Electric field dependence of trapping in one dimension

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(Received 18 February 1983; revised manuscript received 27 June 1983)

We have derived an exact analytic solution for the electric field and time dependence of the survival fraction in the one-dimensional trapping problem. The intermediate- and long-time behavior is discussed below and above a threshold region of the electric field strength. The mean decay rate is given as a function of trap concentration and electric field strength.

Some time ago we derived an exact analytical formula[1] for the survival fraction $n(t)$ of excitations in the presence of deep traps in one-dimensional systems. We showed that the long-time behavior obeyed an $\exp[-(t/t_0)^{1/3}]$ law in the absence of a bias field. The influence of a bias η was analyzed numerically. η is defined by Eq. (2) in the text. From our numerical inversion of the series [see Eq. (24) in Ref. 1], we deduced an effective "threshold" bias $\eta \geqslant x$ (x is the trap concentration) above which the nonexponential behavior of $n(t,\eta)$ changed to an exponential behavior. This was consistent with the physical reasoning presented by Haarer and Möhwald[2] and the results of the "first passage time" approach due to Montroll and Weiss.[3] Unfortunately, we did not have an anlaytic expression for the field dependence at that time and we were thus unable to deduce the strict asymptotic $t\rightarrow\infty$ behavior of $n(t,\eta)$ for small fields ($\eta < x$).

Recently, Grassberger and Procaccia,[4] using a diffusion equation approach, have shown that the asymptotic long-time form of $n(t)$ is exponential however small the bias field. They find

$$\lim_{t\rightarrow\infty} n(t) \sim \exp(-ct^{1/3})\exp(-V_D^2 t/4D) \ ,$$

where V_D is the drift velocity and D is the diffusion constant. These authors state that conclusions regarding the existence of a threshold of $\eta = x$ are incorrect.

We have now succeeded in deriving an exact analytical expression for $n(t,\eta)$ for any value of the bias field and for all times in the trap concentration range of physical interest ($x \leqslant 10^{-2}$). We would like to report this result and at the same time show the following. (a) The long-time decay is exponential as soon as $\eta > 0$. (b) $\lim n(t,\eta)$ is indeed dominated by $\exp(-V_D^2 t/4D)$ $t\rightarrow\infty$ but only when $\eta \leqslant x$. (c) The intermediate- and long-time behavior of the function $n(\eta,t)$ changes drastically at $\eta \approx x$. For $\eta \leqslant x$ the function is a superposition of $\exp(-ct^{1/3})$ laws multiplied by $\exp(-V_D^2 t/4D)$, whereas when $\eta > x$ it is a superposition of exponentials with rate constants now linear in field. In the region $\eta > x$ and $V_D^2 t/4D >> 1$ the survival fraction is a simple exponential law. (d) An exact analytical expression is given for the averaged relaxation time τ or rate constant $\tau^{-1} = k$. This quantity is evaluated explicitly as a function of field.

Starting from the exact series for $n(p,\eta)$ in the space of the Laplace variable p given by Eq. (7) of Ref. 1, we derive the following representation which is exact[5] in the range $x \leqslant 10^{-2}$:

$$n(p,\eta) = \frac{1}{p} + \frac{2x^2\gamma}{p^2}\int_0^\infty d\zeta\, e^{-x\zeta}\left[\frac{\cosh(\eta\zeta)-\cosh(\gamma\zeta)}{\sinh(\gamma\zeta)}\right] \ , \tag{1}$$

where $\gamma = (p/W+\eta^2)^{1/2}$, W is the symmetric zero field jump rate, and the bias is defined by the relation,

$$\frac{1-\eta}{1+\eta} = e^{-eEa/kT} \ , \tag{2}$$

where E, e, and a are electric field strength, electronic charge, and lattice constant, respectively. For small fields ($\eta << 1$) this reduces to $\eta = eEa/2kT$.

Inverting (1), we obtain after some long and tedious algebraic manipulations the result

$$n(t,\eta) = 4x^2\int_0^\infty d\zeta\, e^{-x\zeta}\sum_{n=1}^{\infty}[1-(-1)^n\cosh(\eta\zeta)]\frac{n^2\pi^2\zeta}{(n^2\pi^2+\eta^2\zeta^2)^2}\exp\left[-\left(\frac{n^2\pi^2}{\zeta^2}+\eta^2\right)t\right] \ ; \tag{3}$$

when $\eta \leqslant x$ this can be rewritten in the simple form

$$n(t,\eta) = \frac{4}{\pi^2}e^{-\eta^2 Wt}\int_0^\infty dS\frac{S}{[1+(\eta S/\pi x)^2]^2}e^{-\pi^2x^2Wt/S^2}\left[\frac{e^{-S}}{1-e^{-S}} + \frac{e^{-S(1-\eta/x)}}{2(1+e^{-S(1-\eta/x)})} + \frac{e^{-S(1+\eta/x)}}{2(1+e^{-S(1+\eta/x)})}\right], \quad \eta \leqslant x \ , \tag{4}$$

