

One-dimensional exciton diffusion in a conjugated polymer

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One of the most interesting questions in modern transport theory has been and still is the following: What is the influence of dimensionality (including fractal) on the carrier and exciton dynamics and decay kinetics in quasicrystalline and disordered systems. An enormous amount of theoretical work has been done in this field, extended now to include direct computer simulations. Experimental data have been more difficult to find and are consequently sparse and not always convincing. Certain types of organic compounds and, in particular polydiacetylenes, constitute unique classes of nearly one-dimensional systems. Studies including photoconductive decays have been extended to include picosecond luminescence decay on PDA-1OH [poly(diacetylene-1-hydroxy-hexadiyne-diol)], a continuous highly oriented fibrous polymer. The decay laws are compared with exact results in dimensionalities $d=1$ and near 1. The present data together with the recent work on doped tetramethylammonium manganese trichloride may be evidence for the first time of one-dimensional exciton motion.

I. INTRODUCTION

Diffusion, drift, and trapping of excitations and carriers in quasi-one-dimensional (Q1D) systems is a problem of great current experimental and theoretical interest with a wide range of applications. Applications include exciton diffusion, nuclear-spin diffusion, and relaxation in Q1D systems, superionic conductors, and polymeric chains. Recent theoretical work has led to the recognition that the exact time dependence of the survival probability of a random walker depends on the system parameters, notably its dimensionality, and in general, displays nonexponential kinetics.¹⁻⁴ That this is indeed the case has been observed in low-dimensional materials where deviation from a pure single exponential is most significant.⁵ In three dimensions (3D) and for the deep-trapping model on a regular network, the deviations from single exponentiality is probably outside experimental detectability.⁶

The field effect on the trapping of charge carriers is negligible in 3D at fields of practical interest. This effect is significant in 1D. Constrained to move along 1D, carriers move by diffusion or drift in an applied electric field between sites on the chain separated by a distance a , with a mean jump rate W , until they encounter deep traps. In real solids true one-dimensionality is not achievable. Instead one has to look for highly anisotropic systems in order to observe some of the above effects. Here the class of materials known as the polydiacetylenes [hereafter referred to as PDA's] are unique in several respects.^{7,8} In the "perfect" crystalline forms PDA-TS (poly [diacetylene-bis(toluenesulfonate)]) and PDA-DCH (poly[1,6-di(*N*-carbazolyl)-2,4-hexadiyne]), these materials

consist of polymeric π -conjugated chains separated from each other by distances of up to ~ 0.7 nm (backbone to backbone), while along the chain the π -bond separation is as short as ~ 0.12 nm. Motion of charge carriers or excitons is mainly along the chain direction, with a ratio of interchain to intrachain overlap integral of π orbitals shown by conductivity experiments^{9,10} to be at least 10^3 , but which is in reality most probably in excess of 10^6 . The reason for this is that there is good reason to believe that the "excitations" form polaronic distortions (polarons and exciton-polarons).¹¹ The intrachain to interchain hopping frequency anisotropy of such self-localized excitations can therefore be considerably less than the estimate based on simple π -orbital overlap calculations.

PDA's in the crystalline and film forms represent Q1D semiconductors. Of course, a realistic way of viewing the skeletal nature of the PDA's is one that randomly contains defects which act as traps (or antitraps) with some probability x .¹² Total annihilation of the charge occurs when these carriers eventually encounter recombination centers. Such carriers disappear from the survival fraction of carriers, and therefore, do not contribute to any externally measured electric current. In practice, carrier recombination is achieved only when lateral motion of carriers trapped within the Coulomb capture radius occurs; otherwise, the carrier will remain trapped.¹³

Depending on the time and temperature domain, an ordinary trap may be indistinguishable from a recombination center. It is, therefore, appropriate to recognize two categories of defects, namely (a) traps with particle conservation (release) and (b) traps with particle annihilation (infinitely deep traps) occurring with concentration x . Re-

cent investigations of charge-carrier transport in PDA's (Refs. 14 and 15) have shown that the photocurrent decay can be described extremely well by an $\exp(-bt^{1/3})$ law in accordance with the theory of deep trapping in 1D systems, the theory described in Ref. 3-5 will be, hereafter, referred to as the (MPW) Movaghar-Pohlmann-Würtz theory. Both qualitative and quantitative information on the charge-carrier motion and the material itself has been derived through electric field and temperature studies.¹⁶

II. THE SURVIVAL FRACTION IN A ONE-DIMENSIONAL SYSTEM

The problem of diffusion and trapping in one-dimensional systems with infinitely deep traps has received considerable attention in the scientific literature both past and present, see list in Ref. 17. An exact analytic solution for the electric field and time dependence of the survival fraction in the 1D diffusion problem with randomly distributed deep traps has been derived by Movaghar *et al.*³⁻⁵ using a simple scattering analogy. This theory has been critically assessed against three other well-known approximation methods: the average- t -matrix analysis (ATA), coherent-potential approximation (CPA), and the first-passage-time (FPT) approach of Montroll.^{1,18} We shall first simply consider the 1D-exact case, a theory relevant to PDA's which are probably the closest representation of a 1D system.

Diffusive transport in the presence of traps can be derived using the master equation for the excitation density $n_i(t)$ at site i (Refs. 3 and 4)

$$\begin{aligned} dn_i(t)/dt = & - \left[\sum_j W_{ij} n_i(t) \right] + \left[\sum_j W_{ji} n_j(t) \right] \\ & - \delta_i n_i(t), \end{aligned} \quad (2.1)$$

where W_{ij} is the hopping rate between the pair of sites i and j , δ_i is the trap rate [$=\infty$ with probability x , $=0$ with probability $(1-x)$], x is the concentration of deep traps within the system. This equation is exactly solvable if we simply consider the following. As soon as we specify an initial site i the first trap on the left at site l and the first trap on the right at site m , are also specified. The remaining traps in the chains become irrelevant. This then becomes a two-trap problem which has been solved exactly by Movaghar *et al.*³⁻⁵ by configurationally averaging over all possible positions of l and m . The assumptions required here are that W_{ij} connects nearest neighbors and the initial site i is definitely not a trap.

