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Combination of random-barrier and random-trap models

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Abstract. The temperature dependence of the diffusion coefficient of particles is studied on lattices with disorder. A model is investigated with both trap and barrier disorder that was introduced earlier by Y Limoge and J L Bocquet (1990 *Phys. Rev. Lett.* **65** 60) to explain an Arrhenian temperature dependence of the diffusion coefficient in amorphous substances. We have used a generalized effective-medium approximation (EMA) by introducing weighted transition rates as inferred from an exact expression for the diffusion coefficient in one-dimensional disordered chains. Monte Carlo simulations were made to check the validity of the approximations. Approximate Arrhenian behaviour can be achieved in finite temperature intervals in three- and higher-dimensional lattices by adjusting the relative strengths of the barrier and trap disorder. Exact Arrhenian behaviour of the diffusion coefficient can only be obtained in infinite dimensions.

1. Introduction

Many amorphous substances exhibit linear behaviour in an Arrhenius plot of the diffusion coefficient D, or the mobility B of particles, where $\ln(D)$, or $\ln(B)$, is presented as a function of the inverse temperature $\beta = 1/Tk_B$. The observation of an Arrhenian temperature dependence is not easily understandable from the theory of diffusion in disordered crystals. The commonly used models of diffusion of particles in lattices with disordered transition rates predict different behaviour: the random-trap model predicts generally convex (downward) curvature of $\ln(D)$ versus β, independent of the lattice dimension d, while the random-barrier model gives concave (upward) curvature for three- and higher-dimensional lattices. Limoge and Bocquet [1] suggested that the apparent Arrhenius behaviour of $\ln(D)$ versus β might be due to a compensation of the effects of random barriers and random traps. The aim of this paper is the examination of this appealing proposition by analytical and numerical methods.

The analytical arguments given by Limoge and Bocquet [1] in support of a compensation of the effects of random barriers and of random traps are only partially satisfactory. They employed continuous-time random-walk theory and used a decoupling approximation when performing the disorder averaging. This procedure gives correct results for the random-trap model. For the random-barrier model, however, the ensuing results are not correct, as a consequence of the neglect of important backward correlations in the transitions of the particles. The failure of the decoupling approximation for the random-barrier model in comparison to the Monte Carlo results was already discussed in [1].

Recently a new exact result for the diffusion coefficient of particles in one-dimensional disordered chains has been found [2–4]. The expression contains transition rates that are weighted by the equilibrium occupancies of the sites; this is relevant for random-site

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energies, i.e., random traps. The insight obtained from this result can serve as a basis for approximate treatments of models with site and barrier disorder in higher dimensions, as will be shown here in the form of an effective-medium approximation (EMA). Very recently Limoge and Bocquet [5] tried to take the inherent backward correlations of the random-barrier model into account. The differences between their and our results will be discussed below.

In the remainder of this introduction we present qualitative arguments for the different curvatures in the simple models. The downward curvature of $\ln(D)$ versus β for the random-trap model is easily understood: the deepest trap sites with the lowest energies dominate the behaviour at the lowest temperatures. The convex curvature can be deduced formally from the exact expression for the disorder-averaged diffusion coefficient D (see below), which is valid for all dimensions d. The argument for the random-barrier model is more complicated. At the lowest temperatures, where the ratio of the width of the barrier energy distribution and the thermal energy is large, the diffusion coefficient is determined by the highest barrier along a critical path of bond percolation [6]. The path may be constructed by selecting successively bonds with the lowest barriers possible until the 'infinite' cluster in the lattice appears. If the temperature is raised, additional paths contribute to the diffusivity. These paths comprise also higher barriers, and hence the apparent activation energy is increased.

In the following section we describe the derivation of the exact result for D in disordered linear chains from an expression for the mean first-passage time. In section 3 we give an analytical treatment of the combination of independent random barriers and random traps. Section 4 contains the EMA for the combined model for $d \geqslant 3$. In section 5 we present our conclusions from the results.

