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Photocurrent kinetics in quasi-one-dimensional polymeric crystals with recombination centres

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Abstract. Trapping of charge carriers in a bias field in polymeric crystals with recombination centres is studied in the framework of a one-dimensional model. The dependence of the photocurrent temporal decay on the parameters of the system—electric field E, concentration of centres c and ratio of recombination (capture) rate ω to diffusion rate W—is obtained. In a well known paper by Movaghar, Pohlmann and Würtz (MPW theory) and subsequent papers, the model of immediate capture, $\omega = \infty$, has been used. We have shown that under slow trapping, $\omega/cW \ll 1$, the form of the kinetic curve and its evolution with changing E differ qualitatively from the predictions made with MPW theory, whose range of applicability is determined. Comparison of the new results with those reported previously is made.

1. Introduction and statement of the problem

In recent years attention has been focused on studies of excitation energy and charge transport phenomena in low-dimensional systems, particularly in quasi-one-dimensional (Q1D) crystals and polymers. There exist many organic and non-organic crystals for which a high one-dimensional anisotropy of the motion of neutral and charged quasi-particles is demonstrated experimentally [1–14]. The polydiacetylenes (PDA), forming Q1D polymeric crystals, belong to this class. Comprehensive experimental and theoretical investigations of the PDA, reviewed in [15–19], have been stimulated, in part, by their novel electro-optic qualities [1–6]. The latter can be used in molecular electronic and opto-electronic devices incorporating Langmuir–Blodgett films built-up upon PDA. In this connection the temporal behaviour of dark photocurrent and its dependence on electric field and temperature in PDA are of interest.

Different approaches have been employed to interpret photocurrent kinetics (see for example [20–23]), but the problem still seems far from being solved. Therefore, further development of theoretical models of charge transport in Q1D systems is imperative.

In PDA such as PDA-1-OH with recombination centres (which are of unknown nature [4, 6] or may be created in a special way [5]) the main path of relaxation of charge carriers after they are generated by light is believed to be provided by irreversible capture of free carriers by recombination centres or traps [4, 5, 19]. To explain the observed kinetics of this process, the Movaghar, Pohlmann and Würtz (MPW) theory of charge trapping in one dimension (1D) [22] has been used. In the paper referred to above, a chain with

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chaotically distributed traps has been considered to be the basic structural unit of a Q1D crystal. The motion of charge carriers has been regarded as a Markovian 1D random walk (or diffusion) process resulting in the trapping of a particle with unit probability whenever it occurs at a site neighbouring the trap. The latter assumption in the language of the master-equation formalism is equivalent to an infinite capture rate. Let us summarise briefly the main results of MPW theory.

It was shown in [22] that the influence of a bias electric field E on the time evolution of the charge carrier density $\rho(t)$ is qualitatively different in the cases of weak

$$\eta < c \tag{1}$$

and strong

$$\eta > c \tag{2}$$

fields, where η is the bias parameter ($\eta \propto E$), which defines the charge drift efficiency in the field E (see equations (13) and (15)).

Under the condition (1)

$$\rho(t) = \begin{cases} \exp\{-\frac{3}{2}[2\pi^2(c-\eta)^2 Wt]^{1/3}\} & [2\pi^2(c-\eta)^2 W]^{-1} \ll t \ll t_c \\ \exp(-\eta^2 Wt) & t \gg t_c,\ t_c = (c-\eta)/\eta^3 W \end{cases} \tag{3}$$

and if the second inequality holds, we have

$$\rho(t) = \frac{4(\eta - c)^2}{(2\eta - c)^2} \exp[-(2\eta c - c^2)Wt] \qquad (2\eta c - c^2)Wt \gg 1. \tag{4}$$

As is easily seen, the decay law $\rho(t)$ is controlled by the strength of a bias field. An increase in E will result in a shift to shorter times of the cross-over point at which the dependence $\propto \exp(-t^{1/3})$, which corresponds to Balagurov–Vaks asymptotics [24] caused by trap density fluctuations, is expected to change to an exponential one. At strong fields the intermediate Balagurov–Vaks asymptotics disappear and the definition of the exponential decay rate constant, $K = \eta^2 W$, is replaced by $K = (2\eta c - c^2)W$.

The peculiarities of the dependence $\rho(t)$ on the parameters c, W and η have been related to the observed dark photocurrent kinetics in PDA-1-OH [4, 5].

It should be stressed that in accordance with the MPW theory predictions, the character of the charge-density decay law is defined by the relation of two parameters, η and c, only. This is a direct consequence of the assumption that the charged particle capture (recombination) rate is infinite (this rate is hereafter denoted by ω), although this is hardly realistic. Moreover the MPW model is evidently irrelevant to the capture-rate-limiting process when the finite value of ω should be taken into account. An illustration of such a situation is given in figure 1, where a part of the chain between two traps (deep minima in the potential energy profile) is shown. The energy wall that is to be overcome in the capture process can be rather high due, for example, to distortions introduced by defects which play the role of traps. In this case a particle performing random walks on a chain segment between traps will undergo multiple reflection from a barrier before being trapped.

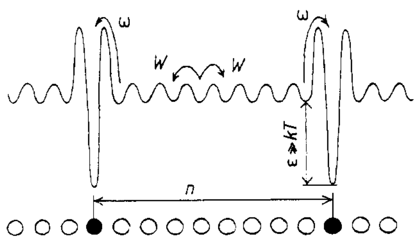

Figure 1. Energy profile of a chain with traps in zero bias field: ○, host molecules; n, their number in a given segment; ●, trap molecules; W, particle jumping rate between host molecules; ω, jumping rate from the host to the trap molecule. The potential energy of a particle at the trap site, ε, is supposed to be much below the energy minimum associated with a particle on a host molecule, i.e. the average thermal energy kT is much less than ε.

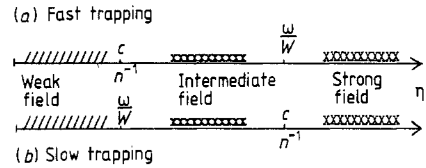

Figure 2. Two different sequences in the heirarchy of the characteristic parameters (increase is from left to right). For (a) fast and (b) slow trapping, the transition from weak to strong bias fields (and also from weak to intermediate ones in case (b)) leads to qualitative changes in the kinetic curve $\rho(t)$ (see figure 3).

The small rate of capture can affect the observed decay kinetics of diffusing and trapped particles in a special way. In the absence of bias, this has been demonstrated by various examples in [25–28]. In particular, in the cases of fast

$$\omega/Wc \gg 1 \tag{5}$$

and slow

$$\omega/Wc \ll 1 \tag{6}$$

trapping, the dependences $\rho(t)_{\eta=0}$ differ qualitatively from each other. In contrast to the first case, when $\rho(t)_{\eta=0}$ deviates weakly from that expected for immediate capture, $\omega = \infty$, there exist intermediate asymptotics in the dependence $\rho(t)_{\eta=0}$ which correspond to the slow trapping. The latter is

$$\rho(t) = \sqrt{\pi}(2c\omega t)^{3/4} \exp[-2(2c\omega t)^{1/2}] \qquad c\omega t \gg 1 \qquad c\omega t \ll (\pi^2 Wc/\omega)^2. \tag{7}$$

Note that the characteristic timescale in (7) does not coincide with that in equation (3) for $\eta = 0$. Besides, the main asymptotics, $\propto \exp(-t^{1/3})$, are realised at such large times, $c\omega t \gg (\pi^2 Wc/\omega)^2$, that the quantity $\rho(t)_{\eta=0}$ is extremely small and the deviation of the particle motion from being strictly one-dimensional may lead to considerable changes in the particle-density decay kinetics. For these reasons the observation of the dependence proportional to $\exp(-t^{1/3})$ may become practically impossible.

