Journal of Statistical Physics, Vol. 1, No. 2, 1969

The Effect of Lattice Vibrations on Trap-Limited Exciton Lifetimes

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Received March 13, 1969

The problem of exciton migration and trapping on a linear polymer is treated as a random walk on a one-dimensional lattice. The average number of steps required for a walker to be trapped is calculated when the probability of stepping to adjacent lattice sites is not symmetrical, and is found to be less than that calculated for a symmetrical walk. An asymmetrical stepping probability is shown to result from the thermal vibrations of the lattice. The magnitude of this effect on the exciton lifetime is estimated and found to be significant.

KEY WORDS: trap-limited exciton lifetimes; asymmetrical random walks; lattice vibrations; displacement correlation functions; phonon-assisted exciton lifetime reduction.

1. INTRODUCTION

A number of physical and biological phenomena can be explained on the basis of the transport of excitation energy through an array of molecules.[1–4] Photosynthesis, for example, involves the excitation of chlorophyll molecules by visible light and the subsequent migration of this excitation energy through the array of chlorophyll molecules to a center where it is trapped, and where it triggers a chemical reaction yielding oxygen and a carbohydrate or sugar.[5] In competition with the removal of energy by this process is the reemission of light by the chlorophyll molecule, that is, fluorescence. The rate of fluorescence is proportional to the number of molecules excited, or excitons present. The decay rate of the fluorescence, when the irradiation

This work was partially supported by the US Office of Naval Research, and by the US Air Force Office of Scientific Research (Grant #611-67).

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of the sample is interrupted, then gives the rate at which excitons are removed by trapping centers and fluorescence. If the trapping is much more efficient than the fluorescence, the decay rate will be due almost entirely to the trapping of excitons. In such cases, the average length of time between the creation and trapping of an exciton can be determined experimentally.[6]

The migration and trapping of an exciton can often be treated as a random walk on a periodic space lattice in which some of the lattice sites are traps.[7,8] In these cases, one assumes that the excitation can be created with equal probability at any nontrapping lattice site, and then calculates the average number of steps required for it to reach a trap for the first time. The lifetime of the exciton is then just this average number of steps times the time interval τ between steps, which is assumed to be constant.

Machine calculations of trap-limited exciton lifetimes have been made by Pearlstein[9,10] and Robinson[11]; ten Bosch and Ruijgrok's[12] analytic results disagreed with these, a discrepancy resolved by Knox.[7] Montroll[8] has given an analytic treatment of random walks on lattices containing a periodic array of traps. He has also treated the case of randomly distributed traps and obtained exact results for the average lifetime in a one-dimensional system.[13]

Inherent in all of these calculations is the assumption that steps to all nearest-neighbor lattice sites are equally probable, although it is known that the excitation transfer rate depends on certain angular factors and on the distance between the sites.[1,14] The problem we shall consider is that of an exciton migrating by steps to nearest-neighbor sites on a linear polymer in which the distance between monomers, due to their thermal motion, is not constant. The probability of an exciton jumping to a neighboring site is greater, the smaller is the distance between the sites. Hence, if an exciton is created at a site which is closer, say, to the site on its right than to the site on its left, it will have a greater probability of jumping to the right (see Fig. 1). If, when it makes its next jump, the lattice motion has been such that the site to the right of its new position is again closer (see Fig. 1), it will again have a higher probability of jumping to the right. If this situation tends to persist for a large number of steps, as one might expect if the time between jumps and the vibrational periods are comparable, the exciton will tend to be driven to the right. One would then expect the number of steps to reach a trap to be reduced from the situation in which a jump in either direction is equally probable.

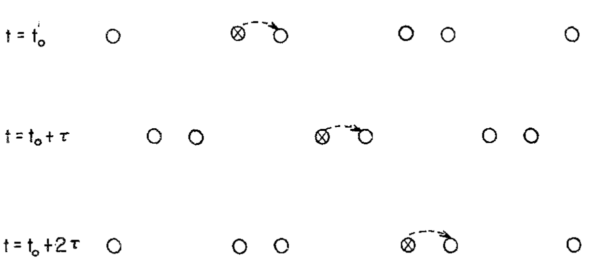

Fig. 1. Motion of an exciton on a vibrating linear chain. The more-probable direction in which the exciton will jump is indicated by the arrows.

Two questions should be resolved: (1) How much is the lifetime of an exciton on a linear chain reduced if the probability of its moving in one direction is greater than in the other direction? (2) Are the lattice vibrations such that motion of the exciton in one direction is consistently more probable for a number of steps at least of the order of the number of steps required for it to be trapped? The first question will be examined in Section 2, and the second in Section 3. It will be shown in Section 4 that the effect on the exciton lifetime can, indeed, be appreciable.

2. ASYMMETRICAL RANDOM WALK

The formalism and notation in the following treatment of the random walk is taken from Montroll.[15] A walker on the infinite one-dimensional lattice without traps of Fig. 2 steps to the right with a probability p and to the left with a proabability $q = 1 - p$. The coefficient p of $e^{i\phi}$ in the expression $(pe^{i\phi} + qe^{-i\phi})$ represents the probability of the first step being to the right, while the coefficient q of $e^{-i\phi}$ represents the probability of the first step being to the left. The coefficient p^2 of $e^{2i\phi}$ in $(pe^{i\phi} + qe^{-i\phi})^2$ represents the probability of a walker being at $l = 2$ after two steps, the coefficient $2pq$ of $e^{oi\phi}$ the probability that he has returned to the origin, and the coefficient q^2 of $e^{-2i\phi}$ the probability that he ends at $l = -2$ after two steps. Generally, $P_n(l)$, the probability that the walker is at l after n steps, is the coefficient of $e^{+il\phi}$ in $(pe^{i\phi} + qe^{-i\phi})^n$, and is given by

$$P_n(l) = (1/2\pi) \int_{-\pi}^{\pi} (pe^{i\phi} + qe^{-i\phi})^n \, e^{-il\phi} \, d\phi \tag{1}$$

since

$$(1/2\pi) \int_{-\pi}^{\pi} e^{-i(m-m')\phi} \, d\phi = \delta_{m,m'} \tag{2}$$

The generating function of all walks which end at lattice point l independently of the number of steps n is defined to be

$$\begin{aligned} U(z, l) &= \sum_{n=0}^{\infty} z^n P_n(l) \\ &= \frac{1}{2\pi} \sum_{n=0}^{\infty} z^n \int_{-\pi}^{\pi} (pe^{i\phi} + qe^{-i\phi})^n \, e^{-il\phi} \, d\phi \\ &= \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{e^{-il\phi} \, d\phi}{1 - z(pe^{i\phi} + qe^{-i\phi})} \end{aligned} \tag{3}$$

