RANDOM WALKS OF A PAIR OF ANNIHILATING QUASIPARTICLES ON DEFECTED CHAINS

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The distribution function and survival probability of a pair of annihilating quasiparticles diffusing in a segment with absorbing or reflecting ends are obtained. The averaged survival probability of a pair on a chain with chaotically distributed defects such as traps or barriers is calculated.

1. Introduction

Models of random walks in one dimension (1D) attract lasting attention of researchers in many fields because of the availability of exact results related to real processes. For example, in recent years much effort has been focused on the interpretation of charge and excitation energy transport phenomena in quasi-one-dimensional (Q1D) systems in terms of random walks [1,2]. But most of the known random walk models are essentially one-particle ones (see the reviews [2,3] and the references therein). Thus, they cannot be used (at least directly) in studying the effects caused by the interparticle interaction. The latter manifests itself at high particle concentrations. In the case of excitons created at sufficiently high levels of pumping the interparticle interaction often leads to an exciton annihilation which may affect considerably the exciton luminescence kinetics. The corresponding observables are the luminescence quantum yield, the time-resolved luminescence intensity, the delayed luminescence intensity, etc. Experimental measurements of these quantities in Q1D molecular structures [4,5] stimulate theoretical studies of the dynamics of an annihilating pair of particles executing 1D random walks.

Keeping this in mind we present some exact results concerning the problem of 1D random walks of a pair of particles which can annihilate when they come into contact. In section 2 the distribution function and the survival probability for an annihilating pair of particles that execute random walks in a chain with absorbing or reflecting boundaries are determined . In section 3 these results are used to calculate the average survival probability of an annihilating pair in a chain with chaotically distributed defects that operate as barriers or traps.

2. Survival probability of an annihilating pair in a chain with absorbing or reflecting ends

When considering charge or excitation energy transfer processes in real Q1D systems it is often instrumental to regard them as a markovian process of random walk motion of particles in an infinite chain with chaotic defect distribution. The typical element of such a chain is a segment of regular sites with absorbing or reflecting ends which model trapping-like or scattering-like defects in the chain. Assuming the motion of particles in a segment to be realized by jumps between the nearest-neighbour sites and supposing that particles annihilate immediately whenever they occur on the same site, one can write the master equation for the pair distribution function in the form

$$\frac{\partial \rho_n(i,j,t)}{\partial t} = -4\rho_n(i,j,t)+\rho_n(i+1,j,t)+\rho_n(i-1,j,t)+\rho_n(i,j+1,t)+\rho_n(i,j-1,t), \quad i+j\neq n,$$

$$\rho_n(i,j,t)=0, \qquad i+j=n, \tag{1}$$

where $\rho_n(i, j, t)$ defines the conventional probability to find particles on sites i and j (see fig. 1) at time t (expressed hereafter in units of W^{-1}, W is the jump probability per second), $\rho_n(0,j,t)=\rho_n(i,n+1,t)=0$ for a segment with absorbing ends, and the boundary conditions $\rho_n(0,j,t)=\rho_n(1,j,t)$, $\rho_n(i,n,t)=\rho_n(i,n+1,t)$ model the reflection of particles from the segment ends.

For most of the practical purposes it is sufficient to solve, instead of (1), the diffusion equation

$$\frac{\partial \rho_n(x,y,t)}{\partial t} = \frac{\partial^2 \rho_n(x,y,t)}{\partial x^2} + \frac{\partial^2 \rho_n(x,y,t)}{\partial y^2} \tag{2}$$

in the region of continuous variables x, y,

$$0\leqslant x+y\leqslant n, \tag{2a}$$

with the boundary conditions

$$\rho_n(x,y,t)|_{x+y=n}=0 \tag{3}$$

(which determines the condition of instantaneous annihilation of particles that have occupied the same site), and the conditions

$$\rho_n(x,y,t)|_{x=0}=\rho_n(x,y,t)|_{y=0}=0 \tag{4}$$

for absorbing and

$$\left.\frac{\partial \rho_n(x,y,t)}{\partial x}\right|_{x=0} = \left.\frac{\partial \rho_n(x,y,t)}{\partial y}\right|_{y=0} =0 \tag{5}$$

for reflecting ends. The distribution function $\rho_n(x, y, t)$ is equivalent to $\rho_n(i, j, n)$ for $n, t\gg 1$.

