Time decay of excitations at quasi-one-dimensional trapping

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The survival probability of a particle that performs a quasi-one-dimensional random walk on a lattice with randomly distributed traps is considered. The derivations are based on the approximation of weak transitions between one-dimensional chains where detailed results on the survival probability are available, neglecting returns to the same chain. It is shown that calculated curves of the survival probability coincide rather well with data of Monte Carlo simulation at times $t \sim 1/\delta_2$, where δ_2 is the degree of quasi-one-dimensionality.

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I. INTRODUCTION

The problem of random walks of electronic excitations in low-dimensional systems with randomly distributed traps is rather actual. There are a number of theoretical papers studying the migration and trapping of excitations in one-dimensional (1D) systems [1–8], and far less in quasi-one-dimensional (Q1D) objects [9]. Wieting, Fayer, and Dlott [9] studied in detail the time dependence of the mean number of new sites visited by a walker in the case of Q1D energy migration in two- and three-dimensional topology. However, their expression for the trapping rate and survival probability is based on the Rosenstock approximation [10], which is rather rough at long times in 1D and Q1D systems.

At the same time in a number of experimental papers the energy migration and trapping are studied by time-resolved luminescence spectroscopy in Q1D crystals (antiferromagnetic [11–15] and molecular [16,17]). These investigations have shown that even the insignificant probability of an excitation off-chain hop results in essential changes in the luminescence decay curves. In all likelihood, while studying the energy migration in multichain biopolymers [18], the Q1D character of transport should be taken into account.

The present paper is concerned with a simple model describing the decay law of survival probability due to Q1D random walks on a lattice with randomly distributed traps. This approach is based on the exact [2,8] or approximated [5,10] solutions for the survival probability at strictly 1D random walks at high and low trap concentrations, respectively. In spite of some simplifications, the calculated survival probability at times corresponding to the time of an off-chain hop is in good agreement with the results of Monte Carlo (MC) simulations.

II. THE DECAY OF SURVIVAL PROBABILITY

Consider the following problem: a walker performs Q1D random walks in three-dimensional topology on the periodic lattice with randomly distributed quenched traps. When a walker hops to a trap site, it is captured instantaneously (efficient trapping). The discrete time and nearest-neighbor transitions are considered. At each step with relative probabilities W_{on}, $W_{\mathrm{off}\,1}$, $W_{\mathrm{off}\,2}$ a walker is able to transit to one of six neighbor sites. These probabilities are determined as

$$\text{on chain (1D direction)}\quad W_{\mathrm{on}}=\frac{F_{\mathrm{on}}}{F_{\mathrm{tot}}}\,,$$
$$\text{off chain}\begin{cases} W_{\mathrm{off}\,1}=\dfrac{F_{\mathrm{off}\,1}}{F_{\mathrm{tot}}}\,,\\[2ex] W_{\mathrm{off}\,2}=\dfrac{F_{\mathrm{off}\,2}}{F_{\mathrm{tot}}}\,,\end{cases} \tag{1}$$
$$F_{\mathrm{tot}}=F_{\mathrm{on}}+F_{\mathrm{off}\,1}+F_{\mathrm{off}\,2}\,,$$

where F_{on} and $F_{\mathrm{off}\,1}$, $F_{\mathrm{off}\,1}$ are hopping rates on the chain and off chain, respectively. It follows from the quasi-one-dimensionality condition that $F_{\mathrm{off}\,1}$, $F_{\mathrm{off}\,2} \ll F_{\mathrm{on}}$. For the sake of simplicity we assume $W_{\mathrm{off}\,1}=W_{\mathrm{off}\,2}=W_{\mathrm{off}}$ and indicate $W_{\mathrm{on}}=\delta_1$, $2W_{\mathrm{off}}=\delta_2$, then $\delta_1+\delta_2=1$.

Let $S(n)$ be the number of new sites visited by a walker in n steps. Then the survival probability (the probability that a walker will be not trapped) is

$$f(n)=p^{S(n)}\,, \tag{2}$$

where $p=1-C$ and C is the trap concentration. Further, consider Q1D random walks for a certain motion route (or configuration). It is assumed that at the $l_1+1, l_2+1, \ldots, l_k+1$ step a walker makes an off-chain hop ($l_k<n$). Thus, after n steps, a walker makes k off-chain hops. If we assume that after leaving the given chain a walker never hops back again, then the mean survival probability for the given configuration is

$$\langle f(n)\rangle=p^k\langle p^{S(l_1)}\rangle\langle p^{S[l_2-(l_1+1)]}\rangle\cdots\langle p^{S[n-(l_k+1)]}\rangle\,. \tag{3}$$