This integral is easily evaluated by setting $s = e^{\pm i\phi}$, accordingly, as l is negative

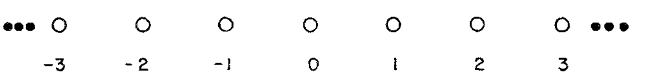

Fig. 2. An infinite one-dimensional lattice without defects.

or positive, to obtain a contour integration around the unit circle $|s| = 1$.Application of the residue theorem then gives

$$\begin{aligned} U(z, l) &= \left[\frac{1-(1-4z^2pq)^{1/2}}{2zq}\right]^l \frac{1}{(1-4z^2pq)^{1/2}}, \qquad l \geqslant 0 \\ &= \left[\frac{1-(1-4z^2pq)^{1/2}}{2zp}\right]^{-l} \frac{1}{(1-4z^2pq)^{1/2}}, \qquad l \leqslant 0 \end{aligned} \tag{4}$$

This is the generating function of random walks from 0 to l on an infinite one-dimensional lattice without defects. The generating function for walks from 0 to l on a ring of N points (that is, a chain of N points with periodic boundary conditions), is equivalent to the sum of the generating functions for all those walks on an infinite chain which represent walks from 0 to l, from 0 to $l + N$, etc., as well as from 0 to $l - N$, $l - 2N$, etc. Hence,

$$\begin{aligned} U_N(z, l) = &\ U(z, l) + U(z, l + N) + U(z, l + 2N) \\ &+ \cdots + U(z, l - N) + U(z, l - 2N) + \cdots \end{aligned} \tag{5}$$

Using Eq. (4), we obtain

$$\begin{aligned} U_N(z, l) &= \frac{1}{(1-4z^2pq)^{1/2}}\left[\frac{x^l}{1-x^N} + \frac{y^{N-l}}{1-y^N}\right], \qquad l \geqslant 0 \\ &= \frac{1}{(1-4z^2pq)^{1/2}}\left[\frac{y^{-l}}{1-y^N} + \frac{x^{N+l}}{1-x^N}\right], \qquad l \leqslant 0 \end{aligned} \tag{6}$$

where

$$x = \frac{1-(1-4z^2pq)^{1/2}}{2zq}, \qquad y = \frac{1-(1-4z^2pq)^{1/2}}{2zp} \tag{7}$$

Let us now consider a chain in which one of the N lattice sites, say l_1, is a trap, and the walker starts at $l_0 \neq l_1$. The probability that the walker not be trapped on the nth step is

$$\sum_{l \neq l_1} f_n(l)$$

where $f_n(l)$ is the probability that the walker is at l after n steps. The probability that he is trapped on the nth step is then

$$\sum_{l \neq l_1} [f_{n-1}(l) - f_n(l)]$$

and the average number of steps required for trapping is

$$\bar{n} = \sum_{n=1}^{\infty} n \sum_{l \neq l_1} [f_{n-1}(l) - f_n(l)] \tag{8}$$

In terms of the generating function defined by

$$F_N(z, l) = \sum_{n=0}^{\infty} z^n f_n(l) \tag{9}$$

we have

$$\bar{n} = \frac{\partial}{\partial z}\left[(1 - z) \sum_{l \neq l_1} F_N(z, l)\right]_{z=1} \tag{10}$$

Since

$$\sum_l F_N(z, l) = \sum_l \sum_{n=0}^{\infty} z^n f_n(l) = \sum_{n=0}^{\infty} z^n \sum_l f_n(l)$$

$$= \sum_{n=0}^{\infty} z^n = \frac{1}{1 - z} \tag{11}$$

we may write

$$(1 - z) \sum_{l \neq l_1} F_N(z, l) = 1 - (1 - z) F_N(z, l_1) \tag{12}$$

and, therefore,

$$\bar{n} = \frac{\partial}{\partial z} [(1 - z) F_N(z, l_1)]_{z=1} \tag{13}$$

The generating function $F_N(z, l)$ can be obtained from the generating function of random walks starting from the origin on a perfect lattice. We note that

$$P_0(l) = \delta_{l,0} \tag{14}$$

and

$$P_n(l) = pP_{n-1}(l - 1) + qP_{n-1}(l + 1) \tag{15}$$

Multiplying this equation by z^n and summing from $n = 1$ to ∞, we obtain

$$U(z, l) - \delta_{l,0} = pzU(z, l - 1) + qzU(z, l + 1) \tag{16}$$

where $U(z, l)$ is defined by Eq. (3). The generating function for walks on an N-point ring then satisfies the difference equation

$$U_N(z, l) - pzU_N(z, l - 1) - qzU_N(z, l + 1) = \delta_{l,0} \tag{17}$$

Now,

$$f_0(l) = \delta_{l,l_0} \tag{18}$$

$$f_n(l) = pf_{n-1}(l - 1) + qf_{n-1}(l + 1); \qquad l \neq l_1, l_1 \pm 1 \tag{19}$$

and, since the walker cannot escape from site l_1,

$$f_n(l_1) = pf_{n-1}(l_1 - 1) + qf_{n-1}(l_1 + 1) + f_{n-1}(l_1) \tag{20}$$

Then, for any l,

$$f_n(l) = pf_{n-1}(l-1)[1 - \delta_{l-1,l_1}] + qf_{n-1}(l+1)[1 - \delta_{l+1,l_1}] + f_{n-1}(l)\,\delta_{l,l_1} \tag{21}$$