We find the solution of the problem (2)–(5) choosing the random initial distribution

$$\rho_n(x,y,t=0)=1, \quad 0<x+y<n. \tag{6}$$

It is convenient to extend it in the following way,

$$\rho_n(x,y,t=0)=-1, \quad x\leqslant n, \quad y\leqslant n, \quad x+y>n, \tag{7}$$

and to find $\rho_n(x, y, t)$ in the square $0\leqslant x, y\leqslant n$ using together with (3)–(5) the boundary conditions

$$\rho_n(x,y,t)|_{x=n}=\rho_n(x,y,t)|_{y=n}=0 \tag{8}$$

and

$$\left.\frac{\partial \rho_n(x,y,t)}{\partial x}\right|_{x=n} = \left.\frac{\partial \rho_n(x,y,t)}{\partial y}\right|_{y=n} =0 \tag{9}$$

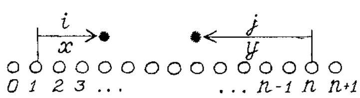

Fig. 1. The discrete coordinates i, j (and continuous ones x, y) which define the displacement of an annihilation particle in a chain.

for the cases of absorbing and reflecting segment ends, respectively (see fig. 2). The solution of eq. (2) with these initial and boundary conditions is equivalent to the desired solution of the problem (2)–(6) in the region $0 \leqslant x+y \leqslant n$.

Using the Green functions of eq. (2) under the boundary conditions (4), (8) [6],

$$G_n^{\mathrm{tr}}(x,y,x',y',t) = \frac{4}{n^2} \sum_{m=1}^{\infty} \sum_{l=1}^{\infty} \exp[-(\pi^2/n^2)(m^2+l^2)t] \sin(\pi m x/n) \sin(\pi l y/n) \sin(\pi m x'/n) \sin(\pi l y'/n) , \tag{10}$$

and (5), (9),

$$G_n^{\mathrm{b}}(x,y,x',y',t) = \frac{1}{n^2}\left(1+2\sum_{\bar{m}=1}^{\infty} \exp(-\pi^2 \bar{m}^2 t/n^2) \cos(\pi \bar{m} x/n) \cos(\pi \bar{m} x'/n)\right) \times\left(1+2\sum_{l=1}^{\infty} \exp(-\pi^2 l^2 t/n^2) \cos(\pi l y/n) \cos(\pi l y'/n)\right) , \tag{11}$$

one can write

$$\rho_n^{\mathrm{tr(b)}}(x,y,t) = \int_0^n \mathrm{d}x' \int_0^n \mathrm{d}y' \, G_n^{\mathrm{tr(b)}}(x,y,x',y',t) \rho_n^{\mathrm{tr(b)}}(x',y',t=0)$$

$$= \int_0^n \mathrm{d}x' \int_0^{n-x'} \mathrm{d}y' \, G_n^{\mathrm{tr(b)}}(x,y,x',y',t) - \int_0^n \mathrm{d}x' \int_{n-x'}^{n} \mathrm{d}y' \, G_n^{\mathrm{tr(b)}}(x,y,x',y',t) , \tag{12}$$

$$\rho_n^{\mathrm{tr}}(x,y,t) = \left(\frac{2}{\pi}\right)^2 \sum_{\bar{m}=1}^{\infty} \sum_{l=1}^{\infty} \frac{\exp[-(\pi^2/n^2)(\bar{m}^2+l^2)t]}{\bar{m}^2-l^2} \frac{\bar{m}}{l} \times [1-(-1)^l][1+(-1)^{\bar{m}}] \, [\sin(\pi \bar{m} x/n) \sin(\pi l y/n) + \sin(\pi l x/n) \sin(\pi \bar{m} y/n)] , \tag{13}$$

and

$$\rho_n^{\mathrm{b}}(x,y,t) = \left(\frac{2}{\pi}\right)^2 \sum_{m=1}^{\infty} \frac{\exp(-\pi^2 m^2 t/n^2)}{m^2} [1-(-1)^m] \, [\cos(\pi m y/n) + \cos(\pi m x/n)] + \frac{8}{\pi^2} \sum_{m=1}^{\infty} \sum_{l=1}^{\infty} \frac{\exp[-(\pi^2/n^2)(m^2+l^2)t]}{l^2-m^2} [(-1)^m-(-1)^l] \cos(\pi l y/n) \, \cos(\pi m x/n) , \tag{14}$$

for the cases of absorbing, eq. (13) (index "tr" denotes traps), and reflecting, eq. (14) (index "b" denotes barriers), segment ends.