The survival fraction $n(t, \eta)$ in the influence of a bias field η was also investigated for all times in the trap concentration range of physical interest ($x \leq 10^{-2}$), η is a dimensionless field parameter as defined by

$$(1-\eta)/(1+\eta) = \exp(-eEa/kT), \quad (2.2)$$

where e , E , and a are the electric charge, electric field strength, and the lattice constant, respectively. For small fields ($\eta \ll 1$) this reduces to $\eta = eEa/2kT$. The derived (exact) equation, in the Laplace frequency domain, can be represented by

$$n(p, \eta) = 1/p + (2x^2\gamma/p^2) \int_0^\infty d\xi e^{-x\xi} \{ [\cosh(\eta\xi) - \cosh(\gamma\xi)] / \sinh(\gamma\xi) \}, \quad (2.3)$$

where $\gamma = [(p/W) + \eta^2]^{1/2}$ and W is the symmetry zero-field jump rate. After some long and tedious algebraic manipulations involved in inverting Eq. (2.3), Movaghar *et al.*⁴ showed that

$$n(t, \eta) = 4x^2 \int_0^\infty d\xi e^{-x\xi} \left[\sum_{n=1}^\infty [1 - (-1)^n \cosh(\eta\xi)] [\pi^2 n^2 \xi / (n^2 \pi^2 + \eta^2 \xi^2)^2] \right] \exp[-(n^2 \pi^2 / \xi^2 + \eta^2) t]. \quad (2.4)$$

For $\eta \leq x$, Eq. (2.4) reduces to

$$n(t, \eta) = (4/\pi^2) e^{-\eta^2 W t} \int ds \frac{se^{-\pi^2 x^2 W t / s^2}}{[1 + (s\eta/x\pi)^2]^2} \left[\frac{e^{-s}}{1 - e^{-s}} + \frac{e^{-s(1-\eta/x)}}{2(1 + e^{-s(1-\eta/x)})} + \frac{e^{-s(1+\eta/x)}}{2(1 + e^{-s(1+\eta/x)})} \right], \quad (2.5)$$

which in the limit of zero-field bias ($\eta=0$) becomes

$$\begin{aligned} n(t) = & (4/\pi^2) \int_0^\infty ds s \cosh(s) \\ & \times \exp(-\pi^2 x^2 W t / s^2). \end{aligned} \quad (2.6)$$

In the asymptotic long-time behavior of the decay form the survival fraction for $\eta=0$ and $x \ll 1$ has been shown to be³⁻⁵

$$n(t) \sim 16 \left[\frac{x^2 W t}{3\pi} \right]^{1/2} \exp \left[-3 \left[\frac{\pi^2 x^2 W t}{4} \right]^{1/3} \right]. \quad (2.7)$$

III. EXPERIMENTAL VERIFICATIONS OF THE MPW THEORY: PHOTOCONDUCTION MEASUREMENTS

The survival fraction of random walkers in 1D $n(t, \eta)$, represented by Eq. (2.4) can be divided into two regimes: $\eta \leq x$ and $\eta > x$. In the former case, it is the diffusion of carriers which dominates their recombination whereas for the latter case, it is the drift of the carriers that dominates. For $0 \leq \eta \leq x$, the survival fraction $n_1(t, \eta)$ can be represented by Eq. (2.5). For $\eta > x$, the survival fraction $n_2(t, \eta)$ is given by

$$n_2(t, \eta) = n_1(t, \eta) + L(t, \eta), \quad (3.1)$$

where

$$L(t, \eta) = 8x^2(\eta - x)^2 e^{-\eta^2 W t} \times \left[\sum_{n=0}^{\infty} \frac{(n + \frac{1}{2}) e^{W t [(\eta - x)/2n + 1]}}{(2n\eta + x)^2 [2(n + 1)\eta - x]^2} \right]. \quad (3.2)$$

The asymptotic long-time forms of n_1 and n_2 are of the following form:

(a) For n_1 ,

$$n_1(t, \eta) \sim \exp[-3(t/\tau_1)^{1/3}] \exp[-t/\tau_2] \quad \text{as } t \rightarrow \infty \text{ with } \eta \leq x, \quad (3.3)$$

where

$$\tau_1 = \frac{4}{\pi^2(x - \eta)^2 W} \quad (3.4)$$

and

$$\tau_2 = \frac{1}{\eta^2 W}. \quad (3.5)$$

At some critical time (transition period) given by

$$t_c = \frac{\pi\sqrt{27}}{2} \frac{(x - \eta)}{\eta^3 W} \quad (3.6)$$

an equal contribution from both exponential terms in Eq. (3.3) is expected. For short and intermediate times ($t < t_c$) we should obtain an $\exp[-3(t/\tau_1)^{1/3}]$ law and for long times ($t > t_c$) an exponential law with $\tau_2 \propto 1/E^2$ is expected.

(b) For n_2 ,

$$n_2(t, \eta) \sim \frac{4(\eta - x)^2}{(2\eta - x)^2} \exp[-(2\eta x - x^2)Wt] \quad \text{as } t \rightarrow \infty \text{ with } \eta \gg x. \quad (3.7)$$

This implies a time constant $\tau \propto 1/E$.

The first observation of electric-field-induced trapping effects was made by Haarer and M \ddot{o} hwald¹⁹ on a material which was however only moderately anisotropic compared to the PDA's. More recent experimental observations carried out by Hunt *et al.*¹⁴ on PDA-1OH (polydiacetylene-1-hydroxy-hexadyne-diol) and by Seiferheld *et al.*¹⁵ on PDA-TS bombarded by He⁺ ions in the time range (1–2) 10⁴ s both verified the predictions of the MPW theory; the two most important striking predictions being (a) for low fields and intermediate times, the decay $\sim \exp[-(t/\tau_1)^{1/3}]$, and (b) for low fields and long times, the decay $\sim \exp(-t/\tau_2)$.

