

Energy Transfer as a Random Walk with Long-Range Steps

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We consider the incoherent energy transport in molecular crystals, where the transfer rates stem from Coulombic and exchange interactions. For substitutionally disordered lattices we present in a first passage model the excitation decay due to trapping by randomly distributed traps; the decay is related to the distribution of the number of distinct sites visited during the time t and is expressible through the cumulants of this distribution. The validity domains of approximate decay laws based on the first few cumulants are also discussed. We exemplify the findings for dipolar transfer rates between randomly distributed molecules on a square lattice, by comparing the random walk on the random system to its CTRW (continuous time random walk) counterpart.

KEY WORDS: Energy trapping; cumulant expansion; continuous time random walk; CTRW; random lattices; long-range steps.

1. INTRODUCTION

From the various applications of the theory of random walks in solid-state physics and chemistry we focus in this paper on the incoherent energy transfer in ordered and disordered crystals. Here the excitation trapping by randomly distributed impurities is particularly revealing, since the trapping determines the time dependence of the luminescence and is therefore directly amenable to experimental observation.

A major feature of the microscopic energy transfer mechanisms is that they are due to Coulombic and to exchange interactions; for these the probabilities of steps to molecules which are not nearest neighbors are

Presented at the Symposium on Random Walks, Gaithersburg, MD, June 1982.

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significant. Setting $w(\mathbf{r})$ for the probability of performing a step \mathbf{r} one has

$$w(\mathbf{r}) \propto r^{-s} \quad (1)$$

for multipolar and

$$w(\mathbf{r}) \propto e^{-\gamma r} \quad (2)$$

for exchange interactions.^(1,2) The constants s and γ denote the interaction type and range (e.g., $s = 6$ for dipolar, $s = 10$ for quadrupolar interactions).

Apart from having to account for long-range steps, the study of energy transfer is quite complex due to the microscopic disorder, which depends on the different types of molecules involved and on the geometrical constraints. Here we consider substitutionally disordered crystals. In the special case of a binary crystal, with *two* molecular components (traps and active, i.e., energy transferring, molecules) the energy decay could be viewed as a random walk on a *regular* lattice, followed by trapping. On the other hand already a ternary crystal with *three* components (traps plus active and inert molecules) leads to the problem of random walks on *random* lattices, which is a major theoretical endeavor. We start by considering the *two*-component case.

2. TRAPPING IN BINARY CRYSTALS

In the models considered here the traps are distributed randomly on the regular lattice and they occupy the lattice sites with probability p . We assume that the microscopic rates do not depend on the nature of the site to which a transfer takes place, i.e., whether the site is a trap or not. Furthermore, the excitation is to be quenched instantaneously at the first encounter of a trap.

For a particular realization of the random walk on the perfect (trap-free) lattice, we let R_n denote the number of distinct sites visited in n steps. For the same realization of the walk we let F_n denote the probability (over the ensemble of lattices doped with traps) that trapping has not occurred up to the n th step. The quantities R_n and F_n are stochastic variables related through

$$F_n = (1 - p)^{R_n - 1} \quad (3)$$

where it is assumed that the origin of the walk is not a trap (see the discussion in Ref. 3). The measurable survival probability $\Phi(t)$ at time t is then the average of Eq. (3) with respect to all possible realizations of the random walk in space and time:

$$\Phi(t) \equiv \langle\langle F_n \rangle\rangle = \sum_{n=0}^{\infty} \langle (1 - p)^{R_n - 1} \rangle \phi_n(t) \quad (4)$$

Here $\phi_n(t)$ is the probability of having performed exactly n steps in time t .^(4,5) Under our assumptions for the binary crystal the transfer rates from each active site are $\tau_1^{-1} = \sum_{\mathbf{r}} w(\mathbf{r})$, independent of the particular site considered. This leads to an exponential probability $\Psi(t)$ not to have left the site:

$$\Psi(t) = \exp\left[-t \sum_{\mathbf{r}} w(\mathbf{r})\right] \tag{5}$$

and to an exponential stepping time distribution $\psi(t) = -d\Psi(t)/dt$:

$$\psi(t) = \tau_1^{-1} e^{-t/\tau_1} \tag{6}$$

from which it follows that the $\phi_n(t)$ are Poisson distributed.^(4,5)