Multiplying this equation by z^n and summing from $n = 1$ to ∞, we find

$$\begin{aligned} F_N(z, l) &- pzF_N(z, l-1) - qzF_N(z, l+1) \\ &= z[\delta_{l,l_1} - p\delta_{l-1,l_1} - q\delta_{l+1,l_1}]\, F_N(z, l_1) + \delta_{l,l_0} \\ &= Q(z, l) \end{aligned} \tag{22}$$

The generating function $U_N(z, l)$ is the Green's function required for the solution of this inhomogeneous equation:

$$\begin{aligned} F_N&(z, l) \\ &= \sum_{l'} U_N(z, l - l')\, Q(z, l') \\ &= U_N(z, l - l_0) \\ &\quad + [zU_N(z, l - l_1) - zpU_N(z, l - l_1 - 1) - zqU_N(z, l - l_1 + 1)]\, F_N(z, l_1) \\ &= U_N(z, l - l_0) + [zU_N(z, l - l_1) - U_N(z, l - l_1) + \delta_{l,l_1}]\, F_N(z, l_1) \\ &= U_N(z, l - l_0) + [(z-1)\, U_N(z, l - l_1) + \delta_{l,l_1}]\, F_N(z, l_1) \end{aligned} \tag{23}$$

We obtain, when $l = l_1$,

$$F_N(z, l_1) = U_N(z, l_1 - l_0)/(1 - z)\, U_N(z, 0) \tag{24}$$

Substituting this into Eq. (13) yields

$$\bar{n} = \frac{\partial}{\partial z} \left[\frac{U_N(z, l_1 - l_0)}{U_N(z, 0)} \right]_{z=1} \tag{25}$$

This is the average number of steps required for a walker starting at l_0 to be trapped at l_1 on a ring of N points. When the starting point can, with equal probability, be any nontrapping point, we must average $\bar{n}$ over all possible starting points to get

$$\begin{aligned} \tilde{n} &= \frac{1}{N-1} \sum_{l_0 \neq l_1} \frac{\partial}{\partial z} \left[\frac{U_N(z, l_1 - l_0)}{U_N(z, 0)} \right]_{z=1} = \frac{1}{N-1} \frac{\partial}{\partial z} \left[\frac{\sum_{l_0} U_N(z, l_1 - l_0)}{U_N(z, 0)} - 1 \right]_{z=1} \\ &= \frac{1}{N-1} \frac{\partial}{\partial z} \left[\frac{1}{U_N(z, 0)(1 - z)} \right]_{z=1} \end{aligned} \tag{26}$$

From Eq. (6),

$$U_N(z, 0) = \frac{1}{(1 - 4z^2pq)^{1/2}} \frac{[1 - (xy)^N]}{(1 - x^N)(1 - y^N)} \tag{27}$$

where x and y are defined in Eq. (7). Let $| p - q | = \delta$; then, Eq. (26) becomes

$$\begin{aligned}\tilde{n} &= \frac{1}{N-1}\left[\frac{N^2}{2\delta} + \frac{N^2}{\delta\{[(1+\delta)/(1-\delta)]^N - 1\}} - \frac{N}{2\delta^2}\right] \\ &= \frac{N^3}{N-1}\frac{1}{2N\delta}\left[\coth(N\tanh^{-1}\delta) - \frac{1}{N\delta}\right]\end{aligned} \tag{28}$$

or

$$\tilde{n} = \frac{N^3}{N-1}\frac{1}{2N\delta} L\left[N\delta\left(1 + \frac{\delta^2}{3} + \frac{\delta^4}{5} + \cdots\right)\right] - \frac{(1/3) + (\delta^2/5) + (\delta^4/9) + \cdots}{2N^2[1 + (\delta^2/3) + (\delta^4/5) + \cdots]} \tag{29}$$

where $L(x) \equiv \coth x - (1/x)$, the Langevin function,[16] goes to zero as $x/3$ as x approaches zero. In the limit $\delta \to 0$, then,

$$\tilde{n} = \frac{N^3}{N-1}\left(\frac{1}{6} - \frac{1}{6N^2}\right) = \frac{N(N+1)}{6}$$

which agrees with the result for a symmetrical walk obtained by Montroll.[8] For δ not zero, but much less than one, we have

$$\tilde{n} \approx \frac{N^3}{N-1}\left[\frac{1}{2N\delta} L(N\delta) - \frac{1}{6N^2}\right] \tag{30}$$

while if $N \tanh^{-1}\delta \geqslant 2$, or, equivalently, since $\tanh^{-1}\delta \geqslant \delta$, $N\delta > 2$, then $\coth(N(N\tanh^{-1}\delta) = 1$ within 5%. Equation (28) then becomes

$$\tilde{n} \approx \frac{N^3}{N-1}\frac{1}{2N\delta}\left(1 - \frac{1}{N\delta}\right) \tag{31}$$

This last equation applies even when δ is not small. In the limit $\delta \to 1$, we get $n \approx N/2$. In this case, the walker steps always in one direction, and $N/2$ is just the average number of lattice sites between the site on which the walker starts and the trap.

The function $y = (1/2N\delta)\, L(N\delta)$ and $y = (1/2N\delta)[1 - (1/N\delta)]$ are plotted in Fig. 3. The reduction in the average number of steps is related to the difference between these curves and the line $y = 1/6$. It is clear from this graph that a significant reduction can be obtained provided $N\delta$ is large enough. Moreover, we see that Eq. (31) is indeed a good approximation when $N\delta \gtrsim 3.0$.

