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Recombination in amorphous materials as a continuous-time random-walk problem

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In this paper we study carrier recombination in amorphous materials. The dynamics is described through continuous-time random walks, for which several stepping-time distributions are used. We determine the probability of the carrier being captured at the recombination centers from the number of distinct sites visited in the walk. The overall process is then modeled in the framework of chemical reactions. Our approach unifies the derivation of decay laws due to recombination and allows a critical evaluation of former results; these conclusions are verified both by analytical and by numerical methods.

I. INTRODUCTION

In the last few years, processes of carrier recombination in disordered materials have attracted considerable theoretical[1-4] and experimental attention.[5-9] For wide classes of materials the decay law due to recombination is highly nonexponential in time. An algebraic decay law provides a good description of the behavior for longer times[7-9]:

$$N(t) \propto ct^{-\beta} . \tag{1}$$

Here $N(t)$ denotes the survival probability of the carrier at time t, and β is a parameter of the process, $0<\beta<1$.

Recombination of two oppositely charged carriers, species A and B (say electrons and holes), is supposed to occur predominantly at particular recombination centers (rc). A general theoretical treatment of the process has to include both the motion of the carriers and also their encounter at the rc. For simplicity, we will assume that one sort of carriers, for example, B, reaches the rc very quickly, so that the recombination is determined by the motion of the A-type carriers to the already B-occupied rc. In the following discussion, only these rc will be considered. Furthermore, we assume that the A carriers recombine at the first encounter of a rc and we describe their motion as a random walk. In the amorphous material the distribution of sites involved in the carrier transport is random, and we are faced with the problem of a random walk on a random lattice. Since no exact approach to this problem is available, we have to use approximate schemes, such as the very successful continuous-time random walk (CTRW).[10-12] In a simple version of the CTRW, one lets the walk take place on a *regular* lattice, and mimics the disorder through stepping-time densities $\psi(t)$ (Ref. 12); this version decouples the temporal process from the spacial one.

In recent theoretical works by Ngai and Liu it was asserted that the decay behavior of Eq. (1) can be explained through a CTRW model with a stepping-time density of the form[4,13]

$$\psi(t)=c\alpha t^{\alpha-1}\exp(-ct^{\alpha}) , \quad 0<\alpha<1 . \tag{2}$$

In Ref. 4 this form was obtained by assuming low-frequency fluctuations, and it is claimed that this equation fits the experimental parameters. We note that this $\psi(t)$ also follows from multipolar transfers in a spatially disordered system.[14-16] On the other hand, Scher and Montroll modeled transport in amorphous media through a $\psi(t)$ which displays a long-time tail[12]:

$$\psi(t) \propto t^{-1-\gamma} , \quad 0<\gamma<1 . \tag{3}$$

The use of this $\psi(t)$ was criticized by Ngai and Liu,[4] who maintain that it does not lead to Eq. (1). The controversy thus touches the fundamental question of the correct description of transport in disordered systems.

Another aspect of the problem connected with Eq. (1) is whether a unimolecular or a bimolecular reaction type applies. References 1 and 3 stress the unimolecular behavior, whereas Refs. 2 and 4, together with interpretations to experimental results,[7–9] favor a bimolecular explanation.

The purpose of this paper is to clarify the situation and to connect the different approximations. In Sec. II we start from a model involving a single random walker on an infinite lattice with randomly distributed rc and calculate the decay law due to recombination. We present approximations to the exact decay law and relate these to the average number of distinct sites $S(t)$ visited during time t. In Sec. III we extend the calculations to the case of several random walkers; in terms of chemical reactions we analyze the recombination both in unimolecular and in bimolecular reaction schemes. Since our analytical expressions are mainly *asymptotic* results valid for long times, we present in Sec. IV the rates for the decay due to recombination also for short and moderately long times; these rates are determined through numerical calculations for the stepping-time density given by Eq. (2). This paper concludes with a critical summary of results.

