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Time Decay of Excitations in the One-Dimensional Trapping Problem

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An exact solution is obtained for the survival fraction in the one-dimensional diffusion problem with randomly distributed deep traps. The time decay is studied both with and without a bias field. The small concentration (x) long time (t) decay behaves as $\exp[-(x^2 t/t_0)^{1/3}]$. The exact results are compared with the coherent potential approximation (CPA) and the first passage time approach (FPT). We find that in most cases of practical interest the FPT is superior to the CPA.

KEY WORDS: Diffusion; trapping; one-dimensional system; excitations; survival fraction; master equation; scattering analogy; coherent potential approximation; first passage time approach.

1. INTRODUCTION

Diffusion and trapping of excitations or carriers in one-dimensional systems is a problem of current experimental and theoretical interest.[1,2] In this paper we present the exact solution of the one-dimensional deep trap problem using a simple scattering theory analogy. Applications range from exciton trapping, to nuclear spin diffusion and relaxation in one-dimensional-like systems, superionic conductors,[3] and polymeric chains.[4] The present results also provide a useful test of well known approximation methods such as the average t matrix (ATA),[5] coherent potential approximation (CPA),[6,7] and the first passage time approach (FPT) of Montroll.[8] The relative merit and validity of these approaches has recently been a subject of some controversy.[9] Since the CPA is always better than the ATA we shall not consider the latter in this paper. In three

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dimensions, CPA and FPT both predict the same (exponential) long time decay and time constant for the survival fraction $n(t)$ in the presence of infinitely deep traps. This is not so in one-dimensional lattices. Here one also has to distinguish between the low and the high trap concentration regimes. Calling x the trap concentration, we find that when $x \leqslant 10^{-2}$ the long time decay can be summarized by writing $n(t) \sim \exp[-(x^2 t/t_\mu)^\mu]$ with $\mu = 1$ (CPA), $\mu = 1/2$ (FPT), and $\mu = 1/3$ for the exact result. Hence in one dimension neither approximation correctly reproduces the concentration and time dependence of the survival fraction. We also find that in concentration ranges of experimental interest, the FPT is a better approximation than the CPA. The CPA is superior only in the limit of very high trap concentration $x \geqslant 1/2$. This is because, unlike the FPT, the CPA becomes exact in the limit that $x \to 1$. However, like all "effective field" theories, the CPA becomes increasingly worse as the dimensionality of the system is lowered. The FPT on the other hand is only meaningful when the concentration of trapping sites is sufficiently small.

The influence of an electric field and off-diagonal disorder is also discussed. The former is treated exactly and the latter is briefly discussed in the framework of the effective medium approximation.[10] The electric field changes the long time decay in the direction of an exponential law with increasing field strength.

2. THE SCATTERING ANALOGY

Diffusive transport in the presence of traps can be described using the master equation for the excitation density $n_i(t)$ at site i

$$\frac{dn_i(t)}{dt} = -\sum_j W_{ij} n_i(t) + \sum_j W_{ji} n_j(t) - \delta_i n_i(t) \tag{1}$$

where W_{ij} is the hopping rate between the pair of sites i and j and δ_i is the trap rate taken here to be either infinite with probability x or zero with probability $(1-x)$; x therefore represents the concentration of traps in the system. We shall present exact results for $n(t)$, the survival fraction of excitations at time t, and $\bar{G}_{00}(t)$, the probability of finding the excitation at the same site at time t. Both are the configurational averaged quantities.

Two cases are considered: (a) $W_{ij} = W_{ji} = W$ and (b) $W_+ = W(1+\eta)$, $W_- = W\,(1-\eta)$; η represents the "bias" and is given by $\eta = eEa/k_BT$. The quantities e, E, a refer to electronic charge, applied field, and lattice constant, respectively. It is assumed that W_{ij} only connects nearest neighbors.