The above analysis has been concerned with a walker on a ring of N lattice points of which one is a trap. However, the problem of a walker on a one-dimensional chain with traps at $l = l_1, l_2, \ldots, l_r$ can be reduced to that of a walker on a ring with a single trap. For, if the walker starts between traps l_j and l_{j+1}, the number of points

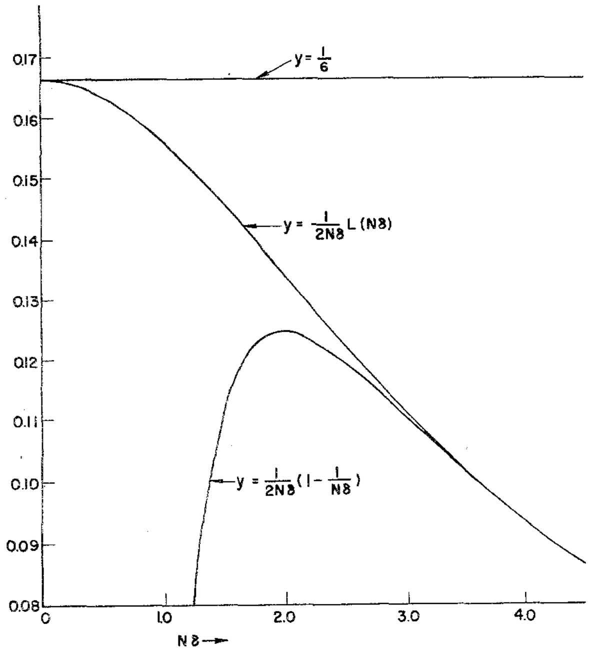

Fig. 3. The functions $(1/2N\delta)\, L(N\delta)$ and $(1/2N\delta)[1 - (1/N\delta)]$.

in the interval is $s_j = l_{j+1} - l_j$, which is the same as a walk on a ring of s_j points, one being a trap. When the traps are distributed periodically with period s, then the average number of steps to be trapped is given by Eq. (28) with s replacing N.

3. LATTICE DYNAMICS

In the development of Section 2, it is assumed that the exciton jumping probabilities p and $q = 1 - p$ were constant over the lifetime of the exciton. However, if p and q are to be related to the instantaneous position of the exciton site and its nearest neighbors when the jump takes place, they must be functions of lattice site and of time. Hence, for the treatment in Section 2 to be applicable, conditions must be found such that p and q do not vary much over the exciton lifetime and from site to site.

In Förster's weak coupled model, the transition rate of an exciton varies as $1/R^6$, where R is the distance between molecules. The distance between lattice sites l and $l+1$ is $u_{l+1}(t) - u_l(t) + a$, where a is the lattice constant. The ratio of the probability of a transition from site l to site $l+1$ to the probability of a transition from site l to site $l-1$ is then

$$\frac{[u_l(t) - u_{l-1}(t) + a]^6}{[u_{l+1}(t) - u_l(t) + a]^6} \approx 1 - \frac{6}{a}\,[u_{l+1}(t) + u_{l-1}(t) - 2u_l(t)] \tag{32}$$

The stepping probabilities of our random walker when at the lth site at time t, $p_l(t)$ and $q_l(t) = 1 - p_l(t)$, must have this ratio. That is,

$$p_l(t) \approx \tfrac{1}{2}\{1 - (3/a)[u_{l+1}(t) + u_{l-1}(t) - 2u_l(t)]\} \tag{33}$$

and we take this to be exact, so that

$$p_l(t) = \tfrac{1}{2}[1 - (3/a)\,\Delta_l(t)], \qquad q_l(t) = \tfrac{1}{2}[1 + (3/a)\,\Delta_l(t)] \tag{34}$$

where

$$\Delta_l(t) = u_{l+1}(t) + u_{l-1}(t) - 2u_l(t) \tag{35}$$

We must now find conditions under which the quantity $\Delta_l(n\tau)$ is, on the average, independent of lattice site l and step number n, with τ being the time interval between steps. That is, given, at the time the exciton is created, that the lattice is in such a condition that a step in one direction is more probable than in the other ($|\Delta_0(0)| > 0$), we want to know whether this situation persists on the average after n steps at different lattice sites. The quantity of interest is then related to the correlation function $\langle \Delta_l(t)\ \Delta_0(0)\rangle$, where the brackets indicate an ensemble average. We take for our average $\Delta_l(t)$

$$\bar{\Delta}_l(t) \approx \langle \Delta_l(t)\,\Delta_0(0)\rangle / \langle \Delta_0^2(0)\rangle^{1/2} \tag{36}$$

and insert this in Eq. (34) to get

$$\bar{p}_l(n\tau) = \tfrac{1}{2}[1 + (3/a)\,\bar{\Delta}_l(n\tau)], \qquad \bar{q}_l(n\tau) = \tfrac{1}{2}[1 - (3/a)\,\bar{\Delta}_l(n\tau)] \tag{37}$$

This gives as initial stepping probabilities

$$\bar{p}_0(0) = \tfrac{1}{2}[1 + (3/a)\langle \Delta_0^2(0)\rangle^{1/2}], \qquad \bar{q}_0(0) = \tfrac{1}{2}[1 - (3/a)\langle \Delta_0^2(0)\rangle^{1/2}] \tag{38}$$

It has been assumed here that $\bar{p}_0(0) > \bar{q}_0(0)$, but this is no restriction, since it was shown in Section 2 that the lifetime of the walker depends only on $\delta = |p - q|$.

