anticipating, we should point out that the results of our numeric experiments unambiguously confirm that the analytically determined $\langle v \rangle$ coincides with the mean jump frequency observed in the course of the simulation, so that the mean stay time is given by $\langle v \rangle^{-1}$ instead of $\langle v^{-1} \rangle$.

II. MODEL

In the present investigation the random barriers define transition probabilities which are governed by Boltzmann statistics in a standard fashion. We impose the restriction that jumps that are made between two specific sites carry exactly the same probability at any time during the calculation. For example, once a forward jump is made in a particular direction, then the backward jump (back to original position) should carry the same probability as the forward jump. For that reason we use a model where the barrier (bond) energies are defined by use of the equation

$$E_{ij} = 0.5 - \sigma(x - 0.5) . \tag{1}$$

Here x is a random number between 0 and 1 from a uniform distribution, and σ is a dispersion parameter ranging also in the interval 0 to 1 that controls the width of the range of the energy values. When $\sigma = 1$, we have the maximum width of energies in the range 0 to 1, and as σ decreases then the energy range correspondingly becomes narrower down to a single value $E = 0.5$. If a directional bias is introduced Eq. (1) becomes

$$E_{ij} = 0.5 - \sigma(x - 0.5) - \varepsilon , \tag{2}$$

where ε is the strength of the bias. In the present paper

$\varepsilon = 0$, as the case with the bias will be treated elsewhere. The jump probabilities P_{ij} from site i to site j are simply the Boltzmann exponentials, i.e.,

$$P_{ij} = (1/z)e^{-E_{ij}/kT} . \tag{3}$$

Here z is the coordination number. The temperature T (in arbitrary units) is a controlling parameter that is to be carefully investigated here. After all P's are summed up, the difference from 1 becomes the probability P_{ii}:

$$P_{ii} = 1 - \sum_{j (\neq i)} P_{ij} , \tag{4}$$

which is the probability for the particles to remain on the same site.

III. METHODS OF CALCULATIONS

Calculations are performed on 2D square lattices (four neighbors), and on 3D simple cubic lattice (six neighbors). Longer-range interactions are neglected. As described above we discern two cases of lattice disorder: (a) the case for which all bond energies are assigned at time $t = 0$, and stay frozen for the duration of the calculation, and (b) the case of dynamic disorder for which there is no memory of the energies, which are randomized at each time step. The latter is computationally simpler, as it requires no lattice at all. It is also free of any finite-size effects, and one can safely go to a very high number of steps. For the first case, we typically build lattices of size 600×600, and $100 \times 100 \times 100$, with cyclic boundary conditions. However, we limit our investigation to times for which the hopping particle basically does not reach the boundary. The particle is placed in the middle of the lattice at time $t = 0$. We use the so-called lattice-growth technique. This means that only the bonds of the lattice that are to be visited by the particle will be given energy values, while the rest are not used at all. Thus, initially the four (or six) neighbor sites are assigned random energies according to Eq. (2), and by drawing on a random number it is decided what step will be taken. Once these bond energies are decided they stay the same (frozen) for the entire calculation. In subsequent steps first it is inquired if the four neighbors have been earlier defined or not. If they have been defined their values are directly used. If not, they are assigned energy values at that time, just like the original bonds. We keep track of the particle coordinates as a function of time, from which the mean-square displacement is calculated. For case (b), as stated above, no lattice is generated. At every time step four (or six) energies are calculated on the basis of the same equation (2), then the four (or six) probabilities are calculated, and the direction of motion is decided by drawing on a random number. The only parameter that is monitored here is the number of displacements in each direction as a function of time. Eventually the mean-square displacement is again calculated. The average values of the data are calculated from a large number of realizations. Depending on inherent noise present the numbers of realizations utilized vary from 1000 to 10 000 different ones.