2. The exact expression for the diffusion coefficient for $d = 1$

Recently an exact expression for the asymptotic diffusion coefficient of single particles on linear chains with disordered transition rates has been derived [2–4]. In [2] a first-passage-time method was used while in [3, 4] the mobility of particles on chains with periodic boundary conditions was derived from the linear response to a driving force. We follow reference [2] for the derivation. The basis is an exact expression for the mean first-passage time of a particle from site 0 to site N on a segment of a disordered chain [7]. Site 0 is regarded as reflecting, while site N is an absorbing site. The expression reads

$$\bar{t}_{0N} = \sum_{k=0}^{N-1} \frac{1}{\Gamma_{k,k+1}} + \sum_{k=0}^{N-2} \frac{1}{\Gamma_{k,k+1}} \sum_{i=k+1}^{N-1} \prod_{j=k+1}^{i} \frac{\Gamma_{j,j-1}}{\Gamma_{j,j+1}}. \tag{1}$$

Here $\Gamma_{i,i+1}$ is the transition rate from site i to site $i+1$, the transitions being restricted to nearest neighbours. Note that (1) gives $\bar{t}_{0N}$ for a particular (quenched) realization of the disordered segment.

We now invoke the condition of detailed balance between two neighbour sites,

$$\rho_i \Gamma_{ij} = \rho_j \Gamma_{ji}. \tag{2}$$

The thermal occupation factors ρ_i are defined by

$$\rho_i = \frac{\exp(-\beta E_i)}{\{\exp(-\beta E_i)\}} \tag{3}$$

where E_i is the energy of site i, counted negative from a common origin. The curly brackets in (3) designate the average over the disordered site energies, for finite segments:

$$\{\exp(-\beta E_i)\} = \frac{1}{N}\sum_{i=1}^{N}\exp(-\beta E_i). \tag{4}$$

The occupation factors are proportional to the thermal equilibrium occupation probabilities of the sites; due to the normalization used they can be larger or smaller than one.

The condition of detailed balance holds in equilibrium, and the occupation factors ρ_i exist for finite segments when all nearest-neighbour transition rates $\Gamma_{ij} \neq 0$. We have to require that unique occupation factors also exist in the limit $N \to \infty$. This requirement excludes certain interesting models, for instance the Sinai model [8], from the further derivations. However, it is fulfilled for the models considered in the next section.

When the condition of detailed balance (2) is introduced into expression (1) a considerable simplification is achieved:

$$\bar{t}_{0N} = \sum_{k=0}^{N-1}\frac{1}{\Gamma_{k,k+1}} + \sum_{k=0}^{N-2}\rho_k\sum_{i=k+1}^{N-1}\frac{1}{\rho_i\Gamma_{i,i+1}}. \tag{5}$$

Taking the disorder average of the equation, we find as the leading term in the limit of long segments, $N \gg 1$,

$$\{\bar{t}_{0N}\} = \frac{1}{2}N^2\left\{\frac{1}{\rho_i\Gamma_{ij}}\right\}. \tag{6}$$

This equation can be interpreted as the inverted relation between time and mean squared displacements of random walks on disordered lattices, $t = (2D)^{-1}\{X^2\}$. We hence deduce the following asymptotic diffusion coefficient from (6):

$$D = \left\{\frac{1}{\rho_i\Gamma_{ij}}\right\}^{-1}. \tag{7}$$

Under the assumption of the existence of unique occupation factors one can also derive, for large N, using again detailed balance

$$\{\bar{t}_{0N}^2\} - \{\bar{t}_{0N}\}^2 \propto N^3. \tag{8}$$

Since $\{\bar{t}_{0N}\}^2 \sim N^4$, the relative dispersion of the disorder average of the mean first-passage times vanishes as $N^{-1/2}$ for long segments. One can say that $\{\bar{t}_{0N}\}$ becomes 'sharp' in the asymptotic limit of large N. In this way the use of the inverted relation (6) to deduce the diffusion coefficient can be justified.

The physical significance of the result (7) is that the diffusion coefficient follows from thermally weighted transition rates. A numerical verification of (7) for the Miller–Abrahams model [9] for $d = 1$ has been given in reference [10].