Thus following the results of [28], one can use the dependence $\rho(t)_{\eta=0}$, obtained for the case $\omega = \infty$ (which is simple and easily comparable with experiment), for a wide range of the parameter ω/W, provided the inequality (5) is satisfied. On the other hand, the *a priori* postulation and the use of the model based on the assumption $\omega = \infty$ to describe the situation that actually corresponds to the case of slow trapping will produce misleading estimations of the diffusion rate and the trap concentration in the sample under investigation.

The above points show that it is of importance to combine models used in [22] and [28] to develop a theory of charge trapping in a bias field in 1D systems, including a finite capture rate. In the framework of such an approach one can get answers to questions which are important for adequate interpretation of experimental results but still remain unclear. Let us specify these questions which stimulated us to perform this study.

From a brief discussion of the previous results it is clear that the definition of weak fields should now read

$$\eta \ll c, \omega/W. \tag{8}$$

It is quite evident that in this case the dependences given in [28] are operative, except for long-time asymptotics. Obviously, the basic MPW theory predictions concerning the charge-density decay kinetics still hold under the condition of fast trapping when $\eta \ll \omega/W$. But the inequality (5) can also be fulfilled for $\omega/W \ll 1$, so that the following situation is possible:

$$\eta > c, \omega/W \tag{9}$$

which correspnds to a new definition of strong fields. Of course, it has not been considered in the MPW approach.

Thus, it is of importance to answer the question: What are the differences in charge trapping kinetics of fast and slow trapping in strong fields? It is also of interest to ask: What kind of kinetic curves describe the process when $\omega/W < \eta < c$? Answering these questions demands a special consideration which starts from the general expression for the density of charge carriers diffusing in a chain with traps (arbitrary values of ω/W and c, $\eta \ll 1$). Below, we obtain kinetic curves for all possible hierarchical sequences of characteristic parameters (see figure 2). Note here that for some particular cases the asymptotic behaviour of $\rho(t)$ has been studied in [29].

2. Survival probability of a diffusing charged particle in a chain with traps

The backbone of a Q1D crystal with chaotically distributed recombination centres, called traps below, may be treated as a set of sequences of linear segments built up of molecules in regular sites (the word 'molecule' has a wide meaning in this context; for example, it also refers to an atom or to a certain group of atoms and molecules). The segments are bounded by defect molecules or distortions of the 1D lattice, which play the role of unsaturated traps for quasi-particles moving along chain segments. A typical example of the defected chain considered is presented in figure 1.

The length distribution of the segments is assumed to be Poisson. This is justified for small trap concentrations. A rigorous definition of the segment (linear cluster) length distribution is given in [30].

A physical quantity of interest in the two-component randomly disordered chain under consideration is a configurational average which reduces to averaging over segment lengths. Measured in experiments, the intensity of a dark photocurrent is proportional to the averaged survival probability of charge carriers in a chain with traps. It reads

$$\rho(t) = c^2 \int_0^\infty \mathrm{d}n\, n\Omega_n(t)\, \mathrm{e}^{-cn} \tag{10}$$

where $\Omega_n(t)$ is the survival probability of a carrier at time t in a segment of the length n, i.e. containing n host molecules. To calculate $\Omega_n(t)$, one needs to choose a model of quasi-particle motion.

Let us suppose that the charge carrier motion in a bias field is a stochastic Markovian process of random walks performed by random jumps between nearest-neighbour chain sites. Then, the conventional probability to find a particle at the site i ($i = 1$ to n) at time t is defined by solving the following set of Pauli master equations:

$$\frac{\partial \rho_n(i,t)}{\partial t} = -(W^+ + W^-)\rho_n(i,t) + W^-\rho_n(i+1,t) + W^+\rho_n(i-1,t) \qquad i \neq 1, n \tag{11}$$

$$\frac{\partial \rho_n(1,t)}{\partial t} = -(\omega^- + W^+)\rho_n(1,t) + W^-\rho_n(2,t) \tag{12a}$$

$$\frac{\partial \rho_n(n,t)}{\partial t} = -(\omega^+ + W^-)\rho_n(n,t) + W^+\rho_n(n-1,t) \tag{12b}$$

where $W^\pm$ is the per second probability (rate) of charge transfer between the host molecules along (+) and against (−) the bias field, and ω^+ and ω^- are the charge capture rates with the above meaning of the subscripts + and −. For thermally activated jumps, one can write

$$W^\pm = W e^{\pm\eta} \qquad \omega^\pm = \omega e^{\pm\eta} \qquad \eta = \frac{eEa}{2kT} \tag{13}$$

where W and ω are, respectively, transfer and capture rates in zero field (figure 1), e is the charge value and a is the lattice constant of the chain.

The use of one-particle equations (11) and (12) to describe the charge carrier dynamics is justified for small carrier concentrations. Some effects of the inter-particle interaction in a defected chain have been considered in [31–33].

In most cases for practical purposes, to find $\rho_n(i, t)$ and to calculate the survival probability in a segment

$$\Omega_n(t) = \sum_{i=1}^{n} \rho_n(i,t) \tag{14}$$

it is sufficient to replace the discrete model (11), (12) by a continuous one, supposing $n \gg 1$, $\eta \ll 1$, $t \gg W^{-1}$. For smooth particle density distribution at distances of the order a, the solution of (11), (12) is equivalent to the solution of the diffusion equation

$$\frac{\partial \rho_n(x,\tau)}{\partial \tau} = \frac{\partial^2 \rho_n(x,\tau)}{\partial x^2} + 2\eta \frac{\partial \rho_n(x,\tau)}{\partial x} \qquad \tau = Wt \tag{15}$$

with the boundary conditions

$$\left.\frac{\partial \rho_n(x,\tau)}{\partial x}\right|_{x=0} = (\tilde{\omega} - 2\eta)\rho_n(0,\tau) \tag{16a}$$

$$\left.\frac{\partial \rho_n(x,\tau)}{\partial x}\right|_{x=n} = -(\tilde{\omega} + 2\eta)\rho_n(n,\tau) \qquad \tilde{\omega} = \frac{\omega}{W} \tag{16b}$$

which follow from equations (12a) and (12b).

The solution of equations (15) and (16) is readily found in the Laplace transform space

$$\tilde{\rho}_n(x, s) = \int_0^\infty \mathrm{d}\tau\, \rho_n(x, \tau)\, \mathrm{e}^{-s\tau}. \tag{17}$$

The substitution of $\tilde{\rho}_n(x, s)$ obtained for the uniform initial density distribution

$$\rho_n(x, t=0) = n^{-1} \tag{18}$$

into the definition

$$\tilde{\Omega}_n(s) = \int_0^\infty \mathrm{d}\tau\, \Omega_n(\tau)\, \mathrm{e}^{-s\tau} = \frac{1}{s} - \frac{\tilde{\omega}}{n}[\tilde{\rho}_n(0, s) + \tilde{\rho}_n(n, s)] \tag{19}$$

gives

$$\tilde{\Omega}_n(s) = \frac{1}{s} - \frac{2\tilde{\omega}}{ns^2} \frac{(2\eta^2 + s)\sinh(\lambda n) + \tilde{\omega}\lambda\cosh(\lambda n) - \tilde{\omega}\lambda\cosh(\eta n) - 2\eta\lambda\sinh(\zeta n)}{(\tilde{\omega}^2 + s)\sinh(\lambda n) + 2\tilde{\omega}\lambda\cosh(\lambda n)}$$

$$\lambda = (\eta^2 + s)^{1/2}. \tag{20}$$

In the limit $\tilde{\omega} = \infty$ equation (20) turns into

$$\tilde{\Omega}_n(s) = \frac{1}{s} - \frac{2\lambda}{ns^2} \frac{\cosh(\lambda n) - \cosh(\eta n)}{\sinh(\lambda n)} \tag{21}$$

which coincides with that used in [21, 22] for calculations of the average survival probability $\rho(t)$.