II. RECOMBINATION IN A RANDOM-WALK SCHEME

In this section we treat the recombination of an A-type carrier at a rc as a first-passage-time problem for a random walk on a regular simple cubic lattice with stepping-time probabilities $\psi(t)$. For a particular realization of the random walk *without* rc we let R_n denote the number of distinct sites visited in n *steps*. For the same realization of the walk T_n denotes the probability (over the ensemble of lattices with rc) that recombination has not occured up to the nth step. The quantities R_n and T_n are stochastic variables related through[17,18]

$$T_n=(1-p)^{R_n-1} . \tag{4}$$

Here the rc (occupied by type-B carriers) are taken to be randomly distributed over the lattice and to occupy its sites with probability p. We take the origin of the walk not to be a rc (otherwise see Ref. 18) and the recombination to occur instantaneously at the first encounter of a rc, i.e., the first-passage-time assumption. For walks with fixed stepping frequency the decay law is the average of Eq. (4) over all realizations of the random walk in *space*:

$$\Phi_n\equiv\langle T_n\rangle=\langle(1-p)^{R_n-1}\rangle , \tag{5}$$

whereas for walks in continuous time the decay also involves a *temporal* average:

$$\Phi(t)\equiv\langle\langle T_n\rangle\rangle=\sum_{n=0}^{\infty}\langle(1-p)^{R_n-1}\rangle\phi_n(t) . \tag{6}$$

Here $\phi_n(t)$ is the probability of having performed exactly n steps in time t, which in the CTRW formalism is related to the stepping-time density $\psi(t)$ through[3,16]

$$\phi_n(u)=[\psi(u)]^n[1-\psi(u)]/u , \tag{7}$$

where $f(u)\equiv\mathscr{L}[f(t)]$ is the Laplace transform of $f(t)$.

Equations (5) and (6) are exact. Analytically, however, the distribution of R_n values is not generally known. One therefore has to resort to approximations.

A canonical way to proceed is to use a cumulant expansion of Eqs. (5) and (6) in terms of $\lambda\equiv-\ln(1-p)$. This approach was discussed by us in Refs. 16, 18, and 19, where we pointed out that the expansion works best for higher-dimensional lattices. In this paper we restrict ourselves to a three-dimensional simple cubic lattice; in this case for random walks with *fixed* stepping-time frequency and for low rc concentrations ($p\ll1$), already the *first* cumulant, i.e., the *mean* number of distinct sites visited, $S_n\equiv\langle R_n\rangle$, allows a satisfactory description of the decay:

$$\Phi_n\simeq(1-p)^{S_n-1}\approx e^{-pS_n}\quad(p\ll1) . \tag{8}$$

A major advantage in using Eq. (8) rests in the fact that much information on S_n is known from the generating function formalism[10]; higher cumulants are much more difficult to evaluate.[17–19] For three-dimensional random walks, S_n behaves asymptotically as $S_n=an+O(\sqrt{n})$, where for nearest-neighbor random walks on cubic lattices the constant a is given by the inverse of the corresponding Watson integral.[10,20]

In the CTRW representation we obtain, therefore, for low rc concentrations and three-dimensional lattices, the following:

$$\Phi(t)\approx\sum_{n=0}^{\infty}e^{-pS_n}\phi_n(t)\quad(p\ll1) \tag{9}$$

where we used Eqs. (6) and (8).

Two approximations to Eq. (9) are now possible. One approximation is to view the sum over n as a time average and to consider a cumulant expansion in time.[16] Here the first cumulant is

$$S(t)=\sum_{n=0}^{\infty}S_n\phi_n(t) ,$$

and in this case one has

$$\Phi(t)\approx e^{-pS(t)} , \tag{10}$$

a form which has been used extensively.[2–4,16,21–23] This is best seen by defining the decay rate $k(t)$ of $\Phi(t)$ through $k(t)=-\dot{\Phi}(t)/\Phi(t)$ and noticing that, from Eq. (10),

$$k(t)\approx p\frac{dS}{dt}\ , \tag{11}$$

the first-passage-time rate of Ref. 23.

The second approximation to Eq. (9) is obtained by making use of $S_n \propto an$, which together with Eq. (7) allows the direct summation of Eq. (9),[3]

$$\begin{aligned}\mathscr{L}[\Phi(t)]&\approx\frac{1-\psi(u)}{u}\sum_{n=0}^{\infty}[e^{-pa}\psi(u)]^n\\ &=[1-\psi(u)]/\{u[1-e^{-pa}\psi(u)]\}\ .\end{aligned} \tag{12}$$

Both forms, Eqs. (10) and (12), have their respective advantages. Equation (10) is certainly superior in describing the short-time decay. As pointed out in Ref. 16, the approximation (10) is convenient for an exponential stepping-time distribution, where it approximates well the true decay form, Eq. (6). The approximate form (10) gets poorer, however, if the stepping-time distribution gets broader,[16] as, for instance, for higher multipolar interactions in Eq. (2). The disadvantage of Eq. (12) is that it is not readily extendable to lower dimensionalities. Its main advantage rests in the long-time description of the decay law, as we now show.