The reason why the one-dimensional deep trap problem is exactly soluble can be simply understood. As soon as the initial site 0, the first trap of the left at site l, and the first trap on the right at site m are specified, the remaining traps in the chain become irrelevant. We therefore have to solve a two-trap problem exactly and carry out the configurational average over all possible positions of m and l. The Laplace transform of the probability of finding the excitation at site n at time t given that it was initially created at site 0, $G_{0n}(m,l)$, is easily found using Eq. (2.3) of Ref. 6. Using elementary scattering theory we have

$$G_{0n}(m,l) = G_{0n}(m) - \frac{G_{0l}(m)\delta_l G_{ln}(m)}{1+\delta_l G_{ll}(m)} \tag{2}$$

and it follows immediately that for infinitely deep traps ($\delta_l \to \infty$)

$$G_{0n}(m,l) = G_{0n} - \frac{G_{0m}G_{mn}}{G_{mm}} - \frac{(G_{0l}G_{mm} - G_{0m}G_{ml})(G_{ln}G_{mm} - G_{lm}G_{mn})}{G_{mm}(G_{ll}G_{mm} - G_{lm}G_{ml})} \tag{3}$$

The "Green functions" G_{kl} on the right-hand side of (3) now refer to the trap-free system. It is easy to check that $G_{0n}(m,l)$ vanishes when n lies outside the region (m,l). For the one-dimensional ordered chain, the renormalized perturbation expansion[6] immediately gives us, for example,

$$G_{0m} = G_{00}(p)h^m(p) \tag{4}$$

where $G_{00} = (p+2g)^{-1}$, $h(p) = g/(g+p)$, and $2g = -p + (p^2 + 4Wp)^{1/2}$. The transform of the survival fraction at time t, $n(p)$, is defined as

$$n(p) = \sum_{m=1}^{\infty} \sum_{l=-1}^{-\infty} \sum_{n=-\infty}^{\infty} x^2 G_{0n}(m,l)(1-x)^{m-1}(1-x)^{|l|-1} \tag{5}$$

where without loss of generality we have assumed that the initial site 0 is definitely not a trap. Substituting (3) in (5), using (4), particle conservation in the trap free system, and rearranging the summation we finally obtain

$$n(p) = \sum_{n=0}^{\infty} \frac{x^2(-1)^n h^{2n}(1-h)^2}{p[1-(1-x)h^n]^2 \cdot [1-(1-x)h^{n+1}]^2} \tag{6}$$

The survival fraction in the presence of an electric field can be evaluated using the same procedure. Here we find that

$$1 - p \cdot n(p,\eta) = \sum_{n=0}^{\infty} \frac{x^2(1-H)H^{2n}}{[1-(1-x)H^n]\cdot[1-(1-x)H^{n+1}]} \times \left[\frac{h_-}{1-(1-x)H^n h_-} + \frac{h_+}{1-(1-x)H^n h_+} \right] \tag{7}$$

where $H = h_+ h_-$, $h_+(p,\eta) = h_-(p, -\eta)$, and

$$h_+(p,\eta) = \frac{\left(p^2 + 4pW + 4\eta^2W^2\right)^{1/2} + 2\eta W - p}{\left(p^2 + 4pW + 4\eta^2W^2\right)^{1/2} + 2\eta W + p} \tag{8}$$

The infinite series (6) and (7) converge rapidly and are simple to compute. The exact solution will now be compared to the CPA and the FPT. From Eq. (4.1) of Ref. 6 we obtain for the CPA

$$n_{\text{CPA}}(p,\eta) = \frac{1 + x}{p^2 + 2x^2W + x\left[4W^2x^2 + p^2 + 4pW + 4\eta^2W^2(1 - x^2)\right]^{1/2}} \tag{9}$$

The zero-field limit is obtained by putting $\eta = 0$ in (9). The CPA expression shows that the bias will modify the long time behavior of $n(t)$ and this only when $\eta \geqslant x/(1 - x^2)^{1/2}$. In the small concentration limit this conclusion can be obtained from a direct physical argument[1] and as we shall see remains valid for the exact result as well. The asymptotic behavior of $n_{\text{CPA}}(t)$ is exponential and of the form $\sim\exp\{-2[1 - (1 - x^2)^{1/2}]Wt\}$.