IV. LUMINESCENCE STUDIES OF 1D SYSTEMS

A. Introduction

The spatial mobility of excited states (i.e., the radiationless transport of excitations) is perhaps the most intriguing feature to researchers in the field. To understand excitation transport requires a close examination of those

processes which affect the wavelike character of the excitons. In situations in which the exciton transport processes and observables relating to it require (do not require) consideration of probability amplitudes, phase relationships, and interference effects, the exciton is said to be *coherence (incoherent)*. In the coherent case, the exciton can be described as a quasiparticle and transport as wavelike in a manner that closely resembles the description of a wave packet. Processes such as exciton-impurity scattering, exciton-defect scattering, and exciton-phonon scattering can destroy exciton coherence, changing the mode of transport to incoherent hopping. In real systems, transport will be mostly of mixed character; coherent and incoherent transport being the limiting cases. An exciton may move with a well-defined group velocity for some distance before losing memory of its velocity (initial state). The distance traveled is referred to as the "coherence length." Under such circumstances, at long times, macroscopic transport will be diffusive in nature. Transport will occur as a random walk, but the step size in the walk will be of the order of the coherence length rather than the lattice spacing. The larger step size will result in a greatly increased macroscopic diffusion coefficient.

Studies on *strictly-* and *quasi-*1D systems have been previously made by Fayer *et al.*^{20–25} Their approach utilized the FPT theory mentioned above.^{1,18} Though in general excellent, the FPT is nevertheless still an approximation and deviates from the exact behavior in 1D well within the experimental domain of observation. A detailed description of the FPT will be given in a later section. We shall first review very briefly the experimental and theoretical developments due to Fayer *et al.* The recently developed MPW theory⁵ will then be used to formulate a new theory for exciton transport in strictly 1D, quasi-1D, 2D and 3D systems. For the latter two dimensions the theory developed will only be discussed briefly, the model used is approximate in relation to the present case but exact in the long-time limit. This new theory will be then compared with the earlier Fayer-Montroll (FM) theory. Attempts will then be made to fit reported data. And finally, we shall analyze luminescence from PDA-10H, a system that is known to display Q1D behavior.

B. Energy migration in strictly- and quasi-1D systems: FM approach

Attempts to study 1D-exciton systems have been made in the past on two molecular solid systems: (a) first triplet (T^1) of 1,2,4,5-tetrachlorobenzene^{20–25} (TCB), and (b) first triplet (T^1) of 1,4-dibromonaphthalene²⁶ (DBN).

In such systems, the 1D exciton transport is believed to arise as a consequence of the intermolecular interactions between molecules arranged along one translational direction in the crystal, such that, the molecules form linear chains along which exciton transport can occur. Impurities, intrinsic scattering species which may be isotopic impurities, chemical impurities or lattice defects, are believed to play a crucial role in the exciton migration in 1D systems and can be of the following two types.

(a) *Impurity scattering sites*—i.e., impurity sites which have an excited state with higher-energy level than the corresponding host crystals exciton band. Such impurities can severely inhibit exciton transport by “caging” a mobile exciton. In such a case, the exciton can either bounce back or tunnel through to the adjacent chain or undergo an intrachain and/or interchain hopping to a different cage.

(b) *Impurity trapping sites*—i.e., impurity sites which have an excited-state energy level below that of the corresponding host exciton band. Such impurities also inhibit exciton transport by localizing, i.e., trapping a mobile exciton.

In either case, the impurity site will exist if the energy difference S between the impurity site excited-state energy level and the exciton band center, is large relative to β , the intermolecular interaction matrix element, responsible for on-chain 1D exciton transport, i.e., $S \gg \beta$. If $S \approx \beta$, the impurity level will be amalgamated into the band and will produce nonlocal scattering.²³

The net result is that independent of the macroscopic mode transport, impurity scattering sites force exciton transport in Q1D systems to be macroscopically diffusive. Thus, exciton migration can be described as a random walk between linear cages or “supersites” on the lattice of cage, a “superlattice,” when viewed on a time-scale long relative to the time required to tunnel out of a particular cage. If the concentration of impurities is such that the on-chain cage stepping frequency becomes comparable to the cross-chain frequency, then the exciton transport may behave as a random walk on a 2D or 3D superlattice. Multidimensional walks therefore increase the total number of distinct sites sampled and consequently increase the ability of an exciton to reach a distant trap site. This has the effect of dramatically altering the exciton transport. On encountering cages which have trap sites, “super-traps,” the exciton will trap on its first visit, even if the single encounter trapping probability is quite small.

Very recently, 1D exciton transport and trapping kinetics has been reported by Auerbach and McPherson²⁷ in doped crystals of $(\text{CH}_3)_4\text{NMnCl}_3$ (TMMC). The luminescence decay curves coupled to a structural analysis have led the authors to suggest an enormous anisotropy of interchain to intrachain exciton motion of the order of 10^8 . A model presented by Fayer *et al.*²⁵ considers the time evolution of an exciton population ensemble interacting with dilute scattering and trap impurities in a 1D system. This model utilizes a Green’s-function formalism for calculating the properties of random walks on lattices of various dimensionality and configuration developed by Montroll. This approach is the FPT approach which relies on the number of distinct lattice sites sampled by an exciton at time t , $S(t)$. The time-dependent populations of the band states $E(t)$ and the trap states $T(t)$ are described by the rate equations:

$$\dot{E}(t) = -[K_E + K_L(t)]E(t), \quad (4.1)$$

$$\dot{T}(t) = -K_T T(t) + K_L(t)E(t), \quad (4.2)$$

where K_E , K_T , and $K_L(t)$ are the decay-rate constant (inverse lifetime) for the band states, decay-rate constant for

trap states, and the instantaneous rate of exciton localization per unit population, the time-dependent trapping rate function, the form of which depends on the effective transport topology. This model does not include thermally assisted promotion from a localized trap state since such an effect will be negligible at sufficiently low temperatures.