Such averaging is possible due to the above assumption of the factors in Eq. (3) being of statistically independent values. By averaging all the configurations $\{l_1,l_2,\ldots,l_k\}$ and all off-chain hops we get the mean survival probability (hereafter the survival probability) for Q1D random walks

$$\Phi(n)=\delta_1^n\langle p^{S(n)}\rangle+\delta_2\delta_1^{n-1}p\sum_{l_1=0}^{n-1}\langle p^{S(l_1)}\rangle\langle p^{S[n-(l_1+1)]}\rangle+\delta_2^2\delta_1^{n-2}p^2\sum_{l_1=0}^{n-2}\sum_{l_2=l_1+1}^{n-1}\langle p^{S(l_1)}\rangle\langle p^{S[l_2-(l_1+1)]}\rangle\langle p^{S[n-(l_2+1)]}\rangle+o(\delta_2^3)\ . \tag{4}$$

The first term of this expression determines the survival probability for a walker that has not gone to a neighboring chain after n steps; the second term corresponds to that for a walker that has made one off-chain hop, the third term to that for a walker that has made two off-chain hops, and so on. It is essential that in Eq. (4) $\Phi(n)$ is expressed by survival probabilities $\langle p^{S[l_{i+1}-(l_i+1)]}\rangle$ for strictly 1D walks. For this case the well-known solutions are exact for high concentrations [2,8] and approximated for low concentrations [2,5–8].

If we consider the times when a walker makes one off-chain hop (the walker's lifetime on a chain) that corresponds to $n\sim 1/\delta_2$, it is possible to leave only the two first terms, without a large error in the series (4). Since the parameter δ_2 is $\sim 10^{-6}-10^{-9}$ for a number of crystals [11–17], a decrease of $\Phi(n)$ at times $\sim 1/\delta_2$ and concentrations $C\sim 10^{-2}-10^{-3}$ will be less than 10^{-2} from the initial value (a similar decrease of $\Phi(n)$ is characteristic of 1D systems at the same concentrations and times [1,2,5–8,11–15]). The latter allows us to use this approximation for comparison with the experimental luminescence decay of an exciton population in a Q1D system with traps.

Proceeding to integration at $n\gg 1$, and taking into account that the integrand is symmetric with respect to the permutation of the l_1 and $n-l_1$ indices,

$$\Phi(n)=\delta_1\langle p^{S(n)}\rangle+2\delta_2\delta_1^{n-1}p\int_0^{n/2}\langle p^{S(l_1)}\rangle\langle p^{S(n-l_1)}\rangle dl_1\ . \tag{5}$$

At low concentrations ($C=0.01$) the integrand can be calculated using the Rosenstock approximation [10] for the short-time limit and the approximation obtained in [5] for the long-time limit. The survival probability in the 1D system as described by the Rosenstock approximation [10] is

$$\langle f(m)\rangle^{\mathrm{Ros}}=\exp(-C\sqrt{8m/\pi})\ . \tag{6}$$

According to [6], at $C=0.01$, the expression (6) correlates fairly well with MC data for $m\le 2\times 10^4$. In the long-time limit, when $n\ge 2\times 10^4$ an approximation obtained by Anlauf [5] is used:

$$\langle f(m)\rangle^{\mathrm{An}}=\frac{8}{\pi}\left[\frac{2}{3\pi}\right]^{1/2}x^{3/2}\left[1+\frac{17}{18}\frac{1}{x}+\frac{205}{645}\frac{1}{x^2}\right]\times\exp(-\tfrac{3}{2}x)\ , \tag{7}$$

with

$$x=(-\pi\ln p)^{2/3}m^{1/3}\ .$$

The substitution of Eqs. (6) and (7) for Eq. (5) and a change of m for $l_1, n-l_1, n$ makes it possible to calculate a number of curves for some δ_2 values by the numerical integration.