In one dimension the survival fraction in the FPT is given by[8]

$$n_{\text{FPT}}(t) = n(0)\exp\left\{-x\int_0^t d\tau\, 2W\exp(-2W\tau)\cdot\left[I_0(2W\tau) + I_1(2W\tau)\right]\right\} \tag{10}$$

where I_0, I_1 are the modified Bessel functions. The quantity in the exponent is the number of new sites visited in a time t multiplied by the concentration of traps. The asymptotic behavior of (10) is given by $\exp[-2x(4Wt/\pi)^{1/2}]$. Approximating $n(t)$ for all times with

$$n_{\text{FPT}}(t) = \exp\left[-2x(4Wt/\pi)^{1/2}\right] \tag{11}$$

we find for the Laplace transform of (11) the expression

$$n_{\text{FPT}}(p) = p^{-1} - (\pi/4)^{1/2}\cdot ap^{-3/2}\exp(a^2/4p)\cdot \text{erfc}(a/2p^{1/2}) \tag{12}$$

with $a = 4x(W/\pi)^{1/2}$. An analysis of the exact and approximate results is presented in the next section.

3. ANALYTICAL BEHAVIOR OF THE SURVIVAL FRACTION $n(t)$ AND ITS TRANSFORM $n(p)$

Recalling that in the bias free case

$$n(p) = \sum_{n=0}^{\infty} \frac{x^2(-1)^n h^{2n}(1 - h)^2}{p\left[1 - (1 - x)h^n\right]^2\cdot\left[1 - (1 - x)h^{n+1}\right]^2} \tag{13}$$

with $h(p)$

$$h(p)=\frac{(p^2+4Wp)^{1/2}-p}{(p^2+4Wp)^{1/2}+p} \tag{14}$$

it follows easily that

$$\begin{aligned} n(p=0) &= 1/2x^2W \\ n(p\to\infty) &\sim 1/p \end{aligned} \tag{15}$$

The infinite series (13) is simple to compute for all p. This is illustrated in Fig. 1 where $n(p)$ is compared to the CPA and Eq. (12) for $x = 10^{-3}$. From Fig. 1 we can immediately infer that the FPT must be a better approximation than the CPA for this particular concentration. We shall now show that this generally holds for $x \leqslant 10^{-2}$.

Since we are interested in the survival fraction $n(t)$ and (13) cannot be analytically Laplace inverted, we look for a good approximation $n_a(p)$ for

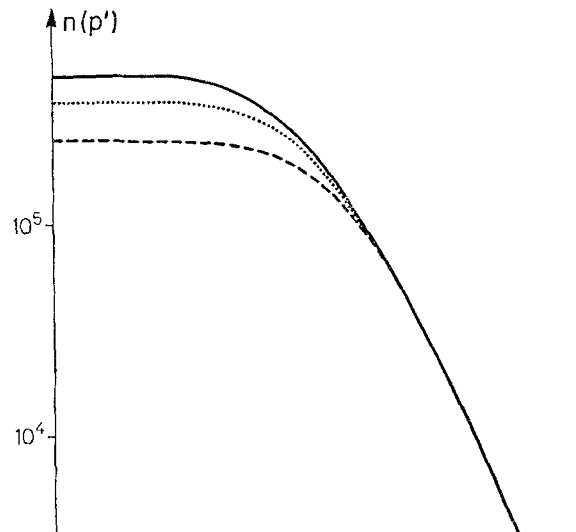


Fig. 1. $n(p')$ is plotted against $p' = p/W$ [Full curve: exact result; dotted curve: Eq. (12); dashed curve: CPA], $x = 10^{-3}$.