Note that the function $\tilde{\Omega}_n(s)$ is not singular at the point $s = 0$. The Laplace transform in this limit defines the lifetime averaged over the initial positions of a particle which diffuses in the bias field in a chain with absorbing boundaries. The corresponding expression is

$$T_n = W^{-1} \lim_{s\to 0} \tilde{\Omega}_n(s) = W^{-1} \left(\frac{(1 + \tilde{\omega}n/2 - \tilde{\omega}/2\eta^2 - \tilde{\omega}^2/4\eta^2)\sinh(\eta n)}{\tilde{\omega}^2\sinh(\eta n) + 2\tilde{\omega}\eta\cosh(\eta n)} + \frac{(\tilde{\omega}/2\eta)(1 + \tilde{\omega}n/2)\cosh(\eta n)}{\tilde{\omega}^2\sinh(\eta n) + 2\tilde{\omega}\eta\cosh(\eta n)} \right). \tag{22}$$

The original of $\tilde{\Omega}_n(s)$ cannot be obtained analytically in the general case. Therefore, we find $\Omega_n(t)$ for a representative series of parameter relations. The details of the calculations are given in Appendix 1. The following equations present the final results

$$\Omega_n(t) = 4\pi^2 \sum_{k=1}^\infty \frac{k^2\exp[-(\eta^2 + \pi^2k^2/n^2)Wt]}{(\eta^2n^2 + \pi^2k^2)^2}[1 - (-1)^k\cosh(\eta n)]$$

$$\tilde{\omega}n \gg 1,\ \eta \ll \tilde{\omega} \tag{23}$$

$$\Omega_n(t) = 8\pi^2\eta\tilde{\omega}n^2 \sum_{k=1}^\infty \frac{k^2(-1)^k\sinh(\eta n)\exp[-(\eta^2 + \pi^2k^2/n^2)Wt]}{[(\eta^2 - \tilde{\omega}^2)n^2 + \pi^2k^2](\eta^2n^2 + \pi^2k^2)^2} + \exp(\tilde{\omega}n - 2\eta\omega t)/\tilde{\omega}n \qquad \tilde{\omega}n \gg 1,\ \eta \gg \tilde{\omega} \tag{24}$$

$$\Omega_n(t) = \exp[-(2\omega/n)t] \qquad \tilde{\omega}n \ll 1,\ \eta n \ll 1 \tag{25}$$

$$\Omega_n(t) = 8\pi^2\eta\bar{\omega}n^2 \sum_{k=1}^{\infty} \frac{k^2(-1)^k \sinh(\eta n)\exp[-(\eta^2 + \pi^2k^2/n^2)Wt]}{(\eta^2n^2 + \pi^2k^2)^3}$$

$$+ \exp(-2\eta\omega t) \qquad \bar{\omega}n \ll 1, \eta n \gg 1. \tag{26}$$

The above expressions are helpful for understanding the relationship between the temporal dependence of $\Omega_n(t)$ and the segment length, magnitude of bias field and capture efficiency. They are also needed for some other applications. But in performing further calculations of $\rho(t)$ one encounters difficulties, since the substitution of equations (23), (24) and (26) into (10) leads to divergent integrals. Thus, the order of summation and integration cannot be changed. In such cases, it is instrumental to use the definition of the average particle-density Laplace transform

$$\tilde{\rho}(s) = c^2 \int_0^{\infty} \mathrm{d}n\, \tilde{\Omega}_n(s)\, \mathrm{e}^{-cn} \tag{27}$$

and to consider separately fast (equation (5)) and slow (equation (6)) trapping.

Fast trapping. After making some identical transformations in (27) and going over from the Laplace image space to its originals, one gets

$$\rho(t) = \frac{1}{2\pi\mathrm{i}} \int_{\gamma-\mathrm{i}\infty}^{\gamma+\mathrm{i}\infty} \mathrm{d}s\, \mathrm{e}^{s\tau}[\tilde{R}_1(s) + \tilde{R}_2(s)] \tag{28}$$

where

$$\tilde{R}_1(s) = 2\bar{\omega}(2\eta + \bar{\omega})\frac{c^2}{s^2}\lambda \int_0^{\infty} \mathrm{d}y \frac{\sinh[(\eta - c)y]}{(\bar{\omega}^2 + s)\sinh(\lambda y) + 2\bar{\omega}\lambda\cosh(\lambda y)} \tag{29}$$

$$\tilde{R}_2(s) = c^2 \int_0^{\infty} \mathrm{d}n \left(\frac{\mathrm{e}^{-cn}}{s} - \frac{2\bar{\omega}}{ns^2} \frac{\lambda[\mathrm{e}^{-(\eta-c)n}(\eta + \bar{\omega}/2) - \mathrm{e}^{-(\eta+c)n}(\eta - \bar{\omega}/2)]}{(\bar{\omega}^2 + s)\sinh(\lambda n) + 2\bar{\omega}\lambda\cosh(\lambda n)}\right.$$

$$\left. - 2\bar{\omega}\frac{\mathrm{e}^{-cn}}{ns^2} \frac{(2\eta^2 + s)\sinh(\lambda n) + \bar{\omega}\lambda\cosh(\lambda n)}{(\bar{\omega}^2 + s)\sinh(\lambda n) + 2\bar{\omega}\lambda\cosh(\lambda n)}\right). \tag{30}$$

Let us, first, exclude the case of strong fields, i.e. let $\eta \ll \bar{\omega}$. With the restrictions on the parameters given, it is seen that the situation coincides basically with that studied in [22]. Since equation (23), with minor corrections disregarded, is the original of (20) and, at the same time, represents (exactly) the inverse Laplace transform of (21), the calculations made in accordance with (28) (see Appendix 2) allow us to rederive the results of MPW theory:

$$\rho(t)_{\eta<c} \equiv L_1(t) = \frac{4}{\pi^2}\exp(-\eta^2Wt) \int_0^{\infty} \mathrm{d}x \frac{\exp(-\pi^2c^2Wt/x^2)}{[1 + (\eta x/\pi c)^2]^2} \left(\frac{\exp(-x)}{1 - \exp(-x)}\right.$$

$$\left. + \frac{\exp[-x(1 + \eta/c)]}{2\{1 + \exp[-x(1 + \eta/c)]\}} + \frac{\exp[-x(1 - \eta/c)]}{2\{1 + \exp[-x(1 - \eta/c)]\}}\right) \tag{31}$$

and

$$\rho(t)_{\eta>c} = L_1(t) + L_2(t) \tag{32}$$

where

$$L_2(t) = 8c^2(\eta - c)^2 \exp(-\eta^2 Wt) \sum_{k=0}^{\infty} \frac{(k+\frac{1}{2}) \exp\{[(\eta - c)/(2k+1)]^2 Wt\}}{[\eta^2(2k+1)^2 - (\eta - c)^2]^2}. \tag{33}$$

At long times, the expressions (31) and (32) reduce to (3) and (4), respectively.