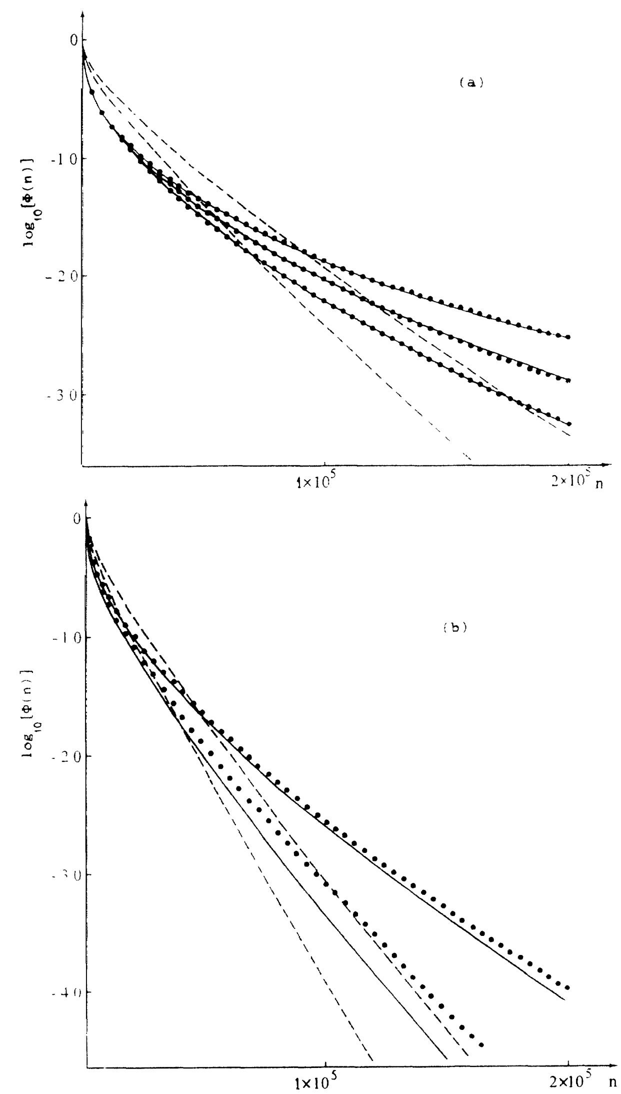

FIG. 1. Decay of $\Phi(n)$ for the trap concentration $C=0.01$ at various values of the quasi-one-dimensionality degree δ_2. The circles denote the MC simulation, the solid lines the results from Eq. (5), and the dashed lines the results from Eq. (8). (a) From top to bottom: $\delta_2\le 10^{-7}$; $\delta_2=5\times 10^{-6}, 10^{-5}$. The thin line is the exact decay form of $\Phi(n)$ for strictly 1D migration as obtained in [8]. (b) From top to bottom: $\delta_2=2\times 10^{-5}, 4\times 10^{-5}$.

III. MC SIMULATION AND DISCUSSION

In order to check Eq. (5), the curves of the survival probability were simulated for Q1D random walks by the MC method. The expression (2) was used as the basis of the algorithm, making it possible to reduce computation time relative to the direct computation of the survival probability when it was necessary to store the trap configuration. For introducing randomness in the stepping a fast random number generator with a sequence period of $2^{49}-1$ was written. Depending on the δ_2 value, realizations from 2×10^3 to 8×10^3 were simulated. The time intervals were $n_{\max}=2\times10^5$ steps for $C=0.01$ and $n_{\max}=4\times10^3$ for $C=0.1$. We used periodic boundary conditions with $L=3600\times10\times10$ sites (L is a site of the lattice) for simulation. The walker started in the center of the lattice with $S(n)=1$ at $n=0$.

Figure 1 presents the dependences of $\Phi(n)$ [Eq. (5), solid lines] and MC simulation (circles) at various δ_2 values. For $\delta_2\le10^{-7}$, MC data coincide with the exact solution [thin line in Fig. 1(a)] for strictly 1D random walks [8]. With an increase of δ_2 the calculated curves coincide well with MC data for $\delta_2=5\times10^{-6}$, 10^{-5}, and a difference between the MC simulation and Eq. (5) is observed only beginning from $\delta_2\ge2\times10^{-5}$. It should be noted that at $\delta_2=2\times10^{-5}$ when $\delta_2=4/n_{\max}$ the approximation still describes the survival probability satisfactorily. Calculated values of $\Phi(n)$ have to be less than those obtained by the MC method, since only the first two terms of the series (4) were taken into account in Eq. (5). With an increasing of δ_2 this difference will increase due to an increasing of the contribution of the series terms, which were not taken into account. This is observed graphically when one compares the curves for $\delta_2=2\times10^{-5}$ and $\delta_2=4\times10^{-5}$ in Fig. 1(b).