Calculating the survival probability of an annihilating pair,

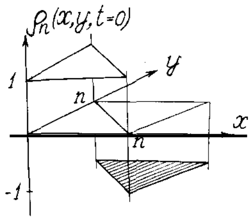

Fig. 2. The extension of the initial condition $\rho_n(x, y, t=0)=1$ given in the region $0<x+y<n$ to the region $x<n$, $y<n$, $x+y>n$ in an additive way (shaded triangle).

$$\Omega_n^{\mathrm{tr(b)}}(t)=\frac{2}{n^2}\int_0^n \mathrm{d}x \int_0^{n-x} \mathrm{d}y\, \rho_n^{\mathrm{tr(b)}}(x,y,t)\,, \tag{15}$$

with the help of (13), (14) one gets

$$\Omega_n^{\mathrm{tr}}(t)=8\left(\frac{2}{\pi}\right)^4 \sum_{m=1}^{\infty}\sum_{l=1}^{\infty} \frac{\exp\{-(\pi^2/n^2)[(2m)^2+(2l-1)^2]t\}}{[(2m)^2-(2l-1)^2]^2}\left(\frac{2m}{2l-1}\right)^2 \tag{16}$$

$$=\frac{32}{9}\left(\frac{2}{\pi}\right)^4 \exp(-5\pi^2 t/n^2),\quad t/n^2\gg 1\,, \tag{16a}$$

and

$$\Omega_n^{\mathrm{b}}(t)=4\left(\frac{2}{\pi}\right)^4 \left(\sum_{l=1}^{\infty}\frac{\exp[-(\pi^2/n^2)(2l-1)^2 t]}{(2l-1)^2}+2\sum_{l=1}^{\infty}\sum_{m=1}^{\infty}\frac{\exp\{-(\pi^2/n^2)[(2m)^2+(2l-1)^2]t\}}{[(2m)^2-(2l-1)^2]^2}\right) \tag{17}$$

$$=4\left(\frac{2}{\pi}\right)^4 \exp(-\pi^2 t/n^2),\quad t/n^2\gg 1\,, \tag{17a}$$

where (16a) and (17a) are obtained with the dominant term in (16) and (17) at $m=1$, $l=1$, being preserved, which is justified at $t/n^2\gg 1$. At small times, calculating $\Omega_n(t)$ at $t/n^2\ll 1$, we use in (13), (14) the Poisson formula (see ref. [6], ch. X)

$$\sum_m^{\infty}\cos[\pi m(x\pm x')/n]\exp(-\pi^2 m^2 t/n^2)=\frac{n}{\sqrt{\pi t}}\sum_{j=-\infty}^{\infty}\exp[-(x\pm x'+2nj)^2/4t]-\tfrac{1}{2}\,.$$

This enables us to pass from a sum such as $\sum_m \exp(-mt/n^2)$ to a sum such as $\sum_j \exp(-j^2n^2/t)$, obtaining

$$G_n^{\mathrm{tr(b)}}(x,y,x',y',t)=\frac{1}{4\pi t}\sum_{j=-\infty}^{\infty}\{\exp[-(x-x'+2nj)^2/4t](\mp)\exp[-(x+x'+2nj)^2/4t]\}$$

$$\times\sum_{j=-\infty}^{\infty}\{\exp[-(y-y'+2nj)^2/4t](\mp)\exp[-(y+y'+2nj)^2/4t]\}\,. \tag{18}$$

Using the definition of $\Omega_n^{\mathrm{tr(b)}}(t)$ (15), we have from (12), (19)

$$\Omega_n^{\mathrm{tr}}(t)=1-\frac{8+4\sqrt{2}}{\sqrt{\pi}}\frac{\sqrt{t}}{n},\quad \frac{t}{n^2}\ll 1\,, \tag{19a}$$

$$\Omega_n^{\mathrm{b}}(t)=1-\frac{4\sqrt{2}}{\sqrt{\pi}}\frac{\sqrt{t}}{n},\quad \frac{t}{n^2}\ll 1\,. \tag{19b}$$