By setting $\lambda = -\ln(1 - p)$ the spatial average on the right-hand side of Eq. (4),

$$\Phi_n \equiv \langle F_n \rangle = \langle (1 - p)^{R_n - 1} \rangle = e^\lambda \langle e^{-\lambda R_n} \rangle \tag{7}$$

can be rewritten as a cumulant expansion^(3,5,6):

$$\Phi_n = e^\lambda \exp\left[\sum_{j=1}^{\infty} \kappa_{j,n} (-\lambda)^j / j! \right] \tag{8}$$

Here the $\kappa_{j,n}$ are the cumulants of the distribution of R_n , e.g., $\kappa_{1,n} = \langle R_n \rangle \equiv S_n$ and $\kappa_{2,n} \equiv \langle R_n^2 \rangle - \langle R_n \rangle^2 = \sigma_n^2$, with S_n and σ_n^2 being the mean and the variance.

In general the distribution of R_n is not known in great detail, so that one has to restrict Eq. (8) to the first N cumulants:

$$\Phi_{N,n} \equiv e^\lambda \exp\left[\sum_{j=1}^N \kappa_{j,n} (-\lambda)^j / j! \right] \tag{9}$$

The form with $N = 1$ then leads to the Rosenstock approximation,⁽⁷⁾ $\Phi_{1,n} = \exp[-\lambda(S_n - 1)]$, whereas $N = 2$ gives $\Phi_{2,n} = \Phi_{1,n} \exp(\lambda^2 \sigma_n^2 / 2)$, which is akin to an expression advanced by Weiss.⁽⁸⁾

The advantage of these simpler, approximate forms is that much information about S_n and σ_n^2 may be obtained through analytical methods. We have discussed these aspects for several three-, two-, and one-dimensional lattices in Refs. 3, 6, and 9, where we have also analyzed the effect of long-range steps. In brief, the numerical evaluation of the distribution of R_n and the comparison of the approximate forms, Eq. (9), with the exact decay form, Eq. (8), show that the Rosenstock approximation works fairly well in three dimensions, for low concentrations of traps, and for times which are not too long. The inclusion of the variance leads to forms which are very good in three dimensions, but whose quality gets poorer for lower dimensions: in two dimensions $\Phi_{1,n}$ is not a good approximation if p is not very small, whereas $\Phi_{2,n}$ is in many cases still acceptable. For a linear chain both

forms are inappropriate even for trap concentrations as low as 1% (see Fig. 1 of Ref. 6). In Refs. 3 and 9 we have also used the analytical expressions^(10,11) for S_n and σ_n^2 to check the accuracy of our numerical results and to establish asymptotic formulas which obtain for different transfer laws, as given by Eqs. (1) and (2). The conclusion is that, apart from singular cases like a nearest-neighbor random walk in one dimension,^(4,6) one is still far from determining the decay law Φ_n in closed form for general interactions and lattice structures. Accurate results, however, may be obtained from numerical simulation, which turns out to be an efficient, versatile tool.

3. TRAPPING IN TERNARY CRYSTALS

As mentioned in the Introduction, trapping in systems composed of active and inert molecules involves random walks on random lattices. From the approximating schemes employed to deal with this problem, the continuous time random walk^(10,12,13) (CTRW) is particularly appealing, since it preserves the migration aspect; in a somewhat simplified form⁽¹³⁾ it lets the migration take place on a *regular* lattice, while the randomness of distinct site environments is accounted for through a random distribution of stepping times $\psi(t)$. We thus first consider the trapping law in the CTRW context and present afterwards the numerically simulated decays.

In our substitutionally disordered crystal we let \tilde{p} be the probability that a site is occupied by a molecule to which the energy can be transferred; $1 - \tilde{p}$ is the probability of finding an inert molecule. If the lattice sites are occupied in a random, uncorrelated way by the different molecular species, then the probability of not having left a particular site is

$$\tilde{\Psi}(t) = \exp\left[-t \sum_{\mathbf{r}}' \zeta(\mathbf{r})w(\mathbf{r})\right] \quad (10)$$

where the $\zeta(\mathbf{r})$ are random variables, which take only the values 1 and 0 with probability \tilde{p} and $1 - \tilde{p}$. The configurational average of Eq. (10) is, exactly (see Ref. 14 for other derivations),

$$\begin{aligned} \Psi(t) &\equiv \langle \tilde{\Psi}(t) \rangle_{\{\zeta(\mathbf{r})\}} = \prod_{\mathbf{r}}' \langle \exp[-t\zeta(\mathbf{r})w(\mathbf{r})] \rangle_{\zeta(\mathbf{r})} \\ &= \prod_{\mathbf{r}}' [(1 - \tilde{p}) + \tilde{p}e^{-tw(\mathbf{r})}] \end{aligned} \quad (11)$$