IV. RESULTS

Figure 1 describes the behavior of the mean-square dispacement $\langle R^2 \rangle$ as a function of time at different temperatures for the case of static disorder, case (a) above. We present data for the range 10 to 10^7 steps. We observe that for all temperatures there is always an early time regime which differs from the diffusive regime $\langle R^2 \rangle \sim Dt$, i.e., at each temperature there is a particular crossover time τ_c. This is in agreement with earlier analytic (EMA) and numeric results [3]. In Fig. 1 we observe that for long times the log-log plot gives a linear relationship. The slope of the line is 1, which is the expected value, i.e., $\langle R^2 \rangle \sim Dt$. As the temperature decreases, linearity is achieved at longer and longer times τ_c. For this reason high T calculations are carried to 10^5 steps, while low T calculations are carried to 10^7 steps. For $T = 0.05$ this diffusive regime sets on after one million steps. Figure 2 shows the data for calculations for 3D lattices, with the same model and algorithm as the 2D one. We observe similar behavior in all respects.

Our interpretation of the observed (temperature-dependent) crossover time τ_c is the following. As the particle starts at some random position, it is most probable that it is localized at some relatively low-energy valley at which it is to be found. Thus, at early times and low temperatures the particle is "trapped" in some limited region of the lattice and cannot escape as the temperature is low and all jumps are consumed to visit the same sites over and over again. The probability for escaping from this position is very small, but after a given time τ_c this probability is realized. It is expected that the crossover time is

$$\tau_c = e^{E_{\mathrm{eff}}/T} , \qquad (5)$$

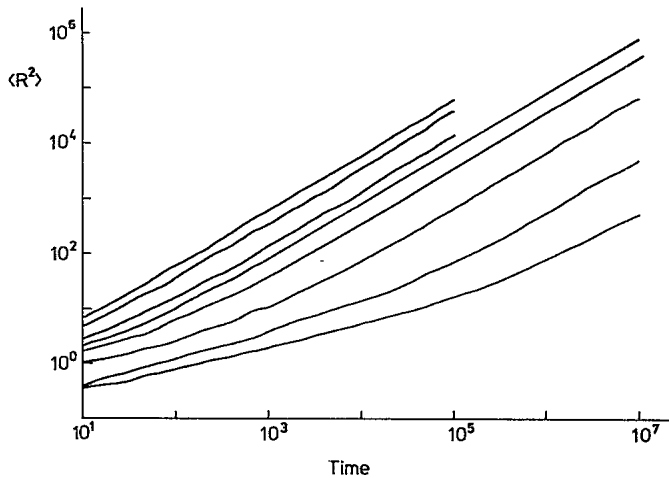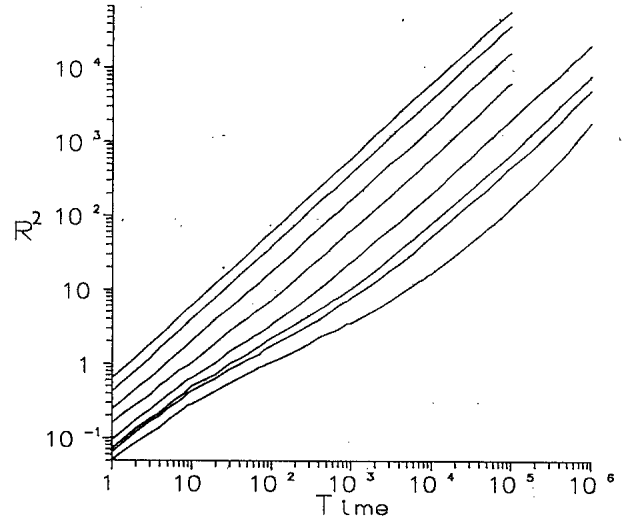

FIG. 2. Mean-square displacement $\langle R^2 \rangle$ as a function of time (number of steps) for several different temperatures for the case of frozen 3D lattices [case (a)], in log-log form. The temperatures are: 1.0, 0.50, 0.25, 0.15, 0.10, 0.075, 0.0667, and 0.05 (top to bottom). The dispersion $\sigma = 1.00$. We used 1000 realizations.

where E_{eff} is some effective activation energy. We can estimate the crossover time τ_c for each temperature, when the phenomenon takes place by plotting in Fig. 3 this crossover time τ_c versus $1/T$ lin-log fashion, for the 2D