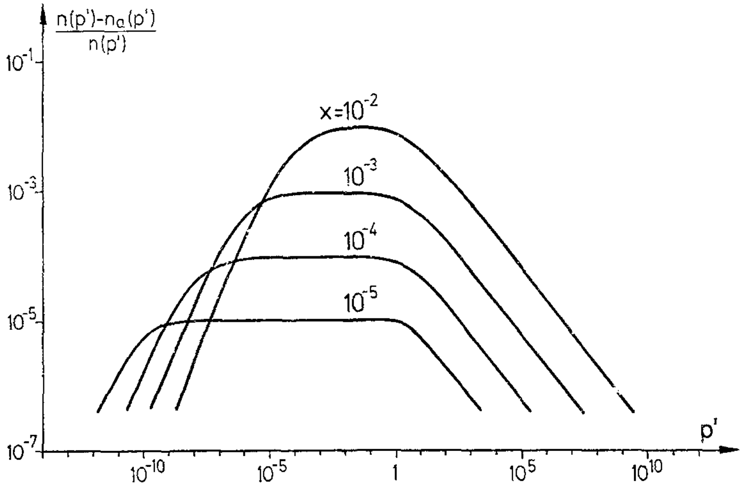


Fig. 2. The relative error $[n(p') - n_a(p')]/n(p')$ is plotted against $p' = p/W$ for $x = 10^{-2}$, 10^{-3}, 10^{-4}, and 10^{-5}.

the infinite series (13). First we carry out an expansion for small values of p and we obtain with $h \sim 1 - (p/W)^{1/2}$

$$n_a(p) = \frac{y^2}{p} \cdot \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+y)^2(n+1+y)^2} \tag{16}$$

where y is defined by $y = x(W/p)^{1/2}$. This infinite series (16) is exact for $p = 0$ and obviously also exact in the $p \to \infty$ limit. This results because for large values of p the first term $n = 0$ dominates the series $n(p)$ and $n_a(p)$, and these terms are identical. To illustrate that $n_a(p)$ is an excellent approximation for $n(p)$ for all values of p we have plotted in Fig. 2 the relative error $[n(p) - n_a(p)]/n(p)$ as a function of p. The maximum error with arises for all values of p is just of the order of the trap concentration x. The function $n_a(p)$ is therefore effectively an exact representation of $n(p)$ as long as $x \leqslant 10^{-2}$.

The infinite series $n_a(p)$ (16) can be rewritten in an integral representation

$$n_a(p) = p^{-1} - \frac{2y^2}{p} \cdot \int_0^{\infty} d\lambda \tanh(\lambda/2)\exp(-y\lambda) \tag{17}$$

which is easier to handle than the infinite series. Writing $\tanh\lambda/2 = 1 - 2/[1 + \exp(\lambda)]$, expanding $\exp(-\lambda y)$ in a power series and then inverting term by term we obtain a power series for $n(t)$ which is convergent for all values of t:

$$n(t) = 4 \sum_{n=0}^{\infty} (-1)^n \zeta(n-1)(1-2^{2-n}) \cdot \left[x(Wt)^{1/2} \right]^n / (n/2)! \quad (18)$$

Here $(n/2)!$ is defined by the gamma function $(n/2)! = \Gamma(n/2+1)$ and ζ is Riemann's zeta function, given for example by the relation

$$\zeta(n-1)(1-2^{2-n}) = 1/(n-2)! \cdot \int_0^{\infty} d\lambda \lambda^{n-2} \left[\exp(\lambda) + 1 \right]^{-1} \quad (19)$$

Considering the first three terms of the power series (18)

$$n(t) = 1 - 4x(Wt/\pi)^{1/2} + \pi/4 \cdot \ln 2 \left[4x(Wt/\pi)^{1/2} \right]^2 \pm \cdots \quad (20)$$

we see that this expression is for short times identical to the asymptotic form (11) of the FPT result. In Fig. 3 we observe that $n(t)$ obtained from