As is evident from Eq. (12) the decay law depends on $\psi(u)$, the Laplace transform of $\psi(t)$. The long-time behavior is crucially determined by the first moment τ_1 of the $\psi(t)$ distribution,

$$\tau_1=\int_0^{\infty}dt\,t\psi(t)\ .$$

If τ_1 is finite then $\psi(u)\approx 1-\tau_1 u$ for small u. In this case one has from Eq. (12), for longer times,

$$\mathscr{L}[\Phi(t)]\approx(u+pa/\tau_1)^{-1}\ .$$

Hence a time domain $\Phi(t)$ compatible to this behavior is

$$\Phi(t)\approx e^{-pat/\tau_1}\ , \tag{13}$$

i.e., an exponential.[16] Long-time tails in $\psi(t)$ may, however, lead to deviations from Eq. (13) for very long times. For the stepping-time distribution of Eq. (3), τ_1 is infinite. One then obtains

$$\psi(u)\approx 1-\Gamma(1-\gamma)u^{\gamma}/\gamma\ ,$$

where $\Gamma(x)$ is the Euler gamma function.[24] In this case one has

$$\mathscr{L}[\Phi(t)]\sim[\Gamma(1-\gamma)/\gamma]u^{\gamma-1}L(u)\ ,$$

with

$$L(u)\sim\{1-e^{-pa}[1-\Gamma(1-\gamma)u^{\gamma}/\gamma]\}^{-1}$$

being a slowly varying function[25] of u, for $u\to 0$. With the use of a Tauberian theorem (Theorem 4, p. 446 of Ref. 25), one obtains

$$\Phi(t)\sim t^{-\gamma}/(pa\gamma) \tag{14}$$

for long times. For $\gamma=\frac{1}{2}$, Eq. (14) was already established through an exact inverse Laplace transform.[1,3]

Consider now the approximate form Eq. (10). We remark that $S(u)$, the Laplace transform of $S(t)$, is given by[10,16]

$$S(u)=\{u[1-\psi(u)]P[\vec{0};\psi(u)]\}^{-1}\ , \tag{15}$$

where $P(\vec{0};z)$ is the generating function of the walk and

$$\lim_{z\to 1^-}P(\vec{0};z)=a^{-1}$$

for three-dimensional lattices. For $\psi(u)\approx 1-\tau_1 u$ one obtains $S(t)\sim at/\tau_1$. Thus Eq. (10) leads in this case also to Eq. (13). For

$$\psi(u)\approx 1-\Gamma(1-\gamma)u^{\gamma}/\gamma$$

the situation is, however, very different. Using Eq. (15) and the same Tauberian theorem leads to

$$S(t)\sim at^{\gamma}/[\Gamma(\gamma)\Gamma(1-\gamma)]\ .$$

Therefore Eq. (10) implies

$$\Phi(t)\sim\exp\{-pat^{\gamma}/[\Gamma(\gamma)\Gamma(1-\gamma)]\}\ . \tag{16}$$

Note the difference between Eqs. (16) and (14). From our numerical experience we view Eq. (14) to be the better approximation at longer times. This is due to the fact that assuming $S_n=an$ works very well in three dimensions for moderate and for large n (see Ref. 20). The summation in Eq. (12) then takes care of all temporal cumulants of $\phi_n(t)$, whose influence is significant for broad distributions, and which are neglected in Eq. (10).

We should emphasize that in the derivation of Eq. (14) no use has been made of the particular form of $S(t)$, the determining factor being $[1-\psi(u)]/u$ in Eq. (12). Nevertheless, one may express Eq. (14) in the form

$$\Phi(t)\sim[p\Gamma(1+\gamma)\Gamma(1-\gamma)S(t)]^{-1}\ , \tag{17}$$

a fact noted already by Scher.[1] The extension of this result to other dimensionalities calls for further attention.

In this section we considered the decay of a single random walker captured by the rc. We are now ready to proceed to the case of several walkers present on the lattice.