In general, it turns out that the trapping rate function is time dependent, and for strictly 1D systems, has the form (FPT approximation)

$$K_L(t) = At^{-1/2}, \quad (4.3)$$

independent of the microscopic mode of transport.²³ The value of the trapping rate coefficient, A , does depend on the mode of transport. It has been shown by Fayer²⁵ that, in the case of dilute concentration of impurities (χ), A is proportional to χ and the χ dependence can be used to assess the transport topology and the cross-chain stepping frequency. For an exciton system which is strictly 1D in its transport, the time-dependent exciton and trap populations have been calculated to be given by

$$E(t) = \exp[-K_E t - 2At^{1/2}], \quad (4.4)$$

$$T(t) = \exp(-K_T t) \left[\frac{A^2 \pi}{(K_E - K_T)} \right]^{1/2} \exp \left[\frac{A^2}{(K_E - K_T)} \right] \\ \times \left[\operatorname{erfc} \left[[(K_E - K_T)t]^{1/2} + \frac{A}{(K_E - K_T)^{1/2}} \right] \right. \\ \left. - \operatorname{erfc} \left[\frac{A}{(K_E - K_T)^{1/2}} \right] \right]. \quad (4.5)$$

Reasonable agreement between theory and experiment has been claimed by the authors. We note that their calculated curve did not involve any adjustable parameters.

An exciton performs a macroscopic random walk amongst the sites of the superlattice in a system that is close to but not strictly 1D. Fayer *et al.* suggest a time-dependent trapping rate function of the form

$$K_L(t) = K_L + B_L t^{-1/2} \quad (4.6)$$

for both types of mode transport. The values of the trapping parameters K_L and B_L depend on all of the physical parameters of the strictly 1D problem and on the rate and relative anisotropy of the exciton walk on the 3D superlattice. The time-dependent exciton and trap populations for Q1D systems can be solved to yield the appropriate rate equations (see Ref. 23 for details).

C. Exact 1D exciton transport: MPW approach

We now derive the exact 1D decay law for excitons using the formalism of the MPW theory discussed earlier. The survival fraction of random walkers in 1D $n(\eta=0, t)$ for the case of physical interest ($\eta \leq x$) can be written as [refer to Eq. (2.6)]:

$$n_1(t) = \frac{8}{\pi^2} \int_0^\infty ds \frac{s \exp(-\pi^2 x^2 W t / s^2)}{(e^s - e^{-s})}. \quad (4.7)$$

1D-decay law from photoconduction experiments is

known to be of the form [refer to Eq. (2.7)]:

$$E(t) = n_1(t)e^{-K_E t}. \quad (4.8)$$

Substituting Eq. (4.8) into Eq. (4.2), we obtain

$$\dot{T}(t) = -K_T T(t) - e^{-K_E t} dn_1(t)/dt. \quad (4.9)$$

We can now solve for $T(t)$ using the appropriate boundary conditions [$T(0)=0$]:

$$T(t) = -e^{-K_T t} \int_0^t e^{\beta t'} \frac{dn_1(t')}{dt'} dt', \quad (4.10)$$

where $\beta = K_T - K_E$. Inserting Eq. (4.7) into Eq. (4.10) and after some algebraic manipulation it is easy to show that

$$T(t) = \frac{8e^{-K_T t}}{\pi^2} \int_0^\infty ds \frac{s [1 - e^{-(\beta - W_1/s^2)t}]}{(e^s - e^{-s})[(s^2(K_E - K_T)/W_1) + 1]}, \quad (4.11)$$

where $W_1 = \pi^2 x^2 W$.

Using

$$Y = \frac{K_T}{W_1} = \frac{16K_T}{\pi^3(P_a)},$$

where $P_a = 16\pi^2 x^2 W/\pi^3$,

$$Z = \frac{K_E - K_T}{W_1} = \frac{16(K_E - K_T)}{\pi^3(P_a)}$$

and

$$t' = W_1 t = \frac{\pi^3(P_a)t}{16},$$

we finally obtain

$$T(t) = \frac{8}{\pi^2} e^{-Yt'} \int_0^\infty ds \frac{s}{(e^s - e^{-s})\gamma} (1 - e^{-\gamma t'/s^2}), \quad (4.12)$$

where $\gamma = 1 + s^2 Z$. Equation (4.12) can now be solved numerically.

Figure 1 is a plot of $T(t)$ versus t and illustrates the effect of increasing the coefficient ($\propto P_a$) of the time-dependent trapping rate function for exact 1D transport based on the MPW formalism, on the time-dependent intensity of trap emission following impulse optical excitation of the exciton band. The rate constants for the exciton and trap decay, K_E and K_T , respectively, are 36 and 27 s^{-1} . As P_a is increased, the population maximum shifts to shorter times and the integrated population of the trap increases.

D. The survival fraction in dimensions greater than 1:

The first-passage-time approach

One of the most reliable methods to evaluate the survival probability in an ordered system is the first-passage-time (FPT) method due to Montroll and Weiss.^{1,18} This technique applies to the situation of infinitely deep traps at low concentrations x . In the FPT one computes the average number of new sites visited by the particle in a time t , $S(t)$. In Laplace space, this quantity

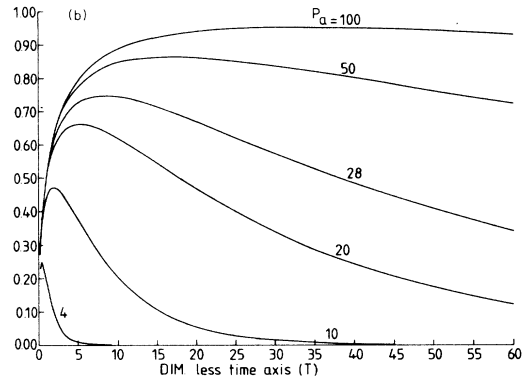
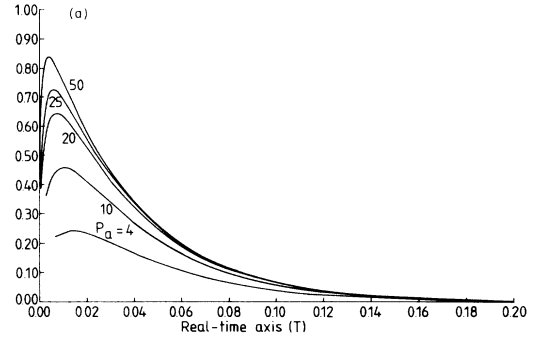


FIG. 1. 1D-exact case—plot of $T(t)$ vs t , effect of varying parameter P_a . (a) P_a vs real-time axis; (b) P_a vs t' (see the text).