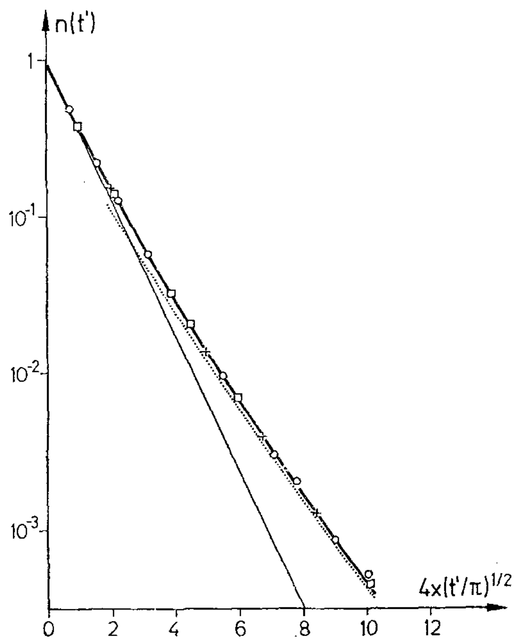


Fig. 3. $\ln n(t')$ is plotted against $4x(t'/\pi)^{1/2}$ with $t' = tW$. Full curve: power series Eq. (20); dotted curve: asymptotic form Eq. (24); thin curve: $\exp[-4x(t'/\pi)^{1/2}]$. The symbols represent the numerical inversion of the exact result Eq. (13) [+: $x = 10^{-2}$, □: 10^{-3}, ○: 10^{-4}].

the power series (20) is in excellent agreement with the numerical inversion of the exact $n(p)$ (13) for trap concentrations $x \leqslant 10^{-2}$.

To obtain the asymptotic long time decay behavior of $n(t)$ we go back to Eq. (17), and change the variables $\lambda y = s$. The expression can then be inverted directly to yield

$$n(t) = 1 - 4x^2 \int_0^t du \int_0^\infty ds \exp(-s)/s \cdot \Theta_2(0\,|\,u \cdot 4x^2/s^2) \qquad (21)$$

where Θ_2 is the second elliptic theta function represented by the following series:

$$\Theta_2(0\,|\,z) = 2 \cdot \sum_{n=0}^{\infty} \exp\left[-\pi^2 z(n+1/2)^2\right] \qquad (22)$$

Inserting this expansion in Eq. (21) and carrying out the u integration we obtain

$$n(t) = \frac{2}{\pi^2} \cdot \sum_{n=0}^{\infty} \frac{1}{(n+1/2)^2} \cdot \int_0^\infty dy\, y \exp\left[-y - 4\pi^2 x^2 Wt(n+1/2)^2/y^2\right] \qquad (23)$$

and by steepest descent the leading term ($n = 0$) becomes

$$n(t \to \infty) \sim 8(4x^2Wt/3\pi)^{1/2} \cdot \exp\left[-3(\pi^2 x^2 Wt/4)^{1/3}\right] \qquad (24)$$

The true asymptotic long time behavior of the one-dimensional deep trap problem behaves in the region of physical interest therefore as $\exp[-(x^2t/t_0)^{1/3}]$ in contrast to CPA and FPT. This is illustrated in Fig. 3, where the exact $n(t)$ is compared with the asymptotic form (24) in the regime $x \leqslant 10^{-2}$. Figure 3 also illustrates the concentration scaling property implicit in (23) and (24).