FIG. 1. Mean-square displacement $\langle R^2 \rangle$, as a function of time (number of steps) for several different temperatures for the case of frozen 2D lattices [case (a)], in log-log form. The temperatures are: 1.0, 0.50, 0.25, 0.20, 0.15, 0.10, 0.067, and 0.05 (top to bottom). The dispersion $\sigma = 1.00$. For $T = 0.067$ and $T = 0.05$ we used 3000 realizations; for all the rest we used 1000 realizations. This was done because there is inherently more noise for the low-T cases.
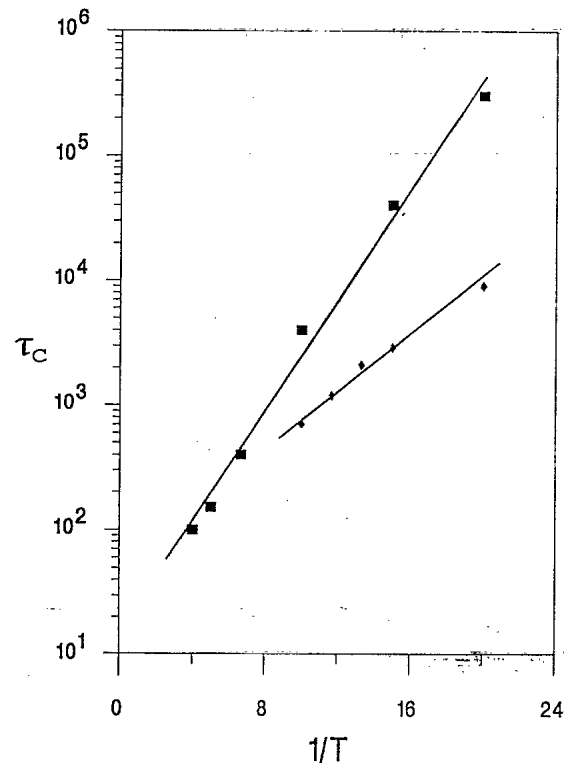

FIG. 3. Plot of the crossover time (the time after which $\langle R^2 \rangle$ is linear), τ_c, as a function of $1/T$, for the temperatures investigated in Fig. 1 (squares) and in Fig. 2 (diamonds). The straight lines are the best fits that give the slopes (see text).

and 3D lattices. We observe for both cases an almost linear relationship. The scattering in the points may well be due to the uncertainties of the exact position of the crossover points. The slope of the line is $E_{\text{eff}}=0.51\pm0.05$ (2D), and $E_{\text{eff}}=0.25\pm0.05$ (3D). According to the conventional chain-reaction theory the reactions with the slowest rate ("bottlenecks") determine the total rate of the process. Reactions that might be bypassed faster do not contribute to the overall rate of the process. The activation barriers which are higher than a given critical value $(E>E_p)$ are practically bypassed. All channels with $E \leq E_p$ will be considered as open, as the hopping particle moves consistently only along these channels. According to the classical chain-reaction theory, the effective activation energy E_{eff} would practically coincide with the upper limit E_p. Clearly this picture will be valid only if the concentration of conducting channels exceeds the percolation threshold p_c. Thus E_p may be viewed as the energy barrier determined in such a way that the concentration of channels with barrier $E \leq E_p$ is p_c. As shown in [15] E_p is determined by

$$\int_0^{E_p} P(E)dE = p_c , \tag{6}$$

where $P(E)$ is the energy barrier probability distribution function while the threshold concentration of the "low enough" barriers p_c depends both on the number of directions available for motion z and on the space dimension d. For $d=2$ $(z=4)$ $p_c=0.5$ (bond percolation) and for $d=3$ $(z=6)$ $p_c=0.25$. Taking into account that $P(E)=1/\sigma$ and that $\sigma=1$ it follows that good estimates for the E_p values are the following: $E_p=0.5$ (2D), and $E_p=0.25$ (3D).

Figure 4 contains the same data for case (b) in linear axes for 2D lattices. Here the situation is simpler as the plot in lin-lin form shows that all lines start at the origin, and are straight throughout time with specific slopes.