The quantity $\bar{\Delta}_l(t)$ can be calculated using standard lattice-dynamics theory. From Eq. (35) and the translational invariance of the lattice we obtain

$$\begin{aligned}\langle \Delta_l(t)\,\Delta_0(0)\rangle = {} & \langle u_{l+2}(t)\,u_0(0)\rangle - 4\langle u_{l+1}(t)\,u_0(0)\rangle \\ & + 6\langle u_l(t)\,u_0(0)\rangle - 4\langle u_{l-1}(t)\,u_0(0)\rangle + \langle u_{l-2}(t)\,u_0(0)\rangle\end{aligned} \tag{39}$$

The displacement–displacement correlation function is given in terms of the phonon Green's function[17] as follows:

$$\langle u_l(t)\,u_0(0)\rangle = \frac{\hbar i}{2\pi} \lim_{\epsilon\to 0^+} \int_{-\infty}^{\infty} \frac{[G_l(\omega + i\epsilon) - G_l(\omega - i\epsilon)]}{(e^{\hbar\omega/kT} - 1)}\, e^{\hbar\omega/kT} e^{-i\omega t}\, dt \tag{40}$$

where

$$G_l(z) = \frac{1}{NM} \sum_q \frac{e^{iqla}}{z^2 - \omega_q^2} \tag{41}$$

Using the equation

$$\lim_{\epsilon\to 0^\pm} \frac{\epsilon}{x^2 + \epsilon^2} = \pm\pi\delta(x)$$

one obtains

$$\lim_{\epsilon\to 0^+} i[G_l(\omega + i\epsilon) - G_l(\omega - i\epsilon)] = \frac{2\pi}{NM} \sum_q e^{iql}\, \mathrm{sgn}\, \omega\ \delta(\omega^2 - \omega_q^2) \tag{42}$$

Performing the integral over ω, we then have

$$\langle u_l(t)\, u_0(0)\rangle = \frac{\hbar}{2NM} \sum_q \frac{e^{iqla}[e^{\hbar\omega_q/kT} e^{-i\omega_q t} + e^{i\omega_q t}]}{\omega_q[e^{\hbar\omega_q/kT} - 1]} \tag{43}$$

Taking the real part of this equation and changing the sum over all q to one over only positive values of q gives

$$\langle u_l(t)\, u_0(0)\rangle = \frac{\hbar}{NM} \sum_{q\geqslant 0} \frac{\cos(qla)\cos(\omega_q t)}{\omega_q} \coth\frac{\hbar\omega_q}{2kT} \tag{44}$$

Substituting this result into Eq. (39) and using the dispersion relation for a linear chain with monomers of mass M and monomer–monomer force constant α

$$\omega_0^2 = (4\alpha/M)\sin^2(qa/2) \tag{45}$$

gives

$$\langle \Delta_l(t)\, \Delta_0(0)\rangle = \frac{16\hbar}{NM\omega_m^4} \sum_{q\geqslant 0} \omega_q^3 \cos(qla)\cos(\omega_q t)\coth\frac{\hbar\omega_q}{2kT} \tag{46}$$

where $\omega_m = 2(\alpha/M)^{1/2}$ is the maximum frequency of the lattice. We transform the sum over q to an integral over frequencies using the lattice density of states:

$$\sum_{q\geqslant 0} f(q) = \frac{1}{2}\int_0^{\omega_m} D(\omega)\, f[q(\omega)]\, d\omega \tag{47}$$

with

$$D(\omega) = \frac{Na}{\pi}\left|\frac{dq}{d\omega}\right| = \frac{2N}{\pi(\omega_m^2 - \omega^2)^{1/2}} \tag{48}$$

Then,

$$\langle \Delta_l(t)\, \Delta_0(0)\rangle = \frac{16\hbar}{M\pi\omega_m^4}\int_0^{\omega_m} \frac{\omega^3 \cos[q(\omega)\, la]\cos(\omega t)}{(\omega_m^2 - \omega^2)^{1/2}} \coth\frac{\hbar\omega}{2kT}\, d\omega \tag{49}$$

This integral can be performed analytically for $l = 0$ if a high-temperature expansion is made:

$$\coth(\hbar\omega/2kT) \approx kT/\hbar\omega \tag{50}$$

This approximation is valid if $kT \gg \hbar\omega_m$, which will be justified later for the physical systems of interest here. Performing the change of variables $x = \omega/\omega_m$ gives

$$\langle \Delta_0(t)\, \Delta_0(0)\rangle = \frac{16kT}{M\pi\omega_m^2}\int_0^1 \frac{x^2\cos(\omega_m t x)}{(1 - x^2)^{1/2}}\, dx \tag{51}$$

This is just an integral representation of the Bessel functions:

$$\langle \Delta_0(t)\, \Delta_0(0)\rangle = \frac{4kT}{M\omega_m^2}[J_0(\omega_m t) - J_2(\omega_m t)] \tag{52}$$

The correlation function for $|l| > 0$ can now be found using the equation of motion satisfied by $\Delta_l(t)$,

$$M \frac{d^2}{dt^2} \langle \Delta_l(t)\, \Delta_0(0)\rangle = \alpha[\langle \Delta_{l+1}(t)\, \Delta_0(0)\rangle - 2\langle \Delta_l(t)\, \Delta_0(0)\rangle + \langle \Delta_{l-1}(t)\, \Delta_0(0)\rangle] \tag{53}$$

and the Bessel function recursion relation

$$4J_n''(z) = J_{n+2}(z) - 2J_n(z) + J_{n-2}(z) \tag{54}$$

Using Eq. (53) to express each correlation function $\langle \Delta_{l+1}(t)\, \Delta_0(0)\rangle$ in terms of the correlation functions $\langle \Delta_l(t)\, \Delta_0(0)\rangle$ and $\langle \Delta_{l-1}(t)\, \Delta_0(0)\rangle$ and noting that $\Delta_l(t) = \Delta_{-l}(t)$, it is easy to deduce that, in general,

$$\langle \Delta_l(t)\, \Delta_0(0)\rangle = (2kT/M\omega_m^2)[-J_{2l+2}(\omega_m t) + 2J_l(\omega_m t) - J_{2l-2}(\omega_m t)] \tag{55}$$