4. HIGH TRAP CONCENTRATION ($x \geqslant 10^{-2}$)

The analytic approximation becomes increasingly worse with increasing x. A corresponding one can presumably be developed for x close to 1 but we shall not pursue this in the present paper. In the regime $x \geqslant 10^{-2}$ we have studied the time decay numerically for $x = 0.1$ and 0.6 and for comparison $x = 10^{-2}$. Figures 4a–4c show that in this concentration range the CPA tends to become a better approximation than the FPT but only when $x \geqslant 1/2$. This is simply because the CPA becomes exact when $x \to 1$ whereas the FPT which relies on the concept of the average number of new sites visited in the trap-free system becomes meaningless in the limit of very high trap concentration.

The effect of a bias field is illustrated in Fig. 5. The field leads as expected to a faster decay in the long time regime when $\eta \geqslant x$; this corresponds to a critical field $E_c = xk_BT/ea$. In general $\ln n(t,\eta) \propto -t^{\mu(\eta)}$, where $\mu(\eta) \to 1$ as $\eta \to 1$. The critical field is several orders of magnitude higher in two- or three-dimensional systems.[1] The analytic treatment of the field-dependent case is more difficult and will be considered in a future paper.

5. THE PROBABILITY OF REMAINING ON THE SAME SITE $G_{00}(t)$

Let us now consider the quantity $\bar{G}_{00}(p)$ which denotes the Laplace transform of the configurational averaged $\bar{G}_{00}(t)$ or probability of finding the excitation on the same site at time t. This quantity is of interest in for example fluorescence line narrowing experiments[11] and NMR relaxation.[4] By definition

$$\bar{G}_{00}(p) = \sum_{m=1}^{\infty} \sum_{l=-1}^{\infty} x^2(1-x)^{m-1}(1-x)^{|l|-1} G_{00}(m,l) \tag{25}$$

Using (3) and (4) this can be rewritten as

$$\bar{G}_{00}(p) = x^2 G_{00}(p) \sum_{n=0}^{\infty} \frac{(1-h^2)^2 h^{4n}}{\left[1-(1-x)h^{2n}\right]^2 \cdot \left[1-(1-x)h^{2n+2}\right]^2} \tag{26}$$

with $\bar{G}_{00}(p=0)$ evaluated to be $(2+x)/6Wx$. In the CPA we obtain

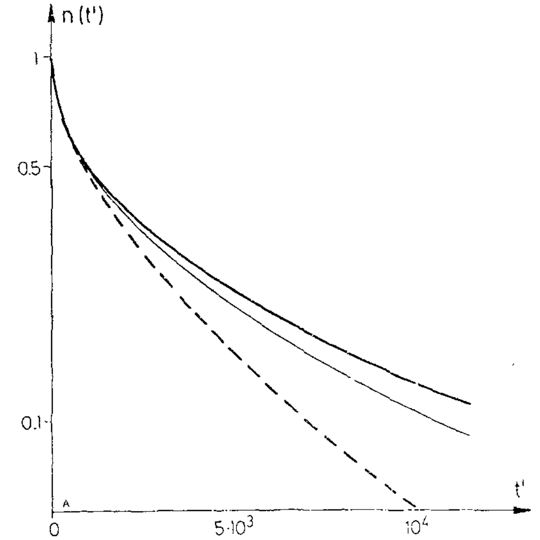
$$\bar{G}_{00}^{\mathrm{CPA}}(p) = \frac{1+x}{xp + 2Wx + (p^2 + 4pW + 4x^2W^2)^{1/2}} \tag{27}$$

We again make the expansion for small values of p using (26) and obtain

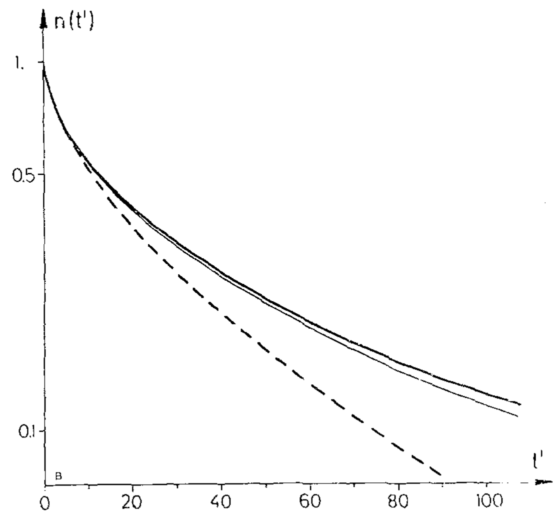
$$\bar{G}_{00}^{a}(p) = y^2 G_{00}(p) \sum_{n=0}^{\infty} \frac{1}{(n+y)^2(n+1+y)^2} \tag{28}$$