3. Combination of random barriers and random traps: analytical results

3.1. The model and exact result for $d = 1$

We now investigate a model for hopping diffusion of particles in lattices with combinations of random barriers and random traps. The random-barrier (RB) model is defined with symmetric transition rates Γ_{ij} between neighbour sites, $\Gamma_{ij} = \Gamma_{ji}$. An Arrhenius form for the transition rates is assumed:

$$\Gamma_{ij} = \Gamma_0\exp(-\beta E_{ij}). \tag{9}$$

The energetic barrier E_{ij} between sites i and j is a random variable and it is taken from a common distribution $\nu_B(E)$. To avoid problems with negative barriers we restrict the range of the barrier energies to $E \geqslant 0$. The random-trap (RT) model is defined by rates Γ_i that originate from the sites i and are independent of the final sites. Also here the Arrhenius form is assumed:

$$\Gamma_i = \Gamma_0 \exp(\beta E_i) \tag{10}$$

where E_i is the energy of site i. The site energies will be counted negative and the range be restricted to $E \leqslant 0$. Again the individual site energies are selected from a common distribution $\nu_T(E)$.

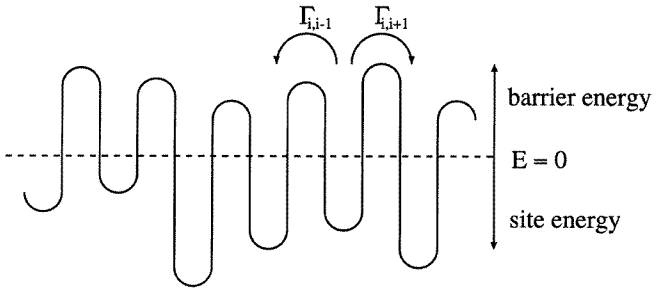

Figure 1. A schematic representation of the combination of random barriers and random traps.

We introduce a combination of the RT and RB models by specifying the transition rates between two neighbour sites as

$$\Gamma_{ij} = \Gamma_0 \exp[-\beta(E_{ij} - E_i)]. \tag{11}$$

The energy E_{ij} with two site indices refers to the barrier $i \to j$ while the energy E_i with one index refers to the site i. (To distinguish between barrier and site energies, we sometimes keep dummy site indices.) A pictorial representation of the model is given in figure 1. Note that the model is different from the Miller–Abrahams model [9] where the site energy of the terminal site j appears explicitly.

The occupation factors ρ_i are required in the weighted transition rates that appear in (7); they are given in (3). The weighted transition rates are then

$$\rho_i \Gamma_{ij} = \frac{\Gamma_0 \exp(-\beta E_{ij})}{\{\exp(-\beta E_i)\}}. \tag{12}$$

The numerator contains only barrier energies while the site energies only appear in the denominator, which can be evaluated directly. An immediate consequence of (12) is the expression for the diffusion coefficient of the RT model:

$$D_{RT} = \Gamma_0 \{\exp(-\beta E_i)\}^{-1} \tag{13}$$

when barrier disorder is absent. Equation (13) follows from (7) for $d = 1$; it is valid for all dimensions [11]. Another consequence of equation (13) is that the derivative of $\ln(D_{RT})$ with respect to the inverse temperature β is given by the mean thermal energy. Since the mean thermal energy can only decrease with decreasing temperature, the slope of $\ln[D_{RT}(\beta)]$ is decreasing with increasing β.

An exact result is obtained from (7) for the diffusion coefficient of the combined RB and RT model for $d = 1$:

$$D_{comb} = \Gamma_0 \{\exp(-\beta E_i)\}^{-1} \{\exp(\beta E_{ij})\}^{-1}. \tag{14}$$

Equation (14) can be cast into another form:

$$D_{comb} = \frac{1}{\Gamma_0} D_{RT} D_{RB}. \tag{15}$$

The diffusion coefficient D_{RT} exhibits generally downward curvature in an Arrhenius plot. Since the average that determines the diffusion coefficient D_{RB} for $d = 1$ has the same form as the one determining D_{RT}, downward curvature is also present in the Arrhenius plot of this coefficient. Also the diffusion coefficient of the combined model has then downward curvature for $d = 1$. In other words, a compensation of the effects of random barriers and random traps is never possible for $d = 1$.

3.2. Results for higher dimensions

The diffusion coefficient of particles in the random-barrier model in simple square lattices is exactly known for symmetric barrier energy distributions $\nu_B(E)$ [12]. For symmetric energy distributions the diffusion coefficient is

$$D_{RB} = \Gamma_0 \exp(-\beta \bar{E}) \tag{16}$$

where $\bar{E}$ is the medium value of the energy distribution. Hence D_{RB} does not show curvature in an Arrhenius plot. Consequently, the diffusion coefficient of the combined model will exhibit downward curvature in simple square lattices.