FIG. 5. Direct comparison between the frozen and the randomizing lattices for two different dispersions $\sigma=1.0$ and $\sigma=0.5$. Same axes as in Fig. 1, but in linear form. Here the temperature $T=0.15$. The top two lines are for the randomizing lattices, the bottom two for the frozen lattices. In each group the $\sigma=1.0$ line is higher than the $\sigma=0.5$ line.

The slopes decrease with decreasing temperature, as expected. This is because the energy barriers generate an average environment, which can be overcome rather easily at high T but with difficulty at lower T. No low-energy valleys are generated here, as all energies are constantly randomized. Thus, temperature here is directly a measure of the efficiency of transport. The log-log plot (not shown here) gives a series of parallel straight lines for $\langle R^2 \rangle \geq 1$.

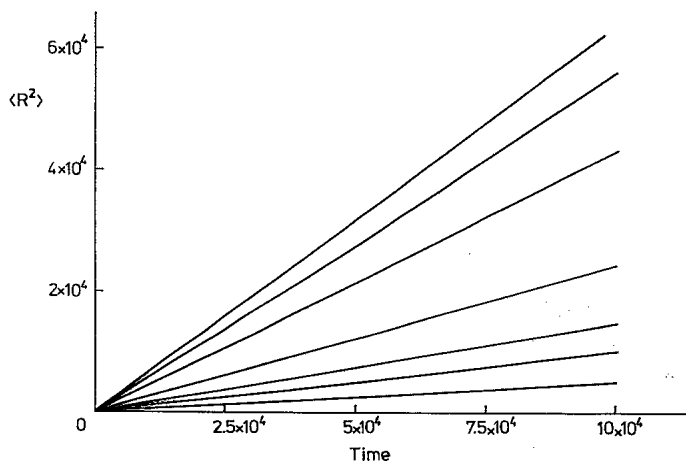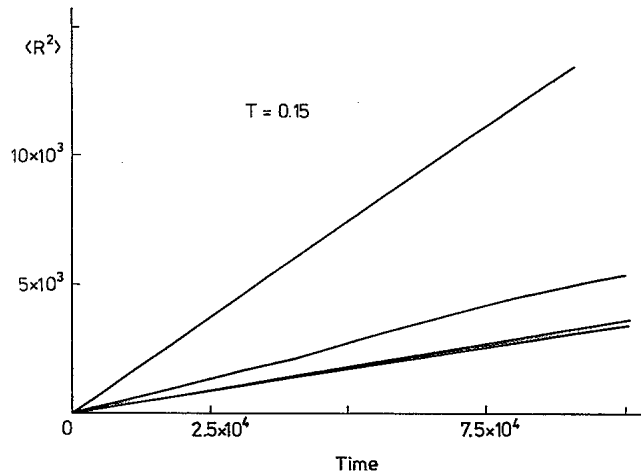Figure 5 shows the effect of the dispersion σ on the

FIG. 4. Mean-square displacement $\langle R^2 \rangle$ as a function of time (number of steps) for several different temperatures for the case of constantly randomizing lattices [case (b)]. The temperatures are $T=1.0$, 0.75, 0.50, 0.25, 0.15, 0.10, and 0.05 (top to bottom). The dispersion $\sigma=1.00$. The results are averages of 10 000 realizations
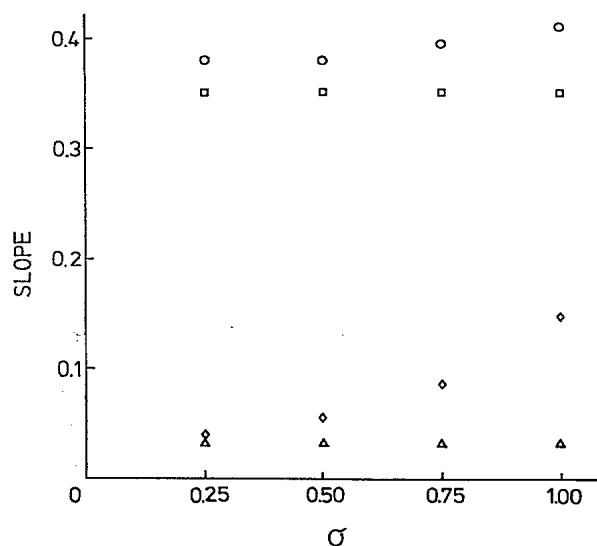