In particular,

$$\langle \Delta_0^2(0)\rangle = 4kT/M\omega_m^2 = kT/\alpha \tag{56}$$

and the quantity defined in Eq. (36) is then

$$\bar{\Delta}_l(t) = \left[\frac{kT}{M\omega_m^2}\right]^{1/2} [-J_{2l+2}(\omega_m t) + 2J_l(\omega_m t) - J_{2l-2}(\omega_m t)] \tag{57}$$

If we consider asymptotically long times,

$$\bar{\Delta}_l(t) \approx 4(-1)^l \left[\frac{2kT}{M\omega_m^2}\right]^{1/2} \frac{\cos[\omega_m t - (\pi/4)]}{(\pi\omega_m t)^{1/2}} \tag{58}$$

and for the time being consider the special case $\tau = \pi/\omega_m$, we have

$$\bar{\Delta}_l(n\tau) \approx \frac{4(-1)^{l+n}}{\pi\sqrt{n}} \left[\frac{kT}{M\omega_m^2}\right]^{1/2} \tag{59}$$

Since once can reach a lattice site with l even (odd) only by an even (odd) number of steps,

$$\bar{\Delta}_l(n\tau) \approx \frac{4}{\pi\sqrt{n}} \left[\frac{kT}{M\omega_m^2}\right]^{1/2} \tag{60}$$

The ratio of this to $\bar{\Delta}_0(0)$ is

$$\frac{\bar{\Delta}_l(n\tau)}{\langle \Delta_0^2(0)\rangle^{1/2}} = \frac{2}{\pi\sqrt{n}} \tag{61}$$

We note that this is always positive and independent of l, and, moreover, varies slowly with the number of steps n. Also, $\bar{p}_l(n\tau)$ will always be greater (less) than $\bar{q}_l(n\tau)$ if $\bar{p}_0(0)$ is greater (less) than $\bar{q}_0(0)$. We conclude that, provided the time interval between steps τ is approximately equal to π/ω_m (or any odd multiple of this quantity), it is reasonable to take for $\delta = | p - q |$ in Section 2 some fraction of $| \bar{p}_0(0) - \bar{q}_0(0)| = 3\bar{\Delta}_0(0)/a \equiv \delta_0$. The fraction will, of course, depend on the average lifetime of the exciton.

4. EXCITON LIFETIMES

If the $\bar{\Delta}_l(n\tau)$ at each step are given equal weight in the calculation of the average δ, we find when $\tilde{n} = 1$, $\delta = \delta_0$; when $\tilde{n} > 1$,

$$\delta = \frac{2\delta_0}{\pi\tilde{n}} \left\{ \sum_{n=1}^{\tilde{n}-1} \frac{1}{\sqrt{n}} + \frac{\pi}{2} \right\} \tag{62}$$

For values of $\tilde{n} \gtrsim 6$, this can be approximated by

$$\delta \approx 4\delta_0/\pi\sqrt{\tilde{n}} \tag{63}$$

to better than 2% accuracy. We can substitute for $\tilde{n}$ from Eq. (28) to obtain the following equation for δ:

$$\delta = \frac{4\delta_0}{\pi\{[N^3/(N-1)][1/2N\delta][\coth(N\tanh^{-1}\delta) - (1/N\delta)]\}^{1/2}} \tag{64}$$

This allows us to find δ in terms of N and δ_0, which, in turn, determines the lifetime of the exciton $\tilde{n}\tau$ by using either Eq. (28) or Eq. (63). Equation (64) can be simplified by using Eq. (31) instead of Eq. (28) if $N\delta > 2$. This gives

$$\delta = \frac{4\delta_0}{\pi\{[N^3/(N-1)](1/2N\delta)[1 - (1/N\delta)]\}^{1/2}} \tag{65}$$

The use of this approximate formula will be justified below, where we will show that $N\delta$ is indeed greater than 2. The effect of this asymmetry on the exciton lifetime will be postponed to that time.

The above discussion assumed that $\tau \approx \pi/\omega_m$. If, instead, τ is some other odd multiple of π/ω_m, say

$$\tau = (2\nu + 1)\,\pi/\omega_m, \qquad \nu = 1, 2, 3,... \tag{66}$$

then the average asymmetry will be

$$\delta = \frac{4\delta_0}{\pi\sqrt{\tilde{n}}} \frac{1}{(2\nu + 1)^{1/2}} \tag{67}$$

rather than that of Eq. (63).

The situation when τ is an even multiple of π/ω_m, say, $\tau = 2\nu\pi/\omega_m$, would seem to give a lengthening of the lifetime, for, referring to Eq. (58), we see that $\bar{\Delta}_l(n\tau)$ then changes sign with each step. That is, the walker would find the probability of a step to the right to be greater at one step, and, at the next step, the probability of a step to the left would be greater. This would tend to keep the walker near his starting point. This situation can be treated within the formalism of Section 2 (see the appendix). The absolute value of the average asymmetry will, in this case, be

$$\delta = \frac{4\delta_0}{\pi\sqrt{\tilde{n}}}\frac{1}{(2\nu)^{1/2}} \tag{68}$$

Putting this into Eq. (A.6) and solving for $\tilde{n}$, we get

$$\tilde{n} \approx \frac{N(N+1)}{6} + \frac{8\delta_0^2}{\nu\pi^2} \tag{69}$$

This means that the average number of steps to be trapped is increased by $8\delta_0^2/\nu\pi^2$, which is negligible except for small N.