can be evaluated using the local propagator as described in Ref. 28. The survival fraction $n(t)$ is then given by (cubic lattice):

$$n_{\bar{d}}(t) = \exp[-xS_{\bar{d}}(t)] \quad (4.13)$$

where

$$\left\{ \begin{array}{l} \sqrt{(8/\pi)}(2W_1 t)^{1/2} \text{ for 1D,} \end{array} \right. \quad (4.14a)$$

$$S_{\bar{d}}(t) = \frac{\pi(4W_2 t)}{\ln(4W_2 t)} \text{ for 2D,} \quad (4.14b)$$

$$6W_3 t/\phi \text{ for 3D.} \quad (4.14c)$$

ϕ is Watson's number and is given¹ by $\approx (0.66)^{-1}$, $W_{\bar{d}}$ is the hopping frequency and x is the trap concentration. For anisotropic lattices in the presence of an electric field one refers to the work of Alexander *et al.*²⁸ The FPT agrees with the mean-field theory (CPA) (Ref. 29) for small x and $\bar{d}=3$. Mean-field theory is more reliable at high concentrations $x \geq 0.1$; the FPT is by its very logic a low-concentration approximation.

The above result [Eqs. (4.13) and (4.14)] should now be compared with the exact asymptotic ($t \rightarrow \infty$) laws valid for any dimension \bar{d} including fractal values. The asymptotic long-time form of the survival fraction $n(\eta=0, t \rightarrow \infty)$ of the excitations or carriers, in the pres-

ence of a small concentration of deep traps ($x \ll 1$), is given by³⁰

$$n(t) \sim \exp[-(x^{2/\bar{d}}/t_0)^{\bar{d}/(2+\bar{d})}\gamma_{\bar{d}}] \text{ as } t \rightarrow \infty, \quad (4.15)$$

where \bar{d} is the fracton or spectral dimensionality of the system. It is rather unfortunate that Eq. (4.15) is only valid under the conditions specified above, i.e., $\eta=0$ and $t \rightarrow \infty$. In practice, in the relevant time domain of interest, it is difficult to experimentally show the validity of Eq. (4.15) because of the smallness of the survival fraction at those times,³¹ exceptions are \bar{d} values equal or near to 1.

Computer simulations for the survival fraction in 2D and 3D have found it extremely difficult to determine crossover points to the asymptotic forms of Eq. (4.15). Recent calculations by Havlin *et al.*⁶ have shown that the survival fraction has to be less than $\sim 10^{-13}$ in $\bar{d} > 2$ before the asymptotic form of Eq. (4.15) appears. This implies that in the experimentally relevant temporal domain the FPT is usually valid for higher dimensionalities ($\bar{d} \sim 3$) and the decay law is well described by a simple exponential.

For the 2D case ($\bar{d}=2$), it follows from Eq. (4.15) that

$$n(t) \sim \exp(-At^{1/2}) \quad (4.16)$$

with $A \propto x^{1/2}$. Note that Eq. (4.16) has the same form as the 1D FPT law except for the very important point that in FPT, $A \propto x$, and that the asymptotic 2D law is in practice probably almost impossible to observe because of the magnitude of $n(t)$ when Eq. (4.16) sets in. Thus $\exp(-At^{1/2})$ in relation to FPT is physically significant whereas the asymptotic forms of Eq. (4.16) with $\bar{d} \geq 2$ cannot certainly be observed in the present experimental conditions.

In order to gain a better understanding of the exact behavior of Eq. (4.16) as $t \rightarrow \infty$, let us briefly show how these forms arise for a 2D system in the presence of an electric field using a simple model. The extensions to "other" values of \bar{d} is then straightforward.

Thus, instead of a purely 1D system consider a rectangle of size aL_x, aL_y with the electric field in the x direction (bias y), jump frequencies W_x and W_y , respectively, and traps all along the boundary of the system. The survival fraction becomes (continuum limit and low-trap concentration $x \ll 1$)

$$n(t, \eta, L_x, L_y) = \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{4n^2\pi^2 L_z}{(n^2\pi^2 + \eta^2 L_x^2)^2} \frac{4L_y}{m^2\pi^2} \exp\left[-\left(\frac{\pi^2 n^2}{L_x^2} + \eta^2\right) W_x t\right] \exp\left[-\frac{\pi^2 m^2 W_y t}{L_y^2}\right] \\ \times [1 - (-1)^n \cos(n\eta L_x)][1 - (-1)^m]. \quad (4.17)$$

The probability of finding a trap-free region of area $L_x L_y$ is $P(L_x, L_y)$ and is of the form

$$P(L_x, L_y) = A(x) e^{-xL_x L_y} e^{-xL_x} e^{-xL_y},$$

where x is the trap concentration and A is chosen so that P be normalized. Averaging $n(t, L_x, L_y)$ using Eq. (4.17) will give us an $\exp(-At^{1/2})$ law for $\eta=0$ in the long-time limit. Extensions to higher dimensionality then trivially follow. Unfortunately we cannot use the above derivation to estimate the actual times at which crossover occurs to the asymptotic form because the above model assumes that the traps are on the total perimeter of the region $aL_x, +aL_y$. In reality x should be replaced by some $\gamma(x)$ where $\gamma(x) \ll x$, but the form, and thus, the asymptotic laws are rigorously valid for the true model. This includes the electric-field dependence. A detailed discussion of the theory of trapping in the presence of an electric field in dimensions $\bar{d} \geq 1$ will be presented elsewhere.³² The above serves only to illustrate the origin of the $\exp[-(t/t_0)^{1/2}]$ law.