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

$$n(t) = \frac{4}{\pi^2}\int_0^\infty dS\, S\,\mathrm{csch}(S)\,e^{-\pi^2 x^2 Wt/S^2}\,, \tag{5}$$

with the asymptotic long-time form[6]

$$n(t) \sim 16\left[\frac{x^2 tW}{3\pi}\right]^{1/2}\exp\left[-3\left[\frac{\pi^2 x^2 Wt}{4}\right]^{1/3}\right]. \tag{6}$$

Defining a mean relaxation time $\tau(\eta)$ as the limit $p \to 0$ of $n(p,\eta)$, we obtain after some manipulations the expression

$$x^2 W\tau(\eta) = \frac{x}{2\eta}\left[1 - \frac{x}{2\eta} + 2\left[\frac{x}{2\eta}\right]^3 \zeta\left[3, 1+\frac{x}{2\eta}\right]\right], \tag{7}$$

where $\zeta(z,q)$ is the Riemann ζ function.

The mean relaxation time $\tau(\eta)$ is the relevant quantity entering, for example, the steady-state photoconductivity. The field dependence of τ can be evaluated using (7) on a desk calculator. The plot of $[x^2 W\tau(\eta)]^{-1}$ vs $(2\eta/x)$ is shown in Fig. 1.

Let us now briefly draw the main conclusions from these results. Noting that $V_D = 2\eta Wa$ and $D = Wa^2$, statements (a) and (b) immediately follow from (4) without further discussion: The asymptotic ($t \to \infty$) limit of $n(t)$ is indeed always $\exp(-V_D^2 t/4D)$ as soon as $\eta > 0$ but only when $\eta \leqslant x$. Statement (c), that the intermediate- and long-time behavior of $n(t,\eta)$ changes drastically at $\eta \geqslant x$, can be seen from (3). To see this we first look at the regime $\eta < x$. Using steepest descent on (4) we obtain a sum of three terms $n(t) = (2n_1 + n_2 + n_3)/2$ with

$$e^{\eta^2 Wt} n_\mu(t,\eta) = \frac{8(x^2 Wt/3\pi C_\mu)^{1/2}}{[1+(2\eta^3 Wt/\pi x C_\mu)^{2/3}]^2} \times \exp\left[-3\left[\frac{\pi^2 x^2 C_\mu^2 Wt}{4}\right]^{1/3}\right], \tag{8}$$

with $C_1 = 1$, $C_2 = (1-\eta/x)$, $C_3 = (1+\eta/x)$. The exponential factor dominates only at times for which

$$\frac{\eta^3 Wt}{xC_\mu} > \sqrt{27}\frac{\pi}{2}\,. \tag{9}$$

The survival fraction obeys the "$t^{1/3}$" law for $\eta << x$ and remains nonexponential up to at least $\eta \leqslant 2x$ in the intermediate-time domain.

When $\eta \geqslant x$, the terms 1 and 3 in Eq. (4) remain unchanged. To the second term in the integrand (4) we obtain an additional contribution which can no longer be represented in this way. This term is dominant in the intermediate- and long-time domain; $n(t,\eta)$ now becomes $n(t) = S(t) + L(t)$, where $S(t)$ is given by (4) and $L(t)$ is

$$L(t,\eta) = 8x^2(\eta - x)^2 e^{-\eta^2 Wt}\sum_{n=0}^{\infty}\frac{(n+\frac{1}{2})\exp\{Wt[(\eta-x)/(2n+1)]^2\}}{(2n\eta + x)^2[2(n+1)\eta - x]^2}\,, \quad \eta > x\,. \tag{10}$$

For long times ($\eta^2 Wt >> 1$)

$$L(t,\eta) \sim \frac{4(\eta - x)^2}{(2\eta - x)^2} e^{-(2\eta x - x^2)Wt}\,, \tag{11a}$$