Approximations are necessary to derive the asymptotic diffusion coefficients in higher-dimensional disordered lattices. It is very plausible that the weighted transition rates (12) should also be used in approximate treatments. The site energy and barrier disorder can be treated independently when they are uncorrelated. Under this assumption, the numerator of equation (12) only contains uncorrelated barrier energies. The EMA gives reasonably accurate results for the RB model when the disorder is not very strong. Hence we will use this approximation to deal with the barrier disorder for $d > 1$. In the EMA, an effective transition rate Γ_{eff} is determined from a self-consistency condition [12, 13]:

$$\left\{ \frac{\Gamma_{eff} - \Gamma}{[(z-2)/2]\Gamma_{eff} + \Gamma} \right\} = 0. \tag{17}$$

The transition rate Γ is a random variable; here it is taken according to equation (12). The rate Γ is symmetric as a consequence of detailed balance; this symmetry is required for the application of equation (17). The curly brackets indicate the disorder average which extends over the barrier disorder. The diffusion coefficient is identical to Γ_{eff} and the lattice constant in the hypercubic lattices that we study is set to unity.

Since the exact result (13) for D_{RT} is contained as a factor in the weighted transition rates, we have in the EMA

$$D_{comb}^{EMA} = \frac{1}{\Gamma_0} D_{RT} D_{RB}^{EMA}. \tag{18}$$

The EMA becomes exact in the limit of coordination number $z \to \infty$, i.e., in infinite-dimensional disordered lattices. We obtain in this limit

$$D_{comb} = \Gamma_0 \{\exp(-\beta E_i)\}^{-1} \{\exp(-\beta E_{ij})\}. \tag{19}$$

The second average is proportional to the average over the rates corresponding to the random barriers. For the RB model and for $d \to \infty$ we have $D_{RB} = \{\Gamma_{RB}\}$, and hence the product form of D_{comb} (15) is also valid for infinite dimensions. We conjecture that (15) is generally valid if the site and barrier energies are uncorrelated. Very recently

Limoge and Bocquet incorporated the backward correlations of the RB model and derived a self-consistency condition for the effective transition rate. However, their self-consistency condition is different from the standard form (17) of the EMA and reproduces neither the exact one-dimensional result (section 3.1) nor the exact two-dimensional result (16).

3.3. The possibility of complete compensation

In this subsection we study the possibility for a complete compensation of the curvatures resulting from the RT and RB models. For this purpose we consider first the case of infinite dimensions, $d \to \infty$. To obtain complete compensation of the curvatures, a special relationship between the site and barrier energy distributions must exist. To determine this relation, we require that the following equation represents simple Arrhenian behaviour of the diffusion coefficient:

$$\Gamma_0\{\exp(-\beta E_i)\}^{-1}\{\exp(-\beta E_{ij})\} = \Gamma_0 \exp(-\beta E_{comb}) \tag{20}$$

with a temperature-independent activation energy $E_{comb} \geqslant 0$.

Let us assume that $\nu_T(E)$ is restricted to the energy interval $[-E_c, 0]$ with E_c a positive quantity. If we identify E_c with E_{comb} we can show by simple manipulations of the left-hand side of equation (20) that it is satisfied when

$$\nu_B(E) = \nu_T(E - E_{comb}). \tag{21}$$

The barrier distribution is then restricted to the interval $[0, E_{comb}]$ and it is simply the trap distribution shifted by E_{comb}. The argument implies that complete compensation, for $d \to \infty$, is only possible for energy distributions that are restricted to a finite interval. Of particular interest are distributions that are symmetric about the midpoint of the interval. Of course it is not necessary that the distributions are not equal to zero throughout the whole interval.

For finite dimensions $1 < d < \infty$ the diffusion coefficient D_{RB} has to be determined using approximations, for instance by the EMA. It is a complicated functional of the energy distribution $\nu_B(E)$ and no general result can be obtained. It seems very implausible that complete compensation can be achieved in general. However, it appears always possible, for dimensions $d \geqslant 3$, to choose the energy distributions $\nu_T(E)$ and $\nu_B(E)$ in such a way that an approximate Arrhenian behaviour is achieved in a restricted temperature interval.