but now with $y = x(W/2p)^{1/2}$. This infinite series approximates the exact $p=0$ value $(2+x)/6Wx$ by $2/6Wx$ and is obviously exact in the $p \to \infty$ limit for the same reason as for $n(p)$. Again we find that $\bar{G}_{00}^{a}(p)$ is an almost exact representation of $\bar{G}_{00}(p)$ as long as $x \leqslant 10^{-2}$. The relative error $[\bar{G}_{00}(p) - \bar{G}_{00}^{a}(p)]/\bar{G}_{00}(p)$ is for all values of p less than half the trap concentration x. The infinite series $\bar{G}_{00}^{a}(p)$ (28) can be rewritten in an integral representation

$$\bar{G}_{00}^{a}(p) = G_{00}(p) \cdot p^{-1/2} \cdot \left[-y + \int_0^{\infty} ds \coth\left(\frac{s}{2y}\right) \exp(-s) \right] \tag{29}$$

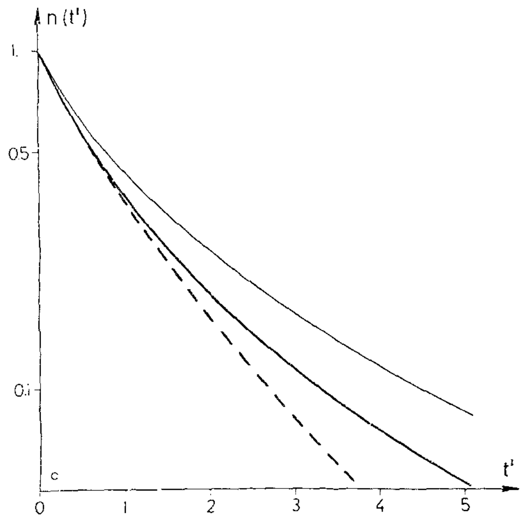


(a)



(b)

Fig. 4. $\ln n(t')$ is plotted against $t' = tW$ for (a) $x = 0.01$, (b) $x = 0.1$, and (c) $x = 0.6$. [Solid curve: exact result; thin curve: FPT Eq. (10); dashed curve: CPA.]



(c)

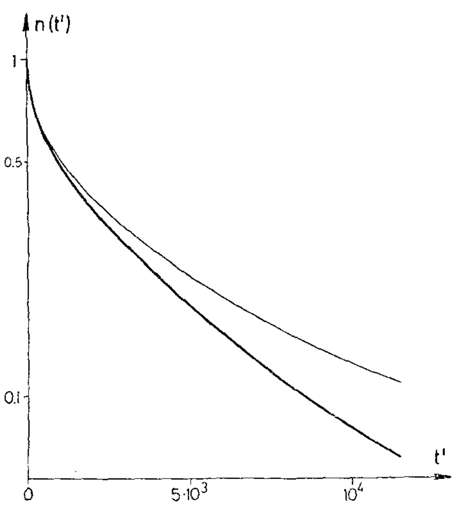


Fig. 5. $\ln n(t')$ is plotted against $t' = tW$ for $\eta = x = 0.01$ (solid curve) and $\eta = 0$ (thin curve).