It is interesting to compare calculations by Eq. (5) and results obtained for Q1D random walks in three-dimensional topology [9]. In this model the survival probability was calculated by the Rosenstock approximation [9,10]

$$\Phi(n)^{\mathrm{Ros}}=\exp\left[-\ln\left[\frac{1}{1-C}\right]R(n)\right], \tag{8}$$

where $R(n)$ is the mean number of new sites visited by a walker in n steps or sampling function (for $C\ll1$ and $R(n)=\sqrt{8/\pi}n^{1/2}$ [19] we obtain Eq. (6)). The expression for $R(n)$ can be obtained on the basis of a procedure developed by Montroll [19], as it was made in [9], too. In accordance with [9]

$$R(n)=\frac{n}{u_0}+\frac{2u_1}{\sqrt{\pi}u_0^2}n^{1/2}+o(n^{-1}), \tag{9}$$

with $u_1=\sqrt{2/(\pi^2\delta_1\delta_2^2)}$ and u_0 depending on δ_2 such that it can be evaluated by numerical integration via an appropriate structure function [19]. The results obtained in accordance with Eqs. (8) and (9) are given in Fig. 1. As

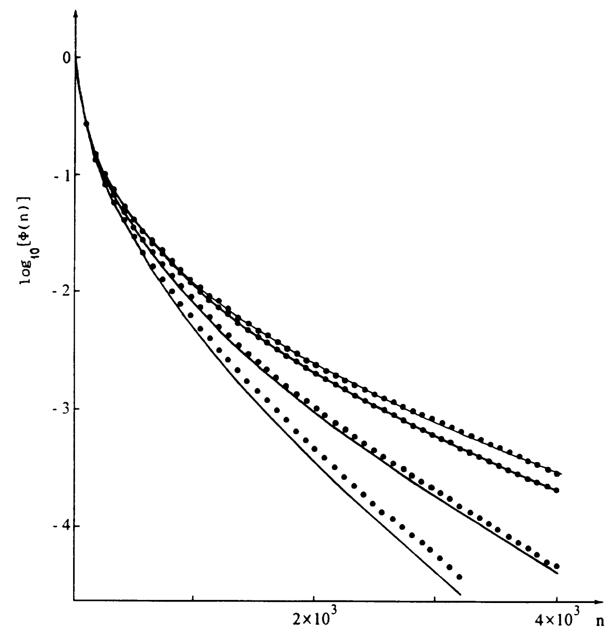

FIG. 2. Decay of $\Phi(n)$ for the trap concentration $C=0.1$ at various values of the quasi-one-dimensionality degree δ_2. The circles denote the MC simulation, and the solid lines the model results from Eq. (5). The thin line is the exact decay form of $\Phi(n)$ for strictly 1D migration as obtained in [8]. From top to bottom: $\delta_2\le5\times10^{-6}$; $\delta_2=10^{-4}$, 5×10^{-4}, 10^{-3}.

is readily seen, these data are rougher than those of Eq. (5). This is most likely due to the Rosenstock approximation being unsatisfactory for Q1D systems at long times.

For high concentrations ($C=0.1$) an exact solution obtained in [2,8] for the survival probability in 1D systems has to be used in Eq. (5). Asymptotics (6) and (7) are not satisfactory for high concentrations [8]. We used results by Onipko and Galchuk [8] since it was not necessary to perform the Laplace transform, distinct from the approach suggested in [2]. As Fig. 2 shows, the calculated curves of $\Phi(n)$ coincide with MC data if $\delta_2\le5\times10^{-6}$. The approximation describes quite satisfactorily the decay of $\Phi(n)$ for $\delta_2=10^{-4}$, although δ_2 exceeds $1/n_{\max}$ ($\delta_2=2/n_{\max}$). It is also of interest to compare the effect of a degree of quasi-one-dimensionality δ_2 on the character of decay curves of $\Phi(n)$ at high and low concentrations.

An increase of the δ_2 parameter by a 1.5 order of magnitude from 5×10^{-6} to 10^{-4} for $C=0.1$ results in an insignificant change of the character of $\Phi(n)$ decay curves (Fig. 2). For example, at $\Phi(n)=0.01\Phi(0)$ [$\Phi(n)$ is related here to $\delta_2=5\times10^{-6}$ and $\delta_2=10^{-4}$] the change is 12%, while this change is 37% for $C=0.01$ with an increase of δ_2 by a 1.5 order of magnitude [from 10^{-7} to 5×10^{-6} Fig. 1(a)]. Thus, at high concentrations the $\Phi(n)$ decay law is less sensitive to the changes in a degree of quasi-one-dimensionality than at low concentrations. This can be explained by taking into account the fact that a fluctuation of the trap density decreases with an increase of their concentration. The quasi-one-dimensional trapping manifests itself most effectively on long chains because a walker should make at least one off-chain hop before it will be trapped. Then due to a decrease of the trap density fluctuation the contribution of long chains into survival probability $\Phi(n)$ will be less at high trap concentrations than at low ones, all things being equal.

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