When the time interval between steps is not exactly equal to π divided by the maximum lattice frequency ω_m, the exciton gets out of phase with the lattice vibrations after some number of steps, with a consequent reduction of the average asymmetry. In this case, when $\tau = (\pi + \epsilon)/\omega_m$, we have from Eq. (58)

$$\begin{aligned} \bar{\Delta}_l(n\tau) &= \frac{4}{[\pi n(\pi + \epsilon)]^{1/2}}\left[\frac{2kT}{M\omega_m^2}\right]^{1/2} \cos\left[n\epsilon - \frac{\pi}{4}\right] \\ &= \frac{2\bar{\Delta}_0(0)}{[n\pi(\pi + \epsilon)]^{1/2}}[\cos(n\epsilon) + \sin(n\epsilon)] \end{aligned} \tag{70}$$

and the average asymmetry would be

$$\delta = \frac{\delta_0}{\tilde{n}}\left\{\sum_{n=1}^{\tilde{n}-1}\frac{2[\cos(n\epsilon) + \sin(n\epsilon)]}{[n\pi(\pi + \epsilon)]^{1/2}} + 1\right\} \tag{71}$$

If one could vary τ, or, equivalently, ω_m, and then measured the exicton lifetime and plotted this against $\pi\omega_m$, the curve would have a minimum at $\omega_m\tau = \pi$. The width of this dip would depend on how quickly the exciton gets out of phase with the lattice vibrations. The width at half-depth can be estimated as follows. For given δ_0 and N, the minimum value of the lifetime is $\tilde{n}\tau$, with $\tilde{n}$ given by either Eq. (28) or by the approximate formulas of Eqs. (30) or (31). One can find from these equations or from these graphs plotted in Fig. 3 that value of $N\delta$, say, $N\delta'$, which would give an $\tilde{n}'$ that would give one half the reduction in the lifetime. These δ' and $\tilde{n}'$, when substituted in Eq. (71), determine ϵ, that is, the width of the dip in the curve.

We will now estimate the magnitude of δ_0 and from this determine the reduction in the lifetime of the exciton that one could expect. To make this estimate, we require typical values of the lattice parameters and the time interval between steps, τ. According to Pearlstein,[6] it may be possible to make lifetime measurements by measuring the decay rate of donor fluorescence in linear polymers. We take for a typical value of the monomer mass 200 proton masses. The exciton transfer rate[1] can be as low as 10^{10} sec^{-1} and as high as 10^{13} sec^{-1}, with $\pi \times 10^{11}$ sec^{-1} being a typical value, that is, $\tau \approx \pi \times 10^{-12}$ sec. Earlier, we found that for an average asymmetry in the stepping probabilities to exist, the maximum lattice frequency ω_m had to be approximately an odd multiple of π/τ, with the largest asymmetry occurring for $\omega_m \approx \pi/\tau$. This means that the force constant would be

$$\alpha = M\omega_m^2/4 = 84 \quad \text{erg/cm}^2 \tag{72}$$

If we take for the temperature $T = 300°\text{K}$, we find from Eq. (56) that

$$\bar{\Delta}_0(0) = \langle \Delta_0^2(0) \rangle^{1/2} = (kT/\alpha)^{1/2} = 2.2 \quad \text{Å} \tag{73}$$

[the high-temperature expansion used to obtain Eq. (48) required $kT \gg \hbar\omega_m$, that is, when $\omega_m = 10^{12}\ \text{sec}^{-1}$, $T \gg 8°\text{K}$, which is certainly satisfied]. The monomer–monomer spacing, the lattice constant, is of the order of 7 Å, so that

$$\delta_0 \equiv 3\bar{\Delta}_0(0)/a = 0.94 \tag{74}$$

This can be used in Eq. (65) to obtain, after multiplying through by N,

$$N\delta = 1.2 \left[\frac{N}{(N-1)} \frac{1}{2N\delta} \left(1 - \frac{1}{N\delta}\right) \right]^{1/2}; \qquad N \geqslant 3 \tag{75}$$

which simplifies to

$$N\delta = 2.88[(N-1)/N] + 1 \tag{76}$$

The minimum value of $N\delta$ occurs when $N = 3$, in which case $N\delta = 2.92$, so that the approximate formulas of Eqs. (31), (63) ,and (69) are valid to within 1 %. (When $N = 2$, $\tilde{n} = 1$ and $\delta = \delta_0 = 0.94$, whence $N\delta = 1.88$. However, this case is of no interest, as the walker is always trapped on the first step whether or not the stepping probabilities are symmetrical.) The maximum value of $N\delta$ is 3.88. For very large N, $N\delta \approx 3.88$ and $N^3/(N-1) \approx N^2$ in Eq. (31), and, therefore,

$$\begin{aligned} \tilde{n} &\approx \frac{N^2}{2(3.88)} \left(1 - \frac{1}{3.88}\right) \\ &= 0.0955N^2; \qquad \text{large } N \end{aligned} \tag{77}$$

For a symmetrical walk and large N, one has

$$\tilde{n}_{\text{sym}} \approx N^2/6 = 0.167N^2 \tag{78}$$

The lifetime is thus reduced by 43 % when N is large and $\delta_0 = 0.94$. The reduction would, of course, be less if δ_0 were smaller. When $N = 30$, Eqs. (76) and (31) give a percentage reduction of the lifetime of 42 %. For smaller values of N, say, $N = 6$, we find a reduction of 36 %. We see that the reduction in the lifetime is not strongly dependent on N, nor, for a periodic distribution of traps, on the period s.

The width of the dip in the curve of lifetime *versus* $\omega_m\tau$ can be calculated accord-

Table I

N	$(\tilde{n}/\tilde{n}_{\text{sym}})_{\max}$	ϵ
6	0.64	−0.050; 0.690
12	0.60	−0.016; 0.177
30	0.58	−0.003; 0.032

ing to the prescription following Eq. (71). When $\tilde{n} \gtrsim 6$, the sum in Eq. (71) can be approximated by an integral to give

$$\delta' = \frac{2}{[\pi(\pi+\epsilon)]^{1/2}} \frac{\delta_0}{\tilde{n}'} \int_0^{\tilde{n}'-1} dn \frac{\cos(n\epsilon) + \sin(n\epsilon)}{\sqrt{n}}$$

$$= \frac{2\sqrt{2}\,\delta_0}{\tilde{n}'[\epsilon(\pi+\epsilon)]^{1/2}} \{C[\epsilon(\tilde{n}'-1)]^{1/2} + S[\epsilon(\tilde{n}'-1)]^{1/2}\} \tag{79}$$

where $C(x)$ and $S(x)$ are the Fresnel integrals.[18]