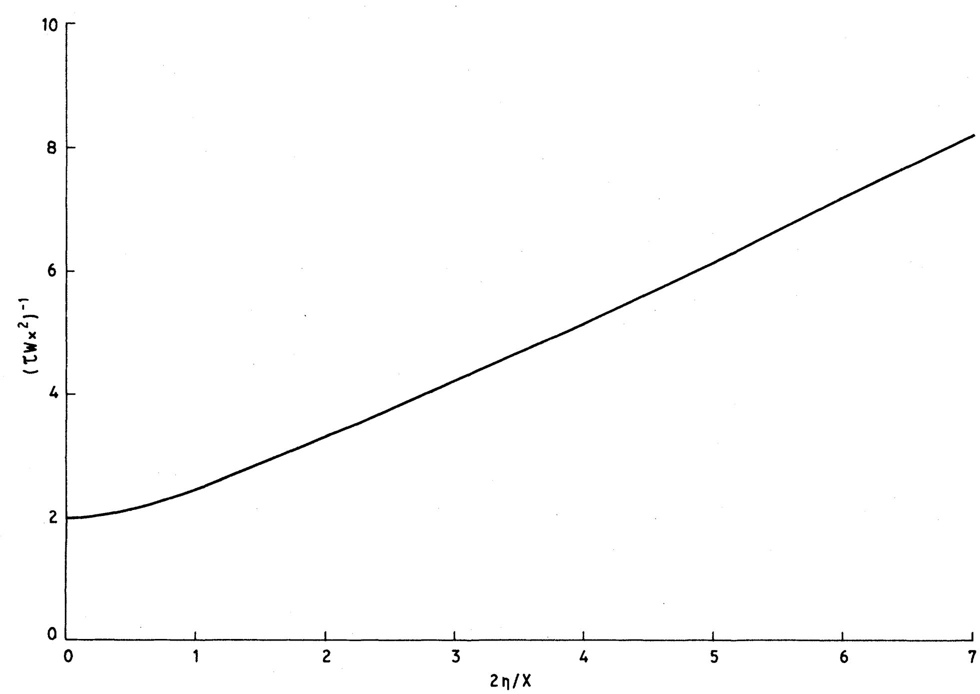

FIG. 1. Function $[\tau(\eta)Wx^2]^{-1}$ is plotted against $2\eta/x$. The effective rate constant is defined as $[\tau(\eta)W]^{-1} = k$ and $V_D = 2\eta aW$. For a given concentration this is therefore essentially a plot of k vs V_D.

so that

$$n(t,\eta) \sim \sqrt{3\pi}e^{-3/2}\left(\frac{x}{\eta}\right)^2 \frac{1}{\eta^2 Wt} e^{-\eta^2 Wt} + n_1 + \frac{n_3}{2} + L \text{ as } t \rightarrow \infty \quad . \tag{11b}$$

Equation (11) gives us the exact asymptotic ($t \rightarrow \infty$) behavior of $n(t,\eta)$ when $\eta \geq x$. It easily follows that when $\eta > x$, L dominates the time dependence of $n(t,\eta)$ in the intermediate- and long-time domain.

Our disucssion in Ref. 1 and the conclusions drawn by Haarer, Möhwald, Montroll, and Weiss remain qualitatively valid in the intermediate-time domain. When the drift velocity exceeds a certain threshold $V_D = 2aW\eta$ ($\eta = x$), the survival fraction $n(t,\eta)$ is nearly a pure exponential law in the intermediate- and long-time domain and exactly $\sim \exp[-(2x\eta - x^2)Wt]$ as $t \rightarrow \infty$. There is, of course, no sharp transition but a smooth crossover between nonexponential to exponential behavior as the drift velocity passes through the threshold region.

Turning our attention now to the effective decay time τ given by (7), we note that for $x/2\eta \ll 1$ and $x/2\eta \gg 1$ we recover the known limits $\tau = 1/2\eta Wx$ and $1/2Wx^2$, respectively. The average rate constant is proportional to the drift velocity at high fields.

We have plotted the function $[x^2 W\tau(\eta)]^{-1}$ vs $2\eta/x$ in Fig. 1 in the range [0,7]. The averaged rate constant is a smooth function for all η. The quadratic behavior with field is present for $(\eta/2x) \ll 1$ and at large fields the function becomes linear as is obvious from (7).

Finally, we would like to point out that the solution of the present model for all field strengths is not only of mathematical interest but that there exists a large class of materials for which such a description is valid. The polydiacetylenes in crystalline and film form represent quasi-one-dimensional semiconductors. Chain and defects act as deep trapping centers for photoconduction. Preliminary measurements of photoconductivity decay on PDA 10H films[7] which have a relatively large trap concentration ($x \sim 10^{-3}$) can be described by an $\exp[-(t/t_0)^{1/3}]$ law over four decades in time. Field and temperature dependence of the photoconductivity decay of quasi-one-dimensional systems are currently under study.

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[5]The relative error is as in Ref. 1 of order x.

[6]The result for $\eta = 0$ previously derived in Ref. 1, Eq. (23), still contained an infinite sum. A change of variables allows the sum to be carried out explicitly and the result is, of course, identical to Eq. (5) in the text. Note the simplicity of the final answer.

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