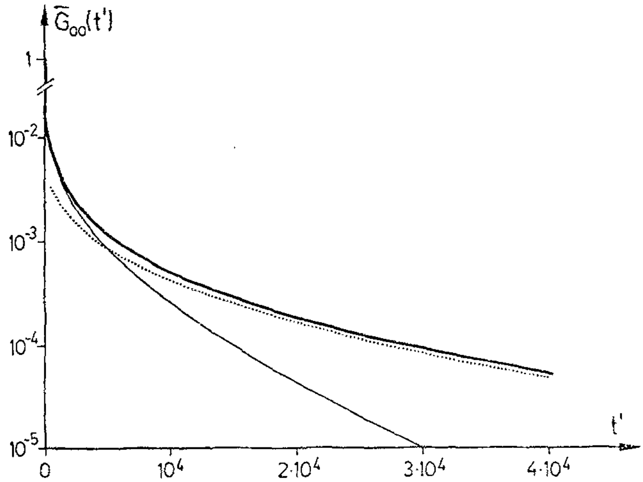


Fig. 6. $\bar{G}_{00}(t')$ is plotted against $t' = tW$ for $x = 0.01$. [Solid curve: exact result; thin curve: CPA; dotted curve: asymptotic form Eq. (32).]

which can immediately be inverted if we use the small p form $\bar{G}_{00}(p)/p^{1/2} \sim 1/2pW^{1/2}$, to yield

$$\bar{G}_{00}(t) \simeq \frac{-x}{2} + \frac{x}{2} \cdot \int_0^\infty ds\, \Theta_3(0 \mid Wtx^2/s^2) \cdot \exp(-s) \tag{30}$$

Using for the third elliptic theta function Θ_3 the following expansion:

$$\Theta_3(0 \mid z) = 1 + 2 \sum_{n=1}^{\infty} \exp(-\pi^2 z n^2) \tag{31}$$

we obtain for the leading term $n = 1$ with the method of steepest descent

$$\bar{G}_{00}(t) \sim x(2\pi/3)^{1/2}(2\pi^2 x^2 Wt)^{1/6} \exp\left[-3(\pi^2 x^2 Wt/4)^{1/3}\right] \tag{32}$$

the long time behavior for the configurational averaged $\bar{G}_{00}(t)$. The exact $\bar{G}_{00}(t)$ is compared to the CPA and the asymptotic form (32) in Fig. 6.

6. DISCUSSION

We have presented exact results for the survival fraction $n(t)$ and the same site probability function $\bar{G}_{00}(t)$ in a one-dimensional ordered system with randomly distributed deep traps. Neither FPT nor CPA predict the correct form of the time and concentration dependence. The influence of fluctuations in one dimensions makes any approximations dangerous although we have shown that the FPT is clearly superior to the CPA in this case. An important extension to treat disordered systems would be to consider the one-dimensional chain with disorder in the hopping rates W_{ij}. In the bond percolation limit, the diffusion problem has been solved exactly by Odagaki and Lax.[2] In the general case of physical interest one has to rely on approximation methods. Odagaki and Lax also discussed the relative merit of approximation methods such as the "effective medium approximation,"[10] continuous time random walk,[12] and CPA.[2] It should be straightforward to include the schemes in the present solution of the trapping problem, because Eqs. (3) and (5) are valid in general. Treating the disorder in the effective medium approximation is, for example, equivalent to replacing the quantity $h(p)$ in (6) with $\langle g\rangle/(p+\langle g\rangle)$ where $\langle g\rangle$ is given by

$$\langle g\rangle = \int dW \rho(W)\left[1/W + 1/(p+\langle g\rangle)\right]^{-1} \tag{33}$$

Once $\langle g(p)\rangle$ is known one can evaluate $n(t)$ using (6). Here $\rho(W)$ is the distribution of hopping rates. In the $p \to 0$ limit we have $D(0) = a^2\langle 1/W\rangle^{-1}$ for the diffusion coefficient and $n(p=0) = \langle 1/W\rangle/2x^2$ for the survival fraction.

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