It is informative to compare the results obtained with similar limits for the survival probability, $\rho_n^{(1)}(t)$, of a single particle that diffuses in a chain with absorbing boundaries for which [7]

$$\rho_n^{(1)}(t)=\frac{8}{\pi^2}\sum_{i=0}^{\infty}\frac{\exp[-(\pi^2/n^2)(2i+1)^2 t]}{(2i+1)^2} \tag{20}$$

$$=1-\frac{4}{\sqrt{\pi}}\frac{\sqrt{t}}{n},\qquad \frac{t}{n^2}\ll 1\,, \tag{20a}$$

$$=\frac{8}{\pi^2}\exp(-\pi^2 t/n^2),\quad \frac{t}{n^2}\gg 1\,. \tag{20b}$$

At large times the exponential decay constants in $\Omega_n^{\mathrm{b}}(t)$ and $\rho_n^{(1)}(t)$ are seen to be the same, whereas the value for $\Omega_n^{\rm tr}(t)$ has turned out to be 5 times as great. At small times the decay rates of $\Omega_n^{\rm b}(t)$ and $\rho_n^{(1)}(t)$ are different, the formal difference of (20b) from (22) being a doubling of the diffusion coefficient (i.e. replacing t with $t/2$ for the case of a particle pair is regarded as an ordinary procedure, because the annihilation rate, unlike the trapping rate, is associated with the diffusion coefficient of a relative motion of a pair (but not of a single particle)). At large times, however, the above difference between $\Omega_n^{\rm b}(t)$ and $\rho_n^{(1)}(t)$ vanishes, whereas in an infinite chain we have a relation such as $\rho_\infty^{(1)}(t)=\Omega_\infty^{\rm b}(t/2)$. Comparing (20) with (22) shows that at small times the rate at which a pair vanishes, $R_n(t)\equiv -{\rm d}\Omega_n^{\rm tr}(t)/{\rm d}t$, is equal to the sum of the rates at which each of the particles is trapped, $R_n^{\rm tr}(t)\equiv -{\rm d}\rho_n^{(1)}(t)/{\rm d}t=2/n\sqrt{\pi t}$ and their annihilation rate $R_n^{\rm an}(t)=-{\rm d}\Omega_n^{\rm b}(t)/{\rm d}t=2\sqrt{2}/n\sqrt{\pi t}$, i.e. the particle disappearance through the trapping and annihilation channels is independent. At large times, however, the processes of particle disappearance caused by trapping and annihilation cannot be regarded as uncorrelated.

3. Average survival probability of an annihilating pair in a defected chain

We now use the result of the previous section to calculate the average annihilating pair survival probability in a chain with chaotic distribution of defects that play the role of traps or reflecting barriers, that is

$$\overline{\Omega^{\rm d}(t)}=\tfrac{1}{2}c_{\rm d}^3\int_0^\infty {\rm d}n\, n^2\exp(-c_{\rm d}n)\Omega_n^{\rm d}(t)\,, \tag{21}$$

where $c_{\rm d}$ is the defect concentration. Substituting (16), (17) into (21), one gets

$$\overline{\Omega^{\rm tr}(t)}=4\left(\frac{2}{\pi}\right)^4\int_0^\infty {\rm d}n\, n^2\sum_{m=1}^\infty\sum_{l=1}^\infty\frac{\exp\{-(\pi^2/n^2)[(2m)^2+(2l-1)^2]t-c_{\rm tr}n\}}{[(2m)^2-(2l-1)^2]^2}\left(\frac{2m}{2l-1}\right)^2 \tag{22}$$

$$=1-\frac{4+2\sqrt{2}}{\sqrt{\pi}}c_{\rm tr}\sqrt{t},\qquad \tau_{\rm tr}\equiv 10\pi^2c_{\rm tr}^2t\ll 1\,, \tag{22a}$$

$$=\frac{16}{9}\left(\frac{2}{\pi}\right)^4\sqrt{2\pi/3}\,\tau_{\rm tr}^{5/6}\exp(-\tfrac{3}{2}\tau_{\rm tr}^{1/3}),\quad \tau_{\rm tr}\gg 1\,, \tag{22b}$$