E. Comparison of 1D FPT with 1D exact (MPW) and 3D FPT in Fayer's exciton trapping model

Inserting the form (4.16) into Eq. (4.10), we obtain

$$T(t) = A e^{-K_T t} \int_{t'=0}^t \frac{t'^{-1/2}}{2} e^{-A(t')^{1/2}} e^{(K_E - K_T)t'} dt'. \quad (4.18)$$

Equation (4.18) is equivalent to

$$T(t) = \frac{A e^{-K_T t} e^{\beta^2}}{\alpha} \left[\int_0^{\beta + \alpha\sqrt{t}} e^{-\gamma^2} d\gamma - \int_0^{\beta} e^{-\gamma^2} d\gamma \right], \quad (4.19)$$

where $\alpha^2 = K_E - K_T$, $\beta^2 = A^2/4(K_E - K_T)$, $A^2 = 16x^2 W/\pi$ for the FM (FPT) approach and $A = 2\alpha\beta$. Recall that $A \propto x^{1/2}$ for the exact asymptotic long-time form. In what follows we shall consider the FM (FPT) treatment. Using

$$A = \alpha \left[\frac{16}{\pi^3} \right]^{1/2} \left[\frac{1}{Z} \right]^{1/2}, \\ \beta^2 = \frac{4}{Z\pi^3},$$

and $Y(P_a)$, $Z(P_a)$, and $t'(P_a)$ —as before, it can be shown that Eq. (4.18) can be rewritten as

$$T(t) = e^{-Yt} \left[\frac{16}{\pi^3} \right]^{1/2} \left[\frac{1}{Z} \right]^{1/2} e^{4/Z\pi^3} \\ \times \left[\operatorname{erfc} \left[\frac{2}{Z^{1/2}\pi^{3/2}} + (Zt')^{1/2} \right] \right. \\ \left. - \operatorname{erfc} \left[\frac{2}{Z^{1/2}\pi^{3/2}} \right] \right]. \quad (4.20)$$

Equation (4.20) can now be solved numerically. A comparison of our computed simulated decay curves for the MPW exact 1D case [Eq. (4.12)] and 1D FM FPT. Equation (4.20) suggests that the curves almost exactly overlay each other.

Assuming simple 3D motion we can similarly write an expression for the survival fraction in the 3D case (approximate)— $\bar{d} = 3$ to be of the form:²⁹

$$n(t) \sim \exp(-St). \quad (4.21)$$

Equation (4.21) is in conflict with the exact asymptotics but is the correct 3D decay law for short and intermediate times.²⁹ One can easily solve for $T(t)$ using Eqs. (4.10) and (4.21):

$$T(t) = \frac{e^{-K_T t}}{1 + [(K_E - K_T)/S]} (1 - e^{-(S + K_E - K_T)t}). \quad (4.22)$$

which can be easily plotted.

F. Luminescence studies of 1,2,4,5—Tetrachlorobenzene (TCB)

Experimental studies of triplet exciton trapping in TCB carried out by Dlott *et al.*^{20–23} led them to conclude that TCB is overwhelmingly 1D with a cross-chain stepping frequency less than $5 \times 10^3 \text{ s}^{-1}$. The effect of impurities by doping TCB crystals with deuterated scattering impurities has also been investigated.²² The Fayer-Montroll model, presented earlier, gave satisfactory agreement with the experimental observations on time-resolved phosphorescence studies of TCB. It is interesting to observe that our calculations using the MPW approach also leads to reasonable agreement with the experimental data on TCB, as shown in Fig. 2. In a way this is not surprising in view of the apparent insensitivity of the time dependence of $T(t)$ in the experimental range to the precise form of the rate “function.” This can be illustrated by taking a simple exponential form as given by Eq. (4.22) and choosing the parameters so as to give the best fit to the TCB data as shown in Fig. 3. The agreement is rather good for $S = 250$ as can be seen from Fig. 3. We conclude therefore that in the case of TCB and the nature of its luminescence kinetics, a deduction on the dimensionality

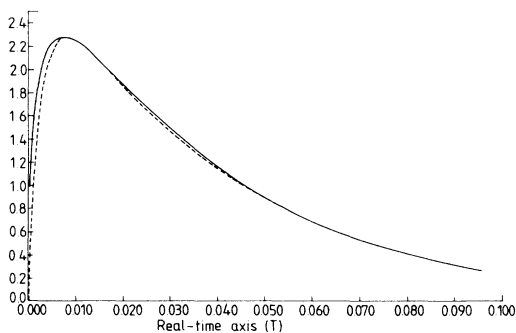


FIG. 2. MPW 1D-exact fit to h_2 -TCB data; for $P_a = 102$, solid line theory.

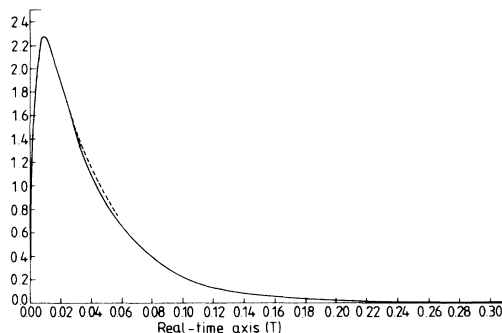


FIG. 3. Simple exponential fit using (4.22) to h_2 -TCB data; for $S = 250$, solid line is (4.22).

of the exciton motion cannot be made from the form of the time dependence alone. The correctness of the analysis due to Fayer and Dlott *et al.*^{20–25} must be inferred from the totality of their analysis and not simply from the time dependence; in other words, the first-principle’s derivation of the parameters and the verification of the concentration dependence as carried out by the authors in Refs. 20–25.

From the point of view of simple time dependence, it is clear that an experimental measurement of the survival fraction $n(t)$ makes it easier to discriminate the dimensionality of the motion. This can be seen in the recent work of Auerbach and McPherson²⁷ which we shall briefly discuss now.

G. Emission dynamics from doped TMMC

Auerbach and McPherson²⁷ have analyzed their emission decay curves from doped crystals of tetramethylammonium manganese trichloride (TMMC) as a function of time, temperature, and doping concentration of Cu^{2+} , using both the (field-free) 1D-recombination model given by Eq. (4.7) and the FPT expression. In the experimentation range the authors were not able to distinguish between the FPT and the exact 1D-diffusion theory. The latter being the exact forms for the given model of 1D diffusion this is not really necessary in this case. From the time, trap concentration, and temperature dependence of the decay curves, we can conclude that these authors have presented impressive evidence for Q1D exciton diffusion and trap kinetics in a strongly anisotropic material. They have suggested an intrachain to interchain jump-frequency anisotropy of 10^8 which is comparable and even larger than our own estimates for the polydiacetylenes. Auerbach and McPherson refer to the theoretical work of Balagurov and Vaks (see Ref. 17) who obtained an identical equation to our Eq. (4.7) using a different approach.