It is worth mentioning that, as the present calculations show, the range of applications of the dependences obtained in [22] is not limited to the case $\omega = \infty$. They can also be used to describe the trapping process characterised by a finite capture rate, including those for which the condition $\tilde{\omega} \ll 1$ is realised. Thus, the decay laws (31) and (32) are relevant to the case of fast trapping and not very strong fields.

Let us now examine the case $\eta \gg \tilde{\omega}$. The calculations carried out in Appendix 3 in accordance with the scheme described in the preceding appendix result in the following expression:

$$\begin{aligned}\rho(t) &= 8\eta^2 \tilde{\omega} c^2 \exp(-\eta^2 Wt) \\ &\quad \times \sum_{k=0}^{\infty} \frac{\exp\{[(\eta - c)/(2k+1)]^2 Wt\}}{(2k+1)(\eta^2 - \xi_k^2)^2[(\xi_k + \tilde{\omega})^2 - \eta^2]} \left(\frac{(\xi_k + \tilde{\omega})^2 - \eta^2}{(\xi_k - \tilde{\omega})^2 - \eta^2}\right)^k \\ &\quad + \mathrm{O}\left(\frac{c}{\tilde{\omega}} \exp(-2\eta\omega t)\right) \\ &\underset{2\eta cWt \gg 1}{\propto} \exp(-2\eta cWt)\end{aligned} \tag{34}$$

where $\xi_k = (\eta - c)/(2k+1)$. It is seen that the decay kinetics described by equation (34) differs from that obtained above, equation (32), for times $2\eta cWt \lesssim 1$ only. The long-time asymptotics of the dependences (32) and (34) coincide.

Note that, as is argued in [29], the asymptotic behaviour of the survival probability can be either of the type $\propto \exp(-\eta^2 Wt)$ which corresponds to (31) or of the type $\propto \exp(-2\eta\omega t)$ (see equation (37) below). Both the asymptotics can be obtained in the smallest pole approximation. But this approximation fails for fast trapping in intermediate and strong fields, i.e. $\eta > c$. To get equations (32) and (34) one needs to take into account the contributions from all poles of the Laplace transform $\tilde{\Omega}_n(s)$.

Slow trapping. Similar to the previous treatment we exclude first the case of strong fields, $\eta > c$. Then the calculations of $\rho(t)$ can be performed directly using (10) together with (25) for $\Omega_n(t)$. As a result one gets for $t \ll \tau$

$$\begin{aligned}\rho(t) &= 2c\omega t K_2(2(c\omega t)^{1/2}) & \tau &= W^2 c/\omega^3 \text{ if } \eta < \tilde{\omega} \\ &\underset{2c\omega t \gg 1}{\propto} \sqrt{\pi}(2c\omega t)^{3/4} \exp[-2(2c\omega t)^{1/2}] & \tau &= c/\omega\eta^2 \text{ if } \eta > \tilde{\omega}\end{aligned} \tag{35}$$

where $K_2(x)$ is the modified Bessel function, and for $t \gg \tau$

$$\rho(t) = L_1(t) = \begin{cases} \exp[-\frac{3}{2}(2\pi^2 c^2 Wt)^{1/3}] & t \ll c/\eta^3 W \\ \exp(-\eta^2 Wt) & t \gg c/\eta^3 W. \end{cases} \tag{36}$$

The expressions (35) and (36) show that in low fields, $\eta < \tilde{\omega}$, the charge-density decay kinetics can follow three different dependences, $\rho \propto \exp(-t^{1/2})$, $\rho \propto \exp(-t^{1/3})$

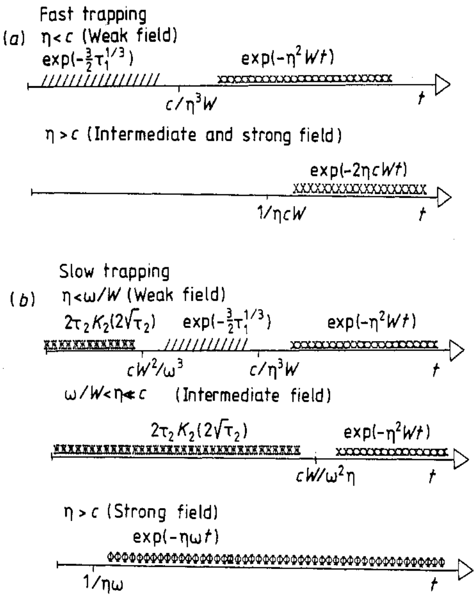

Figure 3. Changes in the temporal dependence of the charge carrier density with increasing bias electric field for (a) fast and (b) slow trapping. Different shaded sections of the time axis (unscaled) are associated with different characteristic dependences $\rho(t)$, $\tau_1 = 2\pi^2c^2Wt$, $\tau_2 = 2c\omega t$.

and $\rho \propto \exp(-t)$, which change into each other as the time increases (figure 3). When $\eta > \tilde{\omega}$, the second intermediate asymptotic does not manifest itself. This means that passing to intermediate fields (see figure 2(b)) one would observe the decay law (35) changing directly to the exponential one defined in (36). A further increase in bias field will result in a shortening of the time interval in which $\rho(t)$ coincides with that describing the density decay of uncharged particles (just as in the case of fast trapping). Accordingly, in stronger fields the exponential decay kinetics will display itself earlier.

With $\eta > c$, it is easy to show (see Appendix 3) that the main contribution to the definition of $\rho(t)$ comes from the second term in (26). Simple calculations lead to

$$\rho(t) = \exp(-2\eta\omega t) + O(\omega/Wc)\exp(-2\eta cWt). \tag{37}$$

In this case the decrease in the charge density is exponential, with the decay rate constant differing from that in equations (3) and (4).

Thus, the change of the kinetic curve in response to the bias increasing should finally result in the decrease in the exponential decay rate, $\eta^2W \rightarrow 2\eta\omega$.

In all the cases considered above, the time interval needed for $\rho(t)$ to decrease by 1–2 orders from its initial value may be evaluated by the average charge carrier lifetime in a chain with traps. The definitions of this time corresponding to the dependence $\rho(t)$ obtained read

$$T = c^2\int_0^\infty \mathrm{d}n\, n\tilde{\Omega}_n(0)\,\mathrm{e}^{-cn} = \begin{cases} 1/2Wc^2 & \tilde{\omega}/c \gg 1,\ \eta \ll \tilde{\omega} \\ 1/2W\eta c & \tilde{\omega}/c \gg 1,\ \eta \gg \tilde{\omega} \\ 1/\omega c & \tilde{\omega}/c \ll 1,\ \eta \ll c \\ 1/2\tilde{\omega}\eta & \tilde{\omega}/c \ll 1,\ \eta \gg c. \end{cases} \tag{38}$$

Summarising the results presented, we would like to emphasise two of them believed to be the most important. It was shown that the predictions of the MPW theory formulated for the case of infinite capture rate remain practically unchanged under the condition of fast trapping (5) for weak and intermediate bias fields. At the same time, when the case of slow trapping (6) is realised, we predict a qualitatively new shape of the kinetic curve expected and its dependence on the bias electric field strength.

3. Concluding remarks

In experiments monitoring the photocurrent after light excitation of a Q1D crystal it is the parameter η (bias field) that can be readily varied [4]. Therefore, it is helpful to trace changes of the kinetic curve $\rho(t)$, connected directly with the dark-current intensity, in response to an increase in bias.