4. Comparison of EMA results and numerical simulations

In this section we present EMA results for the combined model for $d = 3$ and 5 for different forms of the disorder and various temperatures. The results are compared with Monte Carlo simulations of the diffusion coefficient by measuring the mean square displacement $\{\boldsymbol{r}^2(t)\}$ where the asymptotic diffusion coefficient D is given by

$$\left\{\boldsymbol{r}^2(t)\right\} \to 2dDt. \tag{22}$$

Actually we present the whole proportionality factor $2dD$ as the diffusion coefficient in the figures to make results in different dimensions comparable. Compensatory effects of random barriers and random traps are now discussed.

We first calculate D_{comb}^{EMA} for uniform distributions of energies (for the RB model see [12]):

$$D_{comb}^{EMA} = \frac{\Gamma_0}{d-1}\exp\left(-\frac{1}{2}\beta\sigma_B\right)\left[\sinh\left(\frac{d-1}{2d}\beta\sigma_B\right)\Big/\sinh\left(\frac{1}{2d}\beta\sigma_B\right)\right]$$

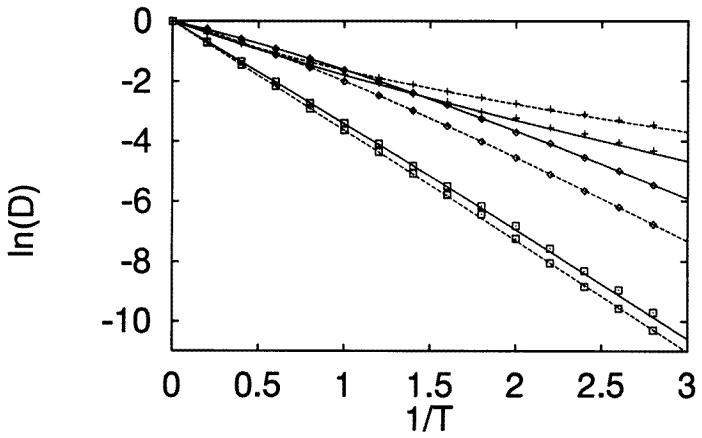

Figure 2. Diffusion coefficients in the RT, RB, and combined model, for uniform distributions of the energies. The parameter Γ_0 is set to unity. The different symbols represent simulation results for the RB (+), RT ($\Diamond$), and the combined model ($\Box$) with $\sigma_T = 3.0, 3.2$ for $d = 3$ (full curves) and $d = 5$ (dashed curves) respectively and $\sigma_B = 4.0$ in both cases. The curves represent the EMA result for $2dD_{comb}$ (23).

$$\times \frac{\beta\sigma_T}{\exp(\beta\sigma_T) - 1} \qquad d \geqslant 2 \tag{23}$$

where

$$\nu(E) = \begin{cases} 1/\sigma_T & -\sigma_T \leqslant E \leqslant 0 \quad \text{(RT)} \\ 1/\sigma_B & 0 \leqslant E \leqslant \sigma_B \quad \text{(RB)} \\ 0 & \text{otherwise.} \end{cases}$$

By comparison with the numerical simulations we find that using

$$\sigma_T \approx \frac{d-1}{d}\sigma_B \tag{24}$$

approximate Arrhenian behaviour is reached. In figure 2 results of Monte Carlo simulations are shown together with the EMA results (23) with parameters chosen according to (24). The upward curvature for the RB model is stronger for $d = 5$ than for $d = 3$ although the width of the distribution is the same. The compensation works in the case of a stronger curvature for the RB and RT models because for larger coordination numbers compensation becomes generally easier. The effect of the coordination number on the possibility of compensation of barrier and site energy disorder was already noted in [1].

We consider as a second energy distribution the Gaussian distribution

$$\nu(E) = \frac{1}{0.95\sqrt{2\pi}\sigma} \exp\left(-\frac{(E-\bar{E})^2}{2\sigma^2}\right) \qquad \text{with } E \begin{cases} \leqslant 0 & \sigma = \sigma_T \text{ for RT} \\ \geqslant 0 & \sigma = \sigma_B \text{ for RB.} \end{cases} \tag{25}$$

We have to cut off the tails of one side of the distributions to get only negative (positive) energy values. We decided to cut off 5% of the distributions. Therefore we take $\bar{E}$ according to

$$\bar{E} = -\sigma \operatorname{erf}^{-1}(0.95) \tag{26}$$

where erf( ) is the error function. For this distribution, the self-consistency condition (17) has to be solved numerically. Results are shown in figure 3. For this example the two