for a chain with traps (d=tr) and

$$\overline{\Omega^{\rm b}(t)}=2\left(\frac{2}{\pi}\right)^4\int_0^\infty {\rm d}n\, n^2\left(\sum_{l=1}^\infty\frac{\exp[-\pi^2(2l-1)^2t/n^2-c_{\rm b}n]}{(2l-1)^4}\right.$$

$$\left.+2\sum_{l=1}^\infty\sum_{m=1}^\infty\frac{\exp\{-(\pi^2/n^2)[(2m)^2+(2l-1)^2]t-c_{\rm b}n\}}{[(2m)^2-(2l-1)^2]^2}\right) \tag{23}$$

$$=1-\frac{2\sqrt{2}}{\sqrt{\pi}}c_{\rm b}\sqrt{t},\qquad \tau_{\rm b}\equiv 2\pi^2c_{\rm b}^2t\ll 1\,, \tag{23a}$$

$$=2\left(\frac{2}{\pi}\right)^4\sqrt{2\pi/3}\,\tau_{\rm b}^{5/6}\exp(-\tfrac{3}{2}\tau_{\rm b}^{1/3})\,,\quad \tau_{\rm b}\gg 1 \tag{23b}$$

for a chain with barriers (d=b).

The average survival probability of a single particle diffusing in a chain with traps is [7–12]

$$\overline{\rho(t)} = \frac{4}{\pi^2} \int_0^\infty dx \frac{x}{\text{sh}\, x} \exp(-\pi^2 c_{tr}^2 t / x^2) \quad (24)$$

$$= 1 - \frac{4}{\sqrt{\pi}} c_{tr} \sqrt{t}, \qquad \pi^2 c_{tr}^2 t \ll 1\,, \quad (24a)$$

$$= 16\sqrt{c_{tr}^2 t / 3\pi} \exp[-3(\tfrac{1}{4}\pi^2 c_{tr}^2 t)^{1/3}], \quad \pi^2 c_{tr}^2 t \gg 1\,. \quad (24b)$$

It is seen that the slowing-down in the decay of the averaged survival probability of an annihilating pair at long times due to defect density fluctuations (i.e. caused by large defect-free chain segments whose length is much larger than the averaged distance between the defects in the chain, c_d^{-1}, enabling an annihilating pair to live much longer) is similar to the effect predicted for $\overline{\rho(t)}$ in ref. [7]. The difference between the pre-exponential factors in the asymptotics (22b), (23b) and (24b) is due to the difference between weight factors used for averaging the cluster values of survival probabilities of a single particle and a pair of particles. This can manifest itself in experimentally observed quantities at not too long times. Yet the most appreciable difference between the dependence $\overline{\rho(t)}$ and $\overline{\Omega^{tr}(t)}$ stems from the five-fold difference in the characteristic time scales of the average survival probabilities for a particle in a chain with traps and for a pair of annihilating particles in the same chain.

The above differences between $\overline{\rho(t)}$ and $\overline{\Omega^{tr}(t)}$ may be experimentally verified, for example, from studies of triplet exciton phosphorescence kinetics and delayed fluorescence (DF) kinetics in the same sample of a Q1D crystal with a high concentration of defects. Indeed, when the dynamics of excitons in such a crystal with impurities playing the role of trapping or scattering centers is modeled, this crystal can be regarded as an infinite chain with chaotically distributed defects – traps or barriers. If the triplet exciton concentration c_T is much lower than the defect (say trap) concentration, most of the trap-free chain segments contain no more than one exciton, so that the exciton–exciton interaction would not affect significantly the exciton phosphorescence intensity under these conditions. In the case of fast trapping the phosphorescence decay kinetics (experimentally studied in refs. [13–15] for some Q1D crystals with traps) is described by the function (24). If the DF can also be observed in the same crystal, the time dependence of its intensity with $c_{tr} \gg c_T$ is determined by the contribution from host molecule segments that contain two excitons initially and thus by the average value of the annihilating pair survival probability, $\overline{\Omega^d(t)}$. A detailed analysis of DF time dependence is given in refs. [16,17].

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