In weak fields (see figure 2) the photocurrent decay due to trapping of the overwhelming majority of charge carriers is indistinguishable from that for uncharged-particle trapping kinetics (studied in detail in [28]), except for the long-time asymptotics which are always exponential when $\eta \neq 0$. For fast trapping this asymptotic has the form $\rho(t) \propto \exp(-\eta^2 Wt)$. An increase in the bias field leads to a decrease in the time interval in which $\rho(t)$ is close to $\rho(t)_{\eta \approx 0}$. At the same time, for stronger fields the transition to exponential kinetics shifts to shorter times, and the exponential decay rate diminishes. An appreciable difference between $\rho(t)$ and $\rho(t)_{\eta=0}$ in the whole range of times has to be expected in fields $\eta > c$, irrespective of the capture rate.

In the case of fast trapping the kinetic curve describing the initial stage of photocurrent decay is defined by equation (32) for intermediate fields, $c < \eta \ll \bar{\omega}$, and by equation (34) for strong fields, $\eta \gg \bar{\omega}$. Both the dependences tend to the same exponential constant $K = 2\eta cW$ ($K = -\eta^2 W$ in weak fields). Taking into account the strong-field asymptotics of $\rho(t)$ obtained in [34], one can expect that a further increase in η (up to values $\eta \gtrsim 1$) will result in the increase in K, governed by the relation $K = 2Wc \tanh \eta$.

The form of the decay curve and its transformation with increasing η differ noticeably from that described above for slow trapping (see figure 3). In weak fields there exist two intermediate non-exponential asymptotics, $\propto \exp(-t^{1/2})$ and $\propto \exp(-t^{1/3})$, which should reveal themselves before an exponential decay (just the same as that for fast trapping) takes place. The first of them, or more precisely, the dependence $\rho(t) = 2c\omega t K_2(2(2c\omega t)^{1/2})$, describes the photocurrent decay at least within two orders of its initial intensity. When passing to intermediate fields, the 'exclusion' of the second asymptotic occurs (see figure 3(*b*)). Thus, distinct from the case of fast trapping, one can observe the matching of the long-time exponential asymptotics, $\propto \exp(-\eta^2 Wt)$, not with dependence $\propto \exp(-t^{1/3})$, but with that $\propto \exp(-t^{1/2})$ when $\eta < c$. In strong fields the intermediate asymptotic disappears (figure 3(*b*)) and the exponential decay law $\propto \exp(-2\eta\omega t)$ controls almost the whole range of dark photocurrent intensity changes, except for a small initial part of its temporal dependence when $\rho(t)$ is close to unity. The decay rate constant acquires a new definition in this case, $K = 2\eta\omega$, which does not include the trap concentration, but depends on the trapping rate as a limiting parameter.

It can be seen that the variation of η in a sufficiently wide range, analysed within the present context, allows one to specify the character of the trapping process: Is it diffusion- or trapping-rate-controlled, or is there any intermediate situation? It is needless to say that a correct choice between the models of slow and fast trapping is a cornerstone for the interpretation of experimental data on quasi-particle trapping kinetics.

In this connection use can be made of the fact that the form of a kinetic curve describing the trapping process is sensitive to the duration of excitation laser pulses. As has been shown in [28] after δ-pulse excitation (i.e. when the quasi-particle creating the pulse is much shorter than the time needed for a considerable change in the particle density due to trapping—average particle lifetime, T) and after stationary excitation (or using laser pulses much longer than T) the dependences $\rho(t)_{\eta=0}$ are quite different. The above change in the excitation duration leads to some kind of a delayed effect in the particle-density decay kinetics. When passing from a δ-pulsed to a stationary excitation the expected rearrangement of the kinetic curve is defined by specific values of the parameters ω, W and c and is predicted to be very much different depending on whether fast or slow trapping is operative [28]. Using this effect seems to be helpful as an additional tool in studies of charge carrier trapping kinetics. The results obtained in [28] are applicable to interpret the experimental dark photocurrent temporal dependence in weak fields. But to deal with experiments with varied excitation duration under intermediate and strong fields, some additional calculations should be made.

Let us emphasise, in conclusion, that the crucial dependence of the observables linked with the diffusion, drift and capture of charge carriers on the trapping rate, which is demonstrated by the discussion presented, shows that a reliable interpretation of experiments [4–6] and analogous ones cannot be achieved without careful analysis on equal footing of both the possibilities available, namely, those referred to as fast and slow trapping in the paper.

Appendix 1. The survival probability of a particle in a segment

To obtain the survival probability of a particle, which diffuses and drifts in a bias electric field in a segment with absorbing boundaries, it is necessary to find the inverse Laplace transform given in (20). So, since $\tilde{\Omega}_n(s)$ is a single-valued function without branch points, its original is defined by the sum of residues

$$\Omega_n(t) = \sum \mathrm{Res}\, \mathrm{e}^{s\tau} \tilde{\Omega}_n(s) \tag{A1.1}$$

taken at the poles of $\tilde{\Omega}_n(s)$. The point $s = 0$ is not singular, see (22); therefore we can write

$$\Omega_n(t) = 2\tilde{\omega} \sum_{s\neq 0} \mathrm{Res} \left(s^{-2}\, \mathrm{e}^{s\tau} \times \frac{\lambda\tilde{\omega}\cosh(\eta n) + 2\lambda\eta\sinh(\eta n) - (2\eta^2 + s)\sinh(\lambda n) - \lambda\tilde{\omega}\cosh(\lambda n)}{(s + \tilde{\omega}^2)\sinh(\lambda n) + 2\lambda\tilde{\omega}\cosh(\lambda n)} \right) \tag{A1.2}$$

where $\lambda = (s + \eta^2)^{1/2}$ and the residues are taken at those values of s at which the denominator in (A1.2) is equal to zero,

$$(s + \tilde{\omega}^2)\sinh(\lambda n) + 2\lambda\tilde{\omega}\cosh(\lambda n) = 0 \tag{A1.3}$$

or, equivalently, they can be found as solutions of the following equations:

$$\tan x_n = \frac{2\tilde{\omega} n x_n}{(\eta^2 - \tilde{\omega}^2)n^2 + x_n^2} \qquad \mathrm{i}x_n = \lambda n \tag{A1.4}$$

and

$$\tanh y_n = \frac{2\tilde{\omega} n y_n}{(\eta^2 - \tilde{\omega}^2)n^2 - y_n^2} \qquad y_n = \lambda n. \tag{A1.5}$$

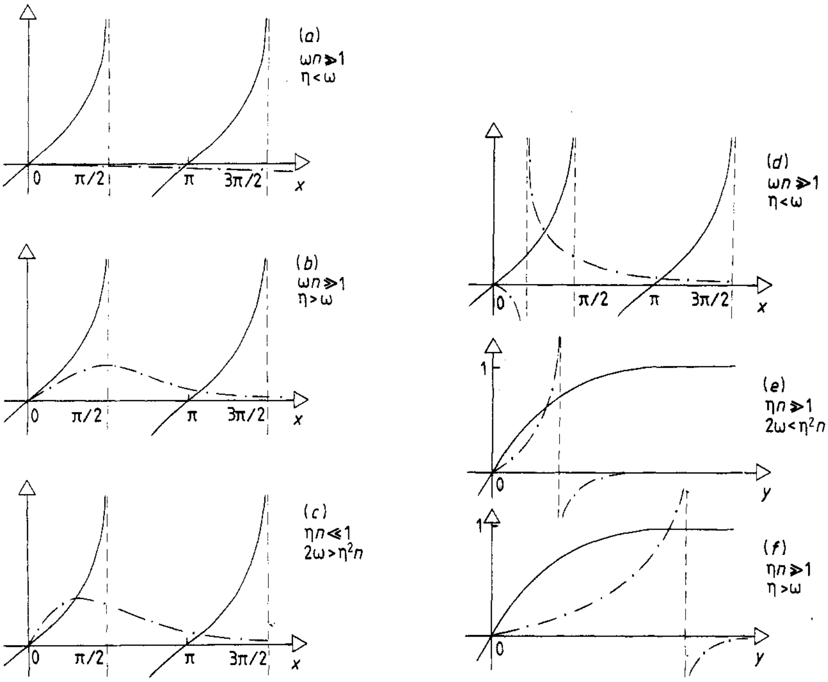

Figure A1. Solutions of equation (A1.4) (*a*)–(*d*) and equation (A1.5) (*e*), (*f*) plotted for different values of the characteristic parameters c, η, ω. Full curves correspond to the left-hand sides of the equations, and chain curves to the right-hand sides. The solutions are defined by the intersection points.