Equation (79) can then be solved numerically for ϵ. Table I lists the values of ϵ which give one half of the maximum reduction in the lifetime for $N = 6$, 12, and 30. The fractional reduction in the lifetime is plotted as a function of $\omega_m\tau$ in Fig. 4. This graph is meant only to show the width of the dip in the lifetime curve, and not its detailed shape. It is clear from Table I and Fig. 4 that the dip in the curve is highly asymmetrical. This is due to the fact that there are no lattice frequencies greater than

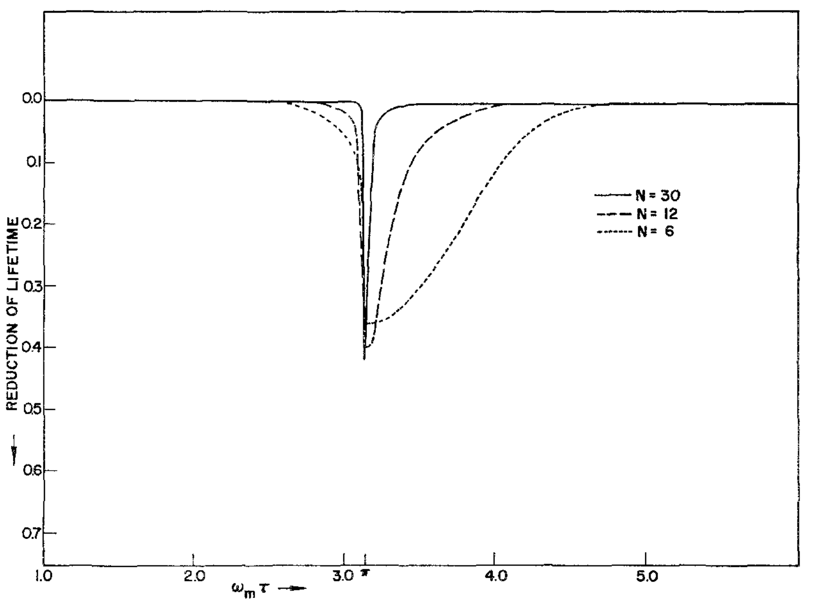

Fig. 4. Lifetime reduction as a function of maximum lattice frequency times the time interval between steps for $N = 6$, 12, and 30. These curves are meant to indicate the half-width of the depression, and not the detailed line shape.

$\omega_m t$, but many that are smaller. The width of the depression, about $\omega_m \tau = (2\nu + 1)\pi$, can be calculated in a similar manner. The resulting curves would be similar to those in Fig. 4.

5. CONCLUSION

We have seen that lattice vibrations can give rise to an asymmetry in the stepping probabilities of the random walk representing exciton motion on a linear polymer, and that this asymmetry can cause a reduction in the exciton lifetime provided $\omega_m \tau$ is approximately an odd multiple of π. For typical lattice parameters, the reduction is of the order of 40% for $\omega_m \tau \approx \pi$, and for moderate trap concentrations (between 5% and 20%), $\omega_m \tau$ could be as much as about 6% greater than π and still give a reduction of the order of 20% in the lifetime. It should be noted that the average asymmetry in the stepping probabilities δ varies as $T^{1/2}$ and, while this is not a strong temperature dependence, it can be experimentally controlled. Studies of the decay rate of donor fluorescence in poly-L-tyrosine and related polypeptides may prove experimental verification of this theory.

Work on extending this analysis to higher dimensions is in progress.

APPENDIX

Let the probability of a step to the right be p if the step number is odd and q if the step number is even. Then the probability of a walker being at site l after $2n$ steps is

$$P_{2n}(l) = \frac{1}{2\pi} \int_{-\pi}^{\pi} d\phi \, [(pe^{i\phi} + qe^{-i\phi})(qe^{i\phi} + pe^{-i\phi})]^n \tag{A.1}$$

and, after $2n + 1$ steps,

$$P_{2n+1}(l) = \frac{1}{2\pi} \int_{-\pi}^{\pi} d\phi \, [(pe^{i\phi} + qe^{-i\phi})(qe^{i\phi} + pe^{-i\phi})]^n \, (pe^{i\phi} + qe^{-i\phi}) \tag{A.2}$$

We obtain, in the same way as in Section 2, the generating function evaluated at $l = 0$,

$$U_{2N}(z, 0) = \frac{1}{z^2\{[p^2 + q^2 - (1/z^2)]^2 - 4p^2q^2\}^{1/2}} \left(\frac{1 + x^N}{1 - x^N}\right) \tag{A.3}$$

$$U_{2N+1}(z, 0) = \frac{(1 + x^{2N+1}) + z(1 + x)\, x^N}{z^2\{[p^2 + q^2 - (1/z^2)]^2 - 4p^2q^2\}^{1/2}\,(1 - x^{2N+1})} \tag{A.4}$$

where

$$x = (-1/2pq)(p^2 + q^2 - (1/z^2) + \{[p^2 + q^2 - (1/z^2)]^2 - 4p^2q^2\}^{1/2}) \tag{A.5}$$

The average number of steps to be trapped is then [see Eq. (26)],

$$\begin{aligned}\tilde{n} &= \frac{1}{N-1}\frac{\partial}{\partial z}\left[\frac{1}{(1-z)\,U_N(z,0)}\right]_{z=1}\\ &= \frac{N^3 - N + 5N\delta^2}{6(N-1)(1-\delta^2)}, \qquad N \text{ even}\\ &= \frac{N^3 - N + 8N\delta^2}{6(N-1)(1-\delta^2)}, \qquad N \text{ odd}\end{aligned} \tag{A.6}$$

ACKNOWLEDGMENTS

The authors wish to thank Professors E. W. Montroll and H. M. Nussenzveig for valuable advice.

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