An approximation to this exact form obtains by disregarding the lattice structure, assuming the concentration $\tilde{p}\rho$ of active molecules to be small⁽¹⁴⁾ (continuum approximation):

$$\Psi(t) = \exp\left(-\tilde{p}\rho \int \{1 - \exp[-tw(\mathbf{r})]\} d\mathbf{r}\right) \quad (12)$$

Equation (12) has been used—and derived—frequently in many fields;

typical forms for Eqs. (11) and (12) for particular microscopic interactions and underlying lattices are given in Refs. 14–16, together with an analysis of the validity domains of Eq. (12). For multipolar interactions given by Eq. (1), one obtains⁽¹⁴⁾ from Eq. (12)

$$\Psi_m(t) = \exp(-At^{\Delta/s}) \tag{13}$$

where Δ is the dimensionality of the lattice considered, and A is time independent. For transfer due to exchange one finds⁽¹⁴⁾

$$\Psi_x(t) = \exp[-Bg_{\Delta}(Ct)] \tag{14}$$

where B and C do not depend on time and $g_{\Delta}(x)$ is an analytical function of x , see the appendix of Ref. 14.

Under the assumptions mentioned above, one can use Eqs. (13) and (14) to determine, via $\psi(t) = -d\Psi(t)/dt$, the corresponding stepping-time distribution functions:

$$\psi_m(t) = \frac{A\Delta}{s} t^{(\Delta/s)-1} \exp(-At^{\Delta/s}) \tag{15}$$

and

$$\psi_x(t) = \frac{B\Delta}{t} g_{\Delta-1}(Ct) \exp[-Bg_{\Delta}(Ct)] \tag{16}$$

We remark that the trapping law for the CTRW is again given by Eq. (4); the probabilities $\phi_n(t)$ of having performed in time t exactly n steps being related to $\psi(t)$ through

$$\tilde{\phi}_n(u) = [\tilde{\psi}(u)]^n [1 - \tilde{\psi}(u)] / u \tag{17}$$

where we let $\tilde{f}(u)$ denote the Laplace transform of $f(t)$, $\tilde{f}(u) = \mathcal{L}[f(t)]$. It should, however, be clear that the forms Eqs. (13) to (16) are valid only for low concentrations of active molecules,^(14–16) i.e., in highly *disordered* situations. This runs counter to the CTRW assumption of letting the random walk take place on a *regular* lattice. We tend thus not to put much weight on the *a priori* determination of the model from the physically underlying structure, but to view the CTRW simply as a mathematical tool, to be used for approximating purposes.

The decay law, Eq. (4), may be put in a convenient form by introducing the function $\rho_n(x)$, the probability density of the distribution R_n :

$$\Phi(t) = e^{\lambda} \sum_{n=0}^{\infty} \int dx e^{-\lambda x} \rho_n(x) \phi_n(t) = e^{\lambda} \int dx e^{-\lambda x} \Omega(x; t) \tag{18}$$

Here we set

$$\Omega(x; t) \equiv \sum_{n=0}^{\infty} \rho_n(x) \phi_n(t) \tag{19}$$

and $\Omega(x; t)$ gives now the probability for having visited exactly x distinct sites during the time t . We remark that the right-hand side of Eq. (18) is very general. Using the cumulants $Y_j(t)$ of the distribution $\Omega(x; t)$ we express the decay law as

$$\Phi(t) = e^\lambda \exp \left[\sum_{j=1}^{\infty} \frac{(-\lambda)^j}{j!} Y_j(t) \right] \quad (20)$$

Evidently, Eq. (8) is the special case of Eq. (20) for a constant stepping frequency. In the following we use Eqs. (18) and (20) to analyze the energy decay laws both for the CTRW model and for the direct simulation of random walks on random lattices.