V. LUMINESCENCE MEASUREMENTS ON PDA-10H

1OH is a monomer which leads to the production of oriented fibrous polymer poly(diacetylene-1-hydroxyhexadiyne-diol) (PDA-1OH) on solid-state polymerization. Detailed methods of preparation of this polymer can be

found elsewhere.^{11,33} PDA-1OH has the structure $(CR-C\equiv C-R')_n$ where R and R' are $-\text{CH}_3$ and $-\text{CH}_2\text{OH}$, respectively, for 1OH and are so far the smallest substituents capable of providing a unique polymerization direction and a reactive lattice packing, primarily as a virtue of hydrogen bonding occurring between the $-\text{CH}_2\text{OH}$ groups.³⁴ On polymerization fibrillation occurs as a result of the considerable strain built up. The latter is due to the difference of the packing nature of the monomer molecules (0.41 nm apart) and the polymer repeat unit length (0.49 nm). The weak van der Waals interactions of the $-\text{CH}_3$ groups are therefore disrupted. This produces fibers having very good crystallinity with a high degree of chain alignment as shown by the optical dichroism. The polymer chain axes lie along the fiber axis as revealed by electron diffraction studies.³⁵ Typically, the fibers are more than 10 μm in length, and about 60 nm in diameter, as obtained from small-angle x-ray scattering studies.³⁶ This polymer is clearly less perfect than PDA single crystals such as PDA-TS and PDA-DCH. Local defects such as chain kinks, dislocations, cross links (unlikely), etc., therefore alter the dimensionality to $\hat{d} \geq 1$, in other words, these systems are quasi-one-dimensional. Misaligned chains have been observed by electron microscopy. The effect of disorder (present only to a small extent) will have important consequences on the diffusivity and drift velocity of carriers or excitations.³⁷

The introduction of defects and/or disorder in PDA chains opens up a weak radiative channel which is, however, in strong competition with an efficient nonradiative channel. PDA-1OH is an interesting material in that it has successfully been used to study both Q1D-charge and -exciton transport. Photoconduction experiments on this polymer (and on PDA-TS) strongly support the 1D-diffusion theory (see Sec. III). Fluorescence lifetime measurements were used in this work as an alternative means not only to probe the (quasi-)1D nature of PDA-1OH, but also to test the state of art of the various proposed theories.

Figure 4 shows linear decay (dotted line) and pump (solid-line) profiles for PDA-1OH (at room temperature) when pumped using the 476.5-nm line of the Ar^+ laser

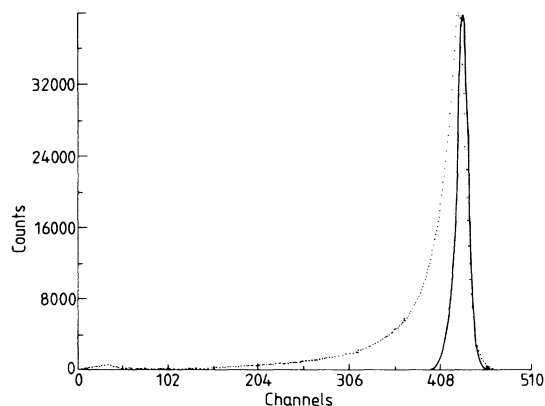


FIG. 4. Fluorescence decay of PDA-1OH (300 K), raw data.

which was employed in the mode-locked and cavity dumped configuration. A detailed description of the experimental set-up can be found elsewhere.³⁸ Analysis of several decay and pump curves revealed good fits to two exponential terms.³⁹ However, the time constants (τ_i) obtained crucially depended on the sampling window of the decay profile we choose. Longer τ values were obtained at longer times; τ values changing from about 20 ps to 2.25 ns. This suggests that the decay is neither single nor double exponential but involves a distribution of decay times. Considerable programming effort would be required to fit this data, after *either* deconvolution of the data *or* reconvolution of the fitting function, to the Eqs. (4.9), (4.13), and (4.16) derived from the MPW theory for 1D-exciton migration. To get over this problem the data were fitted to several exponentials to obtain the best representation of the decay, and then to fit the latter to the appropriate fitting function. It was found that six-exponential terms were adequate for this purpose, as depicted in Fig. 5. The fitting function in this case was the normalized version of Eq. (4.10) without the preexponential term. Plotting this function on a log versus t^0 plot, for the appropriate time domain, reveals a straight line for $\alpha=0.45$. This is very convenient since it allows us to plot the data on similar axes and to visually inspect the fit. It was found that PDA-1OH decay gave a value of $\alpha=0.425$; in close agreement with the predictions of the MPW theory.

Figure 6 shows a typical decay profile of PDA-1OH at 4.2 K when excited using 5-ps, 590-nm-laser pulses; the emission (monitored at 645 nm) being recorded on a streak-camera setup at Clarendon Laboratory (Oxford

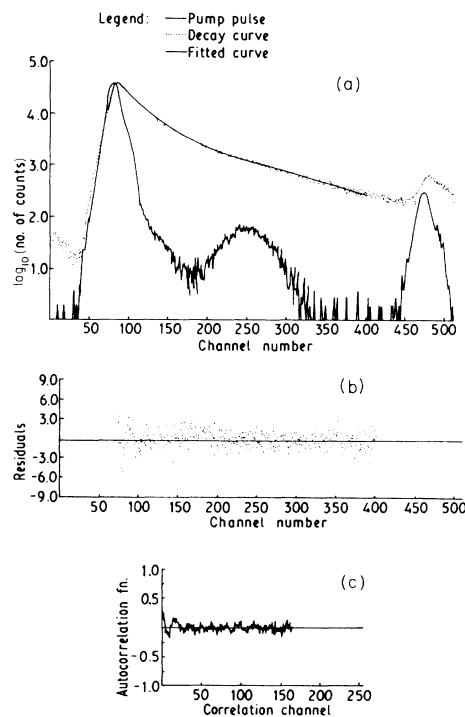


FIG. 5. A six exponential fit to PDA-1OH fluorescence data.