FIG. 6. Slopes of data similar to that of Fig. 5 as a function of the dispersion, both for frozen and randomizing lattices, for two different temperatures $T=0.50$ and 0.15. Frozen lattices: squares, $T=0.50$; triangles, $T=0.15$. Randomizing lattices: circles, $T=0.50$; diamonds, $T=0.15$.
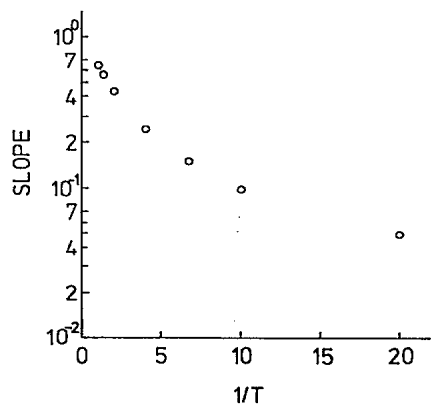
FIG. 7. Slopes of the lines of Fig. 4 vs $1/T$ in a semilogarithmic plot.

mean-square displacement. We observe that for static disorder dispersions of $\sigma = 1$ and 0.5 produce almost identical results in agreement with EMA predictions [3]. For dynamic disorder the impact of σ is stronger and as the dispersion is lowered so is the $\langle R^2 \rangle$. The complete picture is given in Fig. 6 by plotting the slopes of the lines in the previous figure as a function of σ for two different temperatures. Note that the increase of T decreases the impact of σ on $\langle R^2 \rangle$ since the barrier differences are effectively "smeared out". Finally, Fig. 7 gives the behavior of the mean-square displacement (case b) as a function of $1/T$ in lin-log form. Evidently the mobility reveals a non-Arrhenius behavior, as is frequently observed experimentally in typical glass-forming melts and predicted analytically in [15,17].

V. DISCUSSION AND CONCLUSIONS

The present investigation demonstrates that there is a significant difference in the impact of the degree of disorder on the mobility of the particle in media with static and with dynamic energy barrier distribution. This becomes more pronounced when temperature is decreased. One may derive a mean jump frequency as the ratio of the number of successful versus the number of attempted jumps. The Monte Carlo results reveal that this quantity coincides with $\langle v \rangle$, as calculated for the same probability distribution function and assumed in our analytical treatment in [15,17]. The movement of a particle in a "dynamically" disordered medium when the probabilities are randomized at each time step corresponds to self-diffusion or to viscous flow of amorphous systems. It should be noted that the temperature dependence of viscosity of about forty undercooled melts was described successfully [17] within the framework of this model. The theoretical predictions are well in quantitative agreement with experimental data while viscosity varies by more than ten orders of magnitude.

In the case of static disorder we observe characteristic T-dependent crossover times τ_c to the long-time diffusive regime $\langle R^2 \rangle \sim t$ which turn out to be determined by an effective energy barrier for percolation E_p, which is in turn given by the critical threshold concentration of bonds, or "easy channels" p_c. The percolation threshold E_p turns out to be independent of σ in 2D for a symmetric probability distribution $P(E)$. Since the diffusion coefficient is determined unambiguously by E_p, D_{eff} does not change with σ either. This situation differs from the result obtained within the site percolation model [18]. If, however, $P(E)$ is not symmetric and has a cutoff at higher energies and a long tail at low energies, then D_{eff} will increase simultaneously with σ (E_p will decrease). Note that this is in agreement with the experimental observations (see for instance the experimental data on resistivity of amorphous and crystalline lithium acetate upon changes of structure and temperature [16]). In this way the present model is able to predict temperature behavior of ionic conductivity in the crystalline (highly ordered) and amorphous state.

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