The solutions of these equations, just as the dependence $\Omega_n(t)$, for arbitrary values of the parameters can only be obtained numerically. Therefore, it is instrumental to consider representative limiting cases when the explicit form of $\Omega_n(t)$ can be found. Keeping this in mind, let us distinguish, similar to (5) and (6), fast

$$\tilde{\omega} n \gg 1 \tag{A1.6}$$

and slow

$$\tilde{\omega} n \ll 1 \tag{A1.7}$$

trapping.

For the case of fast trapping, the hierarchical sequence of the characteristic parameters is shown in figure 2(*a*). If $\eta < \tilde{\omega}$, so that $\tilde{\omega} n \gg 1$ (weak and intermediate fields), the solutions of (A1.4) can be represented in the form (see figure A1(*a*))

$$x_n^{(k)} = \pi k \qquad k = 1, 2, \ldots \tag{A1.8}$$

with unimportant corrections omitted. The equation (A1.5) has no solutions for the restrictions on the parameters given. Thus, the definition of the poles in (A1.2) is

$$s_k = -\eta^2 - \pi^2 k^2 / n^2. \tag{A1.9}$$

Using (A1.9) to calculate the residues in (A1.2), one gets the expression (23) coinciding with that obtained for the particle survival probability in a segment with immediately absorbing boundaries, $\tilde{\omega} = \infty$. For such boundaries equation (23) is exact. When $\tilde{\omega} \neq 0$ the evaluation of the terms correcting (23) shows that their contributions do not exceed 1% of the value of $\Omega_n(t)$ at any times if the above inequalities are fulfilled.

If $\eta > \tilde{\omega}$ and $\eta n \gg 1$ (for fast trapping such relations can be realised in strong fields only (see figure 2(*a*))), the solution of (A1.4) is the same but equation (A1.5) also has a solution such as

$$y_n = (\eta - \tilde{\omega})n \tag{A1.10}$$

which defines a pole additional to (A1.9)

$$s = -2\eta\tilde{\omega} + \tilde{\omega}^2. \tag{A1.11}$$

The solutions of (A1.4) and (A1.5) discussed are plotted in figures A1(*b*) and (*f*). The calculation of the survival probability in accordance with (A1.2) yields the expression (24).

To conclude our discussion of fast trapping, we give the major terms in the definition of the average lifetime of a particle in the segment (see (22))

$$T_n = \begin{cases} n^2/12W & \eta n \ll 1 \quad \text{(A1.12)} \\ n/4\eta W & \eta n \gg 1. \quad \text{(A1.13)} \end{cases}$$

In the case of slow trapping, equation (A1.4) may have, apart from (A1.8), an additional root under the condition of weak or intermediate fields

$$x_n = (2\tilde{\omega}n - \eta^2 n^2)^{1/2}. \tag{A1.14}$$

The corresponding pole of $\tilde{\Omega}_n(s)$ is

$$s = -2\tilde{\omega}/n. \tag{A1.15}$$

The solution of (A1.4) is plotted in figures A1(*d*) or (*c*) depending on whether $\eta < \tilde{\omega}$ or $\eta > \tilde{\omega}$.

It is seen that the additional root of (A1.4) always exists in weak fields. In intermediate fields, $\eta > \tilde{\omega}$, the necessary and sufficient condition for the pole to exist is $2\tilde{\omega} > \eta^2 n$. But when this condition is violated (this is the case when $\eta \gg \tilde{\omega}$), equation (A1.5) has such a solution (figure A1(*e*)) that the definition of the additional pole coincides with (A1.15) if $\eta n \ll 1$.

Calculating $\Omega_n(t)$ and making use of (A1.2), (A1.9), (A1.15) and the inequalities given, one gets (25).

In strong fields the additional pole definition differs from that given above. It follows from the solution of (A1.5) and coincides with (A1.11) for $\eta n \gg 1$. In that case the calculation of $\Omega_n(t)$ gives (26).

For slow trapping the average lifetime of a particle in the segment is

$$T_n = \begin{cases} n/2\omega & \eta n \ll 1 \quad \text{(A1.16)} \\ 1/2\eta\omega & \eta n \gg 1. \quad \text{(A1.17)} \end{cases}$$

Appendix 2. Calculation of $\rho(t)$ for fast trapping in weak and intermediate fields

To calculate $\rho(t)$ let us first average $\tilde{\Omega}_n(s)$, equation (21), over the random trap distribution

$$\tilde{\rho}(s) = c^2 \int_0^\infty \mathrm{d}n\, \mathrm{e}^{-cn} \left[\frac{n}{s} + \frac{2\lambda}{s^2}\left(\frac{\cosh(\eta n) - \cosh(2\lambda n)}{\sinh(\lambda n)}\right)\right] \tag{A2.1}$$

and make an identical transformation of the integrand, adding and subtracting the term $2\lambda \exp(c-\eta)n/s^2 \sinh(\lambda n)$

$$\tilde{\rho}(s) = c^2 \int_0^\infty \mathrm{d}n \left(\frac{n}{s}\mathrm{e}^{-cn} + \frac{\lambda}{s^2}\frac{\mathrm{e}^{-(c+\eta)n} + \mathrm{e}^{(c-\eta)n} - 2\mathrm{e}^{-cn}\cosh(\lambda n)}{\sinh(\lambda n)} + \frac{2\lambda}{s^2}\frac{\sinh[(\eta-c)n]}{\sinh(\lambda n)}\right). \tag{A2.2}$$

Inverting (A2.2) to the original space, we get

$$\rho(t) = R_1(t) + R_2(t) = \frac{1}{2\pi\mathrm{i}}\int_{\gamma-\mathrm{i}\infty}^{\gamma+\mathrm{i}\infty} \mathrm{d}s\, \mathrm{e}^{s\tau}[\tilde{R}_1(s) + \tilde{R}_2(s)] \tag{A2.3}$$

where

$$\tilde{R}_1(s) = \frac{2\lambda c^2}{s^2}\int_0^\infty \mathrm{d}n \frac{\sinh[(\eta-c)n]}{\sinh(\lambda n)} \tag{A2.4}$$

$$\tilde{R}_2(s) = c^2 \int_0^\infty \mathrm{d}n \left(\frac{n}{s}\mathrm{e}^{-cn} + \frac{\lambda}{s^2}\frac{\mathrm{e}^{-(c+\eta)n} + \mathrm{e}^{(c-\eta)n} - 2\mathrm{e}^{-cn}\cosh(\lambda n)}{\sinh(\lambda n)}\right) \tag{A2.5}$$

and the cut of a complex plane is taken to the right of all singular points of $\tilde{R}_1$, $\tilde{R}_2$.