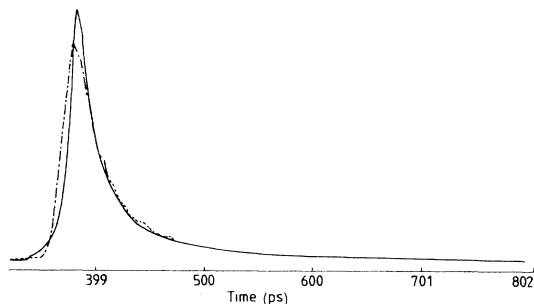


FIG. 6. PDA-1OH luminescence decay at 4.2 K, raw data from Ref. 41. Solid line is an $\exp[-(t/t_0)^{1/3}]$ fit.

University) by Hayes *et al.*^{40,41} These authors suggest the fitting function to be double exponential.⁴⁰ More recently, the same authors suggest a more complex fitting function to describe the decay:⁴¹

$$a_1 \exp(-b_1 t) + a_2 \exp(-b_2 t) + ct^{-\alpha}. \quad (5.1)$$

We note that no physical significance was attached to the latter function. On the other hand, fitting the data on a log versus t^α plot where $\alpha=0.45$ [as a close representation to the MPW theory, viz, Eq. (4.9)], reveals a straight line, as shown in Fig. 7. One must appreciate that the MPW 1D-diffusion model to be the simplest model consistent with the data. The inclusion of several other parameters, as suggested by Hayes *et al.*, requires therefore justification. Of course, the addition of more parameters will evidently yield better fit to the data.

In this connection it may be worth pointing out that a 1D-diffusion model has been used to describe the decay of photoinduced absorption in polyacetylene.⁴² The motion

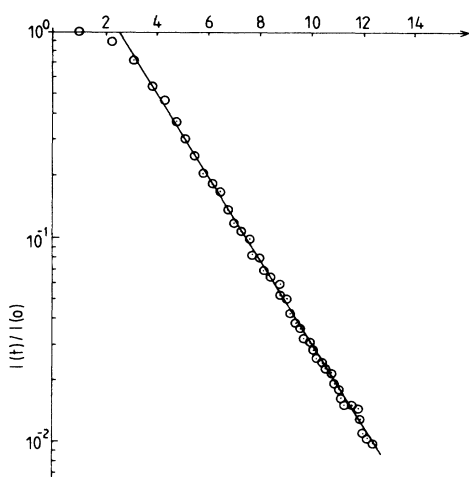


FIG. 7. Experimental fit [$\exp(-t^a)$] to PDA-1OH fluorescence at 4.2 K with $a=0.45$. $a=0.45$ gives a slightly better representation both of the data and the theory law from (2.6) over this range in time.

of a carrier to a recombination site, as observed in PDA-1OH, is field dependent and is given by Eq. (3.3), while for recombining mobile polarons in polyacetylene the decay is of the form $\text{erfc}[-(t/\tau)^{1/2}]$, which can be approximated by $t^{-1/2}$ over a wide temporal range.⁴² The reason is that in this case we are dealing with a single (mobile) trap, which is the other polaron, rather than with two fixed traps at random positions. The exact decay dynamic in the former case is $\text{erfc}(-t/\tau)^{1/2}$, whereas in the latter it is given by Eq. (4.12). It is evident that the room-temperature luminescence decay of PDA-1OH cannot be described by a function of the form $t^{-\alpha}$.

The data obtained from this work and Refs. 40 and 41 exhibit a different slope (q) of the decay functions when plotted on log versus t^α plot: $q(300 \text{ K}) \approx -0.015$ and $q(4.2-55 \text{ K}) \approx -0.08$. This discrepancy could be due to a number of reasons: (1) the different excitation energies employed, (2) systematic error due to different instrumentation and data-acquisition techniques, and (3) sample-to-sample variation.

It is difficult to see how different initial distribution of hot excitons can affect the ultimate decay after thermalization. Systematic errors should be small but studies of photoconductivity in PDA-1OH have revealed sample-to-sample variations in properties. These are a result of small differences in sample preparation and storage producing marked differences in the fibril diameter length, orientation, etc., in the sample. The differences in the values of q are probably, a consequence of the different defect densities.

From Eq. (2.6) one obtains

$$\pi^2 x^2 W = \beta, \quad (5.2)$$

where $\beta (=1.5 \times 10^9)$ is a normalization factor between theory and experiment at $T=300 \text{ K}$. This yields

$$W = \begin{cases} 1.5 \times 10^{14} \text{ s}^{-1} & \text{for } x \sim 10^{-3}, \\ 1.5 \times 10^{12} \text{ s}^{-1} & \text{for } x \sim 10^{-2}. \end{cases}$$

The probability of creating an exciton in a PDA chain exceeds that of creating an electron-hole pair.¹¹ Photoexcitation thus results in the production of excitons which diffuse rapidly (at a rate $\sim 10^{12}-10^{14} \text{ s}^{-1}$) along the chains containing the defects. On encountering the death centers the excitons decay nonradiatively (the most likely fate) to the ground state. Those excitons that escape death centers during their (natural) lifetime, eventually decay by emitting from the exciton band states by either falling into shallow traps (present in high density) or through relaxation to (intrinsic) polaronic states. In PDA-1OH the peak in emission is red-shifted by 0.75 eV from the peak in absorption; so that the initially excited state must relax before emission. Sixl and Warta⁴³ observed a similar luminescence from short PDA chains, which they attributed to polaron formation and recombination. This emission has a much longer red-shift ($\approx 1.5 \text{ eV}$) from the peak of the excitation spectrum, and a larger lifetime than those observed from PDA-1OH. The failure to observe spins from photoinduced ESR studies on PDA-1OH under an inert atmosphere suggest that the excitations are not polarons but exciton-polarons.

These excitations are short-lived as expected and undergo a 1D motion before decaying.

We conclude by saying that it appears as if the 1D-diffusion model can be applied with confidence to PDA-1OH luminescence data at any temperature. Further experimentation and, in particular, a study of the temperature dependence of the decay is however highly desirable. The excitations in these highly ordered polymers appear to be exciton polarons. Like photoconductivity, the luminescence appears to further support the picture that

we have of the PDA's: probably the most one-dimensional semiconductor observed until now.

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