4. NUMERICAL RESULTS

According to Eqs. (18) and (20), the knowledge of the distribution $\Omega(x; t)$ completely determines the decay law $\Phi(t)$ for the first passage model. Therefore, we determine through numerical simulation $\Omega(x; t)$ and calculate from it both the exact decay law, Eq. (18), and approximate forms, obtained by restricting the sum in Eq. (20) to the first N terms:

$$\Phi_N(t) = e^\lambda \exp \left[\sum_{j=1}^N \frac{(-\lambda)^j}{j!} Y_j(t) \right] \quad (21)$$

Since we have already presented in Refs. 3, 6, and 17 the decay laws which obtain for walks with fixed stepping frequency on regular lattices, we focus here on the CTRW model and on random lattices. For reasons of comparison we take in both cases the same underlying lattice, a square lattice, and the same, dipolar, interaction. Other cases will be considered elsewhere.⁽⁵⁾

For the CTRW model the stepping time distribution $\psi(t)$ is taken to be given by Eq. (15), with $\Delta = 2$ and $s = 6$; in the CTRW-spirit the displacements of the walk are nearest-neighbor steps on the regular lattice. We simulated 2000 walks, by determining the step directions as well as the stepping times through a random number generator (RN1 of the ETH-Rechenzentrum). The time is parametrized in units of the average stepping time

$$\tau_1 \equiv \int_0^{\infty} \Psi(t) dt$$

The decay laws for the (relatively high) trap concentrations $p = 0.1$ and $p = 0.5$ are plotted in Fig. 1, together with their approximate forms $\Phi_1(t)$ and $\Phi_2(t)$. Evidently, here none of the two forms is even qualitatively correct. We emphasize, however, that for $p \leq 0.01$, $\Phi_2(t)$ turns out to be a

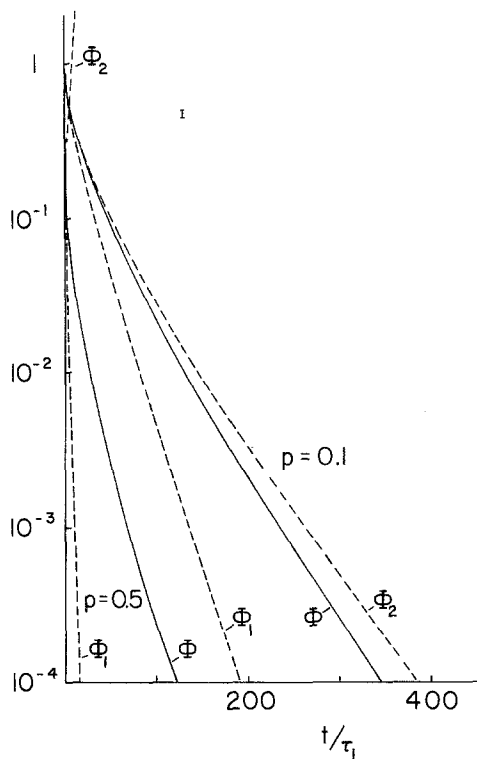


Fig. 1. Decay law due to trapping for a CTRW on a square lattice for the dipolar stepping time density, Eq. (15), with $s = 6$, $\Delta = 2$. The full line Φ denotes the exact decay whereas Φ_N are approximate forms, Eq. (21). The probabilities that a site is a trap are $p = 0.1$ and $p = 0.5$. The vertical bar marks the standard deviation between simulated and smoothed results.

very good approximation⁽⁵⁾ for the decay range $1 \leq \Phi(t) \leq 10^{-4}$ plotted. The exact decay $\Phi(t)$ is nonexponential, mainly due to the wide x distribution of the $\Omega(x; t)$ values, compared to which the effect of the nonlinearity of $S(t)$ with t is almost insignificant.

The random lattice considered was constructed by placing molecules on a square lattice, with a probability $\tilde{p} = 0.1$ for having a site occupied by an active molecule. We started from a 114×114 grid, so that we had 1300 active molecules inside this unit, which was then periodically repeated. The cutoff of the dipolar interaction was chosen so that each molecule could transfer its energy to typically 400 neighboring molecules. On this system 350 walks were performed. The results for $\Phi(t)$, $\Phi_1(t)$, and $\Phi_2(t)$ are plotted in Fig. 2, for trap concentrations of $p = 0.01$ and $p = 0.05$, i.e., $p/\tilde{p} = 0.1$ and 0.5 ; this should parallel the CTRW model of Fig. 1. As is evident, the