The integration of (A2.4) gives

$$\tilde{R}_1(s) = \frac{c^2\pi}{s^2}\tan\left(\frac{(\eta-c)\pi}{2\lambda}\right). \tag{A2.6}$$

According to (A2.6), $\tilde{R}_1(s)$ is a many-valued function with the branch point $s = -\eta^2$. To find $R_1(t)$ we take an integration contour, as shown in figure A2. In the limit $r \to 0$ and $R \to \infty$, the integrals over the contours c_r and C_R go to zero, so that one has for $R_1(t)$

$$R_1(t) = \sum_{s\neq 0} \mathrm{Res}\, \mathrm{e}^{s\tau}\tilde{R}_1(s) + \frac{1}{2\pi\mathrm{i}}\int_{\mathrm{I}} \mathrm{d}s\, \mathrm{e}^{s\tau}\tilde{R}_1(s) + \frac{1}{2\pi\mathrm{i}}\int_{\mathrm{II}} \mathrm{d}s\, \mathrm{e}^{s\tau}R_1(s) \tag{A2.7}$$

where $\Sigma\mathrm{Res}$ denotes the summation over the residues of the function $\exp(s\tau)\tilde{R}_1(s)$. Calculation of the residues and of the integrals in (A2.7) gives for $\eta > c$

$$R_1(t) = 8c^2(\eta-c)^2\exp(-\eta^2 Wt)\sum_{k=0}^{\infty}\frac{\exp\{[(\eta-c)/(2k+1)]^2 Wt\}}{[\eta^2(2k+1)^2 - (\eta-c)^2]^2}(k+\tfrac{1}{2})$$
$$+ \frac{4}{\pi^2}\exp(-\eta^2 Wt)\int_0^\infty \mathrm{d}x\, x\frac{\exp(-\pi^2c^2Wt/x^2)}{(\eta^2x^2/\pi^2c^2+1)^2}$$
$$\times\left(\frac{\exp[-x(1-\eta/c)]}{2\{1-\exp[-x(1-\eta/c)]\}} - \frac{\exp[x(1-\eta/c)]}{2\{1+\exp[x(1-\eta/c)]\}}\right). \tag{A2.8}$$

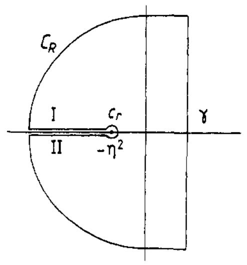

Figure A2. The contour of integration in (25) and (A2.3). The integrand $\tilde{R}_1(s)$ has the branch points, $s = -\eta^2$.

The function $R_2(t)$ is obtained by taking an inverse Laplace transform of equation (A2.5) and then integrating over n. The result is

$$R_2(t) = \frac{4}{\pi^2} \exp(-\eta^2 Wt) \int_0^\infty \mathrm{d}x\, x \frac{\exp(-\pi^2 c^2 Wt/x^2)}{(\eta^2 x^2/c^2\pi^2 + 1)^2}$$
$$\times \left(\frac{\mathrm{e}^{-x}}{1 + \mathrm{e}^{-x}} + \frac{\exp[x(1 - \eta/c)]}{2\{1 + \exp[x(1 - \eta/c)]\}} + \frac{\exp[-x(1 + \eta/c)]}{2\{1 + \exp[-x(1 + \eta/c)]\}} \right). \tag{A2.9}$$

Thus, $\rho(t) = R_1(t) + R_2(t) = L_1(t) + L_2(t)$, where the functions $L_{1,2}(t)$ are defined in (31) and (33).

Appendix 3. Calculation of $\rho(t)$ for fast trapping in strong fields

Let us represent the temporal dependence of charge carrier density in a form analogous to (A2.3):

$$\rho(t) = R_1(t) + R_2(t) \tag{A3.1}$$

where $R_{1,2}(t)$ are the originals of Laplace transforms (29) and (30), respectively. For the given definitions of $\tilde{R}_1(s)$, $\tilde{R}_2(s)$, equation (A3.1) is exact.

First we consider $R_1(t)$. Performing the integration in (29), one can write

$$\tilde{R}_1(s) = \frac{8\eta^2 \tilde{\omega} c^2 \lambda}{s^2(\tilde{\omega} + s + 2\tilde{\omega}\lambda)} \sum_{k=0}^{\infty} \frac{[(\tilde{\omega}^2 + s - 2\tilde{\omega}\lambda)/(\omega^2 + s + 2\tilde{\omega}\lambda)]^k}{(2k+1)^2(\eta^2 + s) - (\eta - c)^2}. \tag{A3.2}$$

Again, $\tilde{R}_1(s)$ is a many-valued function in the complex plane with the branch point $s = -\eta^2$. Calculation of $R_1(t)$ is made by integrating over the contour (figure A2) in the limit $c_r \to 0$, $C_R \to \infty$. As a result, we obtain

$$R_1(t) = -4\eta^2 \tilde{\omega} c^2 \exp(-\eta^2 Wt) \int_0^\infty \mathrm{d}x \sqrt{x} \frac{\mathrm{e}^{-xWt}}{(\eta^2 + x)} \sum_{k=0} \frac{1}{(2k+1)^2 x + (\eta - c)^2}$$
$$\times \left(\frac{\{[\eta^2 + (\sqrt{x} + \mathrm{i}\tilde{\omega})^2]/[\eta^2 + (\sqrt{x} - \mathrm{i}\tilde{\omega})^2]\}^k}{\eta^2 + (\sqrt{x} - \mathrm{i}\tilde{\omega})^2} \right. \tag{A3.3}$$
$$\left. + \frac{\{[\eta^2 + (\sqrt{x} - \mathrm{i}\tilde{\omega})^2]/[\eta^2 + (\sqrt{x} + \mathrm{i}\tilde{\omega})^2]\}^k}{\eta^2 + (\sqrt{x} + \mathrm{i}\tilde{\omega})^2} \right) + \sum_{s \neq 0} \operatorname{Res} \mathrm{e}^{s\tau} \tilde{R}_1(s)$$

where the first two terms correspond to the integrals of the function $\exp(sWt)\tilde{R}_1(s)$ taken over the edges of the cut I and II and the last term is the sum of the residues taken at the poles

$$s_{le} = -\eta^2 + [(\eta - c)/(2l+1)]^2 \qquad l = 1, 2, \ldots \tag{A3.4}$$

and

$$s = -2\tilde{\omega}\eta + \tilde{\omega}^2. \tag{A3.5}$$

Equations (A3.4) and (A3.5) follow from the condition that the denominator in (A3.2) is zero.