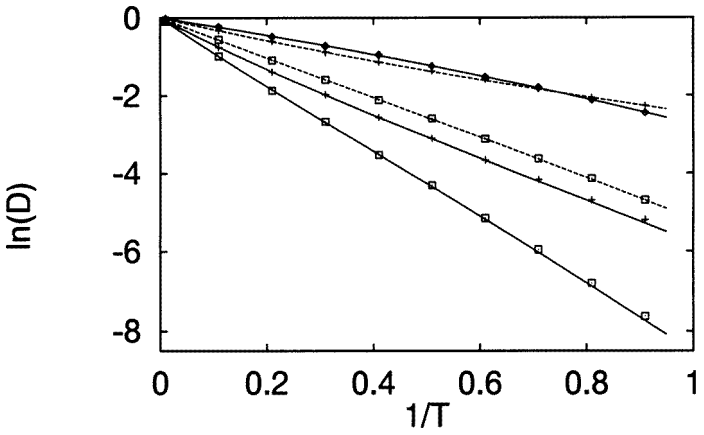

Figure 3. Diffusion coefficients in the RT, RB, and combined model, for the Gaussian distributions of energies. The parameter Γ_0 is set to unity. The different symbols represent simulation results for the RB (+), RT ($\Diamond$), and the combined model ($\Box$) with $\sigma_B = 4.0$, $\bar{E} \approx 6.58$ for $d = 3$ (full curves), $\sigma_B \approx 1.74$, $\bar{E} \approx 2.86$ for $d = 5$ (dashed curves), and $\sigma_T = 1.2$, $\bar{E} \approx -1.97$ in both cases. The curves represent the EMA result for $2dD_{comb}$.

curves for the RT model lie on top of each other because we took the same width for $d = 3$ and 5 and then determined the width of the barrier distribution to get compensation in the combined model. Again the upward curvature of the RB model is stronger for $d = 5$ than for $d = 3$ although we took a smaller width of the barrier distribution for the higher dimension. Nonetheless compensation of the curvature is still possible and the numerical procedure to find the correct parameters of the distribution for the best possible compensation is even more stable for the higher dimension. Though the curves of the combined model in figure 3 look linear, the numerical results show that no perfect compensation is possible.

5. Conclusion

Our theory of the diffusion coefficients of models with combined site energy and barrier disorder was based on weighted transition rates where the thermal site occupancies enter explicitly. Due to the exponential form of the assumed Arrhenius law for the individual transition rates, the contributions from the site energies and the barrier energies factorize. If the site energy and barrier disorder are uncorrelated, the resulting diffusion coefficient factorizes into the random-trap and random-barrier contributions. A consequence is that compensation of the effects of random site energies and random barriers on the curvature in an Arrhenius plot of D_{comb} versus β is not possible for $d = 1$ and $d = 2$. The simple square lattice represents a boundary case.

Partial compensation is possible in a finite temperature interval for three and higher dimensions, if the strength of the disordered site and barrier energies is adjusted properly (stronger disorder in the barriers than in the site energies for finite dimensions $d \geqslant 3$).

In this context we should mention that our conclusions refer to the hypercubic lattices (square, simple cubic, etc). The relevant parameter for the temperature dependence of the diffusion coefficient in the RB model is the coordination number z. Lattices with $z \neq 2d$ were investigated by Limoge and Bocquet [5].

We conclude that partial compensation of the effects of random barriers and random site

energies is possible for $d = 3$, in a finite temperature interval, if two premises are fulfilled:

(i) the assumption of independent site energies and barrier heights; and
(ii) the properly adjusted strength of the disorder.

Point (i) may be somewhat alleviated by including short-range correlations, but point (ii) seems to be generally necessary. We leave the question open of whether the points (i) and (ii) are reasonable descriptions of real amorphous substances.

Instead we point to one serious deficiency of the present theories of diffusion in disordered systems. The present theories are based on regular lattices with the disorder put into the transition rates. Real materials have topologically disordered structures. There exist a range of coordination numbers of the equilibrium sites, and the jump distances vary considerably. The treatment of these effects remains as a task for the future.

Acknowledgments

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