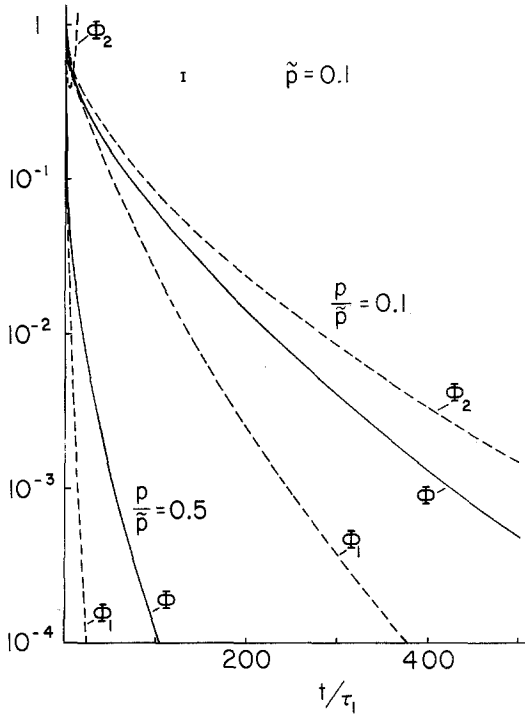


Fig. 2. Decay law due to trapping for random walks on a random lattice (built on a square lattice with occupancy $\tilde{p} = 0.1$). The relative probabilities that an active site is a trap are $p/\tilde{p} = 0.1$ and $p/\tilde{p} = 0.5$. The steps follow the dipolar interactions. The symbols are as in Fig. 1.

qualitative behavior of the decay laws is similar, and the approximations fail in the same way. Quantitatively, however, the decay laws do not agree: They cannot be even brought into agreement by a change in the mean stepping time τ_1 , since for $p = 0.5$ the CTRW decay law lies above its corresponding one for the random lattice, whereas for $p = 0.1$ the situation is just the opposite. A detailed analysis indicates that both shortcomings may be traced to the behavior of the stepping time distribution $\psi(t)$, Eq. (15). Furthermore, we note that, compared to the more pathological forms in use for exchange interactions, the $\psi(t)$ for the dipolar case is extremely well behaved. All this supports our viewing the CTRW approach as an approximate, qualitative tool.

To summarize our findings, we have shown that numerical analyses supplement nicely the analytical results in the theory of random walks since numerically one obtains the complete distribution of distinct sites visited.

This method is particularly adequate in complex cases like CTRW and for random walks on random lattices. For the first-passage decay model cumulant expressions represent a canonical expansion in terms of the distribution of distinct sites visited.

ACKNOWLEDGMENTS

We thank Professor K. Dressler, Dr. K. Allinger, and Mr. W. Toller for helpful discussions and technical assistance. We acknowledge a grant of computer time from the Computer Center of the ETH Zürich and the support of the Deutsche Forschungsgemeinschaft.

REFERENCES

1. T. Förster, *Z. Naturforsch.* **4a**:321 (1949).
2. D. L. Dexter, *J. Chem. Phys.* **21**:836 (1953).
3. G. Zumofen and A. Blumen, *J. Chem. Phys.* **76**:3713 (1982).
4. G. H. Weiss and R. J. Rubin, *Random Walks: Theory and Selected Applications*, Vol. 52, p. 363 (1982).
5. A. Blumen and G. Zumofen, *J. Chem. Phys.* **77**:5127 (1982).
6. G. Zumofen and A. Blumen, *Chem. Phys. Lett.* **88**:63 (1982).
7. H. B. Rosenstock, *Phys. Rev.* **187**:1166 (1969); *SIAM J. Appl. Math.* **27**:457 (1974).
8. G. H. Weiss, *Proc. Natl. Acad. Sci. US* **77**:4391 (1980).
9. A. Blumen and G. Zumofen, *J. Chem. Phys.* **75**:892 (1981).
10. E. W. Montroll and G. H. Weiss, *J. Math. Phys.* **6**:167 (1965).
11. N. C. Jain and W. E. Pruitt, *Proceedings of the Sixth Berkeley Symposium on Mathematical Statistics and Probability* (Univ. California, Berkeley, 1973), Vol. III, p. 31.
12. H. Scher and M. Lax, *Phys. Rev. B* **7**:4491, 4502 (1973).
13. H. Scher and E. W. Montroll, *Phys. Rev. B* **12**:2455 (1975).
14. A. Blumen and J. Manz, *J. Chem. Phys.* **71**:4694 (1979).
15. A. Blumen, *J. Chem. Phys.* **72**:2632 (1980).
16. A. Blumen, *Nuovo Cimento* **63B**:50 (1981).
17. A. Blumen and G. Zumofen, *J. Lumin.* **24/25**:781 (1981).