To calculate $\tilde{R}_2(t)$ we can change the order of taking an inverse Laplace transformation and of integrating over n. Now taking into account that $\tilde{R}_2(s)$ is a single-valued function of s, we find

$$\begin{aligned} R_2(t) = {} & 2\tilde{\omega}c^2 \int_0^\infty \mathrm{d}n \sum_{s\neq 0} \operatorname{Res} \frac{\mathrm{e}^{sWt}}{s^2} \frac{\lambda[\mathrm{e}^{-(\eta-c)n}(\eta + \tilde{\omega}/2) - \mathrm{e}^{-(\eta+c)n}(\eta - \tilde{\omega}/2)]}{(\tilde{\omega}^2 + s)\sinh(\lambda n) + 2\tilde{\omega}\lambda\cosh(\lambda n)} \\ & - 2\tilde{\omega}c^2 \int_0^\infty \mathrm{d}n \sum_{s\neq 0} \operatorname{Res} \frac{\mathrm{e}^{sWt}}{s^2} \frac{(2\eta^2 + s)\sinh(\lambda n) + \tilde{\omega}\lambda\cosh(\lambda n)}{(\tilde{\omega}^2 + s)\sinh(\lambda n) + 2\tilde{\omega}\lambda\cosh(\lambda n)}. \end{aligned} \tag{A3.6}$$

In the case of fast trapping the calculation of the residues of $\exp(sWt)\tilde{R}_1(s)$ at the poles (A3.4) and (A3.5) gives for $s_k = -\eta^2 + [(\eta - c)^2/(2k+1)]$

$$\begin{aligned} \sum \operatorname{Res} \mathrm{e}^{sWt}\tilde{R}_1(s) = {} & 8\eta^2\tilde{\omega}c^2 \exp(-\eta^2 Wt) \times \sum_{k=0}^{\infty} \frac{\exp\{[(\eta - c)/(2k+1)]^2 Wt\}}{(2k+1)(\eta^2 - \xi_k^2)^2[(\xi_k + \tilde{\omega})^2 - \eta^2]} \\ & \times \left(\frac{(\xi_k + \tilde{\omega})^2 - \eta^2}{(\xi_k - \tilde{\omega})^2 - \eta^2}\right)^k \propto \exp(-2\eta c Wt)[1 + \mathrm{O}(c/\tilde{\omega})] \end{aligned} \tag{A3.7}$$

where $\xi_k = (\eta - c)/(2k+1)$,

$$\operatorname{Res} \mathrm{e}^{sWt}\tilde{R}_1(s) \propto (c/\tilde{\omega})^2 \exp[(-2\eta\omega + \omega^2/W)t] \qquad s = -2\tilde{\omega}\eta + \tilde{\omega}^2. \tag{A3.8}$$

It can be shown that the first term in (A3.3) does not exceed the value $\propto \eta\tilde{\omega}c^2 \exp(-\eta^2 Wt)$. Estimating $R_2(t)$ using (A3.6), we derive the upper bound of R_2 as

$$R_2(t) < \mathrm{O}\left(\left(\frac{\tilde{\omega}c}{\eta^2}\right)^2\right) \exp(-\eta^2 Wt) + \mathrm{O}\left(\left(\frac{c}{\eta}\right)^2 + c\eta\right) \exp(-2\eta\omega t). \tag{A3.9}$$

Thus, in the case under consideration the dependence $\rho(t)$ is defined by the sum in (A3.7), which includes the term with the smallest value of the exponential decay rate, $K = 2\eta c W$, and with the greatest pre-exponential factor $\simeq 1$. Just this result is presented in the main body of the paper.

Let us also outline here a simple way to obtain the dependence (37). Note that the first term in the expression (26) for the survival probability $\Omega_n(t)$ is the original of the function

$$\tilde{\Omega}_n^{(1)}(s) = \tilde{\omega}\eta \frac{\lambda}{s^3} \frac{\sinh(\eta n)}{(\lambda n)} \qquad s \neq 0. \tag{A3.10}$$

Substituting (A3.10) into (27) and performing an inverse Laplace transformation, we get

$$\rho^{(1)}(t) \propto (\omega/Wc)\exp(-2\eta cWt) \qquad \tilde{\omega} < \eta < c. \tag{A3.11}$$

As is easily seen, the main contribution to (37) comes from averaging (in accordance with equation (10)) the second term of (26).

References

[1] Siddiqui A S and Wilson E G 1979 *J. Phys. C: Solid State Phys.* **12** 4237
[2] Siddiqui A S 1980 *J. Phys. C: Solid State Phys.* **13** 2147
[3] Soumann T, Donovan K J and Gold E 1984 *Mater. Sci.* **10** 23
[4] Hunt I G, Bloor D and Movaghar B 1983 *J. Phys. C: Solid State Phys.* **16** L623
[5] Seiferheld V, Bassler H and Movaghar B 1983 *Phys. Rev. Lett.* **51** 813
[6] Rughooputh S, Bloor D, Phillips D *et al* 1987 *Phys. Rev.* B **35** 8103
[7] Hochstrasser R M and Whithman J D 1972 *J. Chem. Phys.* **56** 5945
[8] Dlott D D, Fayer M D and Wieting R D 1978 *J. Chem. Phys.* **69** 2752
[9] Kauffman H F, Molley B, Weixelbaumer W-D *et al* 1986 *J. Chem. Phys.* **85** 3566
[10] Auerbach R A and McPherson G L 1987 *Phys. Rev.* B **33** 6815
[11] Buijs M and Blasse G 1986 *J. Luminesc.* **34** 263
[12] Yoshizawa M, Kobayashi T, Fujimoto H *et al* 1988 *Phys. Rev.* B **37** 9888
[13] Yoshizawa M, Kobayashi T, Aikagi K *et al* 1988 *Phys. Rev.* B **37** 10301
[14] Avde'enko A A, Eremenko V V and Karachevtsev V A 1988 *Zh. Exp. Teor. Fiz.* **94** 281
[15] Wegner G 1979 *Molecular Metals* ed. W E Hatfield (New York: Plenum)
[16] Bloor D and Movaghar B 1983 *IEEE Proc.* **130** 225
[17] Sixl H and Warta R 1985 *Electronic Structures of Polymers and Related Compounds* (Berlin: Springer)
[18] Bloor D and Chance R R (ed.) 1985 *Polydiacetylenes* (Dordrecht: Martinus Nijhoff)
[19] Movaghar B 1987 *J. Mol. Electron.* **3** 183; 1988 *J. Mol. Electron.* **4** 79
[20] Donovan K J and Wilson E G 1981 *Phil. Mag.* B **44** 31
[21] Movaghar B, Murray D and Pohlmann B 1984 *J. Phys. C: Solid State Phys.* **17** 1677
[22] Movaghar B, Pohlmann B and Würtz D 1985 *Phys. Rev.* A **31** 1568
[23] Movaghar B, Würtz D and Pohlmann B 1987 *Z. Phys.* B **66** 523
[24] Balagurov B Ya and Vaks V G 1973 *Zh. Exp. Teor. Fiz.* **65** 1939 (Engl. trans. 1974 *Sov. Phys.–JETP* **38** 968)
[25] Onipko A I and Galchuk L I 1987 *Khim. Fiz.* **6** 825
[26] Galchuk L I and Onipko A I 1987 *Ukr. Fiz. Zh.* **32** 1005
[27] Onipko A I 1988 *Teor. Exp. Khim.* **24** 8
[28] Onipko A I, Malysheva L I and Zozulenko I V 1988 *Chem. Phys.* **121** 99
[29] Burlatsky S F and Ivanov O F 1988 *Zh. Exp. Teor. Fiz.* **94** 331
[30] Galchuk L I and Onipko A I 1987 *Dokl. Akad. Nauk Ukr. SSR* A **2** 11
[31] Zozulenko I V and Onipko A I 1988 *Fiz. Tverd. Tela* **30** 2665
[32] Onipko A I and Zozulenko I V 1989 *J. Luminesc.* **43** 173
[33] Gaididei Yu B, Onipko A I and Zozulenko I V 1988 *Phys. Lett.* A **132** 329
[34] Aldea A, Dulea M and Gartner P 1988 *J. Stat. Phys.* **52** 1061