III. RECOMBINATION AS A CHEMICAL REACTION

The purpose of this section is to relate the recombination process described in the Introduction to a chemical reaction and to quantify it with the help of the results of Sec. II. Let $N_A(t)$ denote the number of A-type carriers at time t and $N_B(t)$ the number of rc occupied by B-type carriers. Recombination is then described through

$$A + B \rightarrow AB \, , \tag{18}$$

from which (in the absence of other processes) conservation of particles implies

$$N_A(t) + C = N_B(t) \, , \tag{19}$$

where C is a constant. We denote the reaction rate of (18) by $K(t)$ and have

$$\frac{d}{dt} N_A(t) = -K(t) N_A(t) N_B(t) \tag{20}$$

which, with Eq. (19), is easily integrated by a variable separation:

$$r[N_A(t)] - r[N_A(0)] = \int_0^t K(t')dt' \, , \tag{21}$$

where $r(x) \equiv C^{-1} \ln(1 + C/x)$.

Two limiting cases are of interest. If $N_B(0) \gg N_A(0)$ then $C \gg N_A(t)$, and therefore we are in the low x/C limit. In this limit $r(x) \approx C^{-1} \ln(C/x)$ and

$$N_A(t) = N_A(0) \exp\left[-C \int_0^t K(t')dt' \right] \, , \tag{22}$$

which is a quasiunimolecular decay. If $N_A(0) = N_B(0)$, then $C = 0$. From the limit $C \rightarrow 0^+$ one has $r(x) \approx 1/x$ and thus

$$[N_A(t)]^{-1} = [N_A(0)]^{-1} + \int_0^t K(t')dt' \, , \tag{23}$$

a bimolecular decay, which for longer times behaves as

$$N_A(t) \sim \left[\int_0^t K(t')dt' \right]^{-1} . \tag{24}$$

Other cases are easily obtainable from Eq. (21).

Let us relate $N_A(t)$ to $\Phi(t)$ of the preceding section. We again have to distinguish between the different cases for $\psi(u)$, depending on the existence of τ_1.

For finite τ_1 the form of $\Phi(t)$ is given by Eq. (13), from which we have $k(t) = pa/\tau_1$. We remark that p of $\Phi(t)$ is the number density of rc, so that we have to identify p with $N_B(t)/N_T$, where N_T is the total number of sites. This is now an approximation, since in the previous derivations p was assumed to be constant. We note, however, that the hopping occurs on a shorter time scale than the recombination, so that on the time scale of $\psi(t)$, $N_B(t)$ is quasistationary. By identifying in Eq. (20) $k(t)$ with $K(t)N_B(t)$, $K(t)$ turns out to be $K(t) = a/(N_T \tau_1)$. Setting now this value into Eqs. (22) and (24) we obtain

$$N_A(t) = N_A(0) \exp\left[-\frac{Cat}{N_T \tau_1} \right]$$
$$\approx N_A(0) e^{-pS(t)} = N_A(0) \Phi(t) \tag{25}$$

in the unimolecular case, and

$$N_A(t) \sim \frac{N_T \tau_1}{at} = N_T / S(t) \tag{26}$$

in the bimolecular case of Eq. (23). We remark here that *neither* Eq. (25) *nor* Eq. (26) corresponds to the decay law of Eq. (1). This point will be stressed further in the discussion of Sec. IV. It should be noted here, however, that for a limited range of t values a behavior as in Eq. (1) could obtain simply due to other values of C than the special cases which we explicitly considered.

For a stepping-time distribution as in Eq. (3), whose first moment τ_1 does not exist, we have to refer to the decay law Eq. (14). The unimolecular behavior obtains, as before,[1,3,26]

$$N_A(t) = N_A(0) \Phi(t) \sim N_A(0) / (pa\gamma t^\gamma) \, , \tag{27}$$

which has the same form as Eq. (1). Calculating $k(t)$ from $-\dot{\Phi}(t)/\Phi(t)$ we now obtain $k(t) = t^{-1}$. Thus for longer times $k(t)$ is *independent* of the concentration of rc and of the parameter γ.

The independence of $k(t)$ on p renders now quite arbitrary an identification relating $k(t)$ to $K(t)$. As also noted in Ref. 1, an investigation of the *bimolecular* decay *cannot* be readily inferred from Eq. (14). The reason for the difference from the previous case (finite τ_1) rests in the fact that for finite τ_1 both approximations of Sec. II, Eqs. (10) and (13), lead to the same decay. As noted, Eq. (10) is more appropriate at shorter times. One can thus safely extend the information on the asymptotic behavior of the decay rate to also cover the shorter times needed for the integral in Eq. (21). For infinite τ_1 the situation is different, and a naive insertion of $k(t) = t^{-1}$ into Eq. (21) leads to divergent behavior at short times.

In this section we have connected the recombination in the random-walk scheme to the chemical reaction Eq. (18). Here, as in previous investigations,[1–4,26] the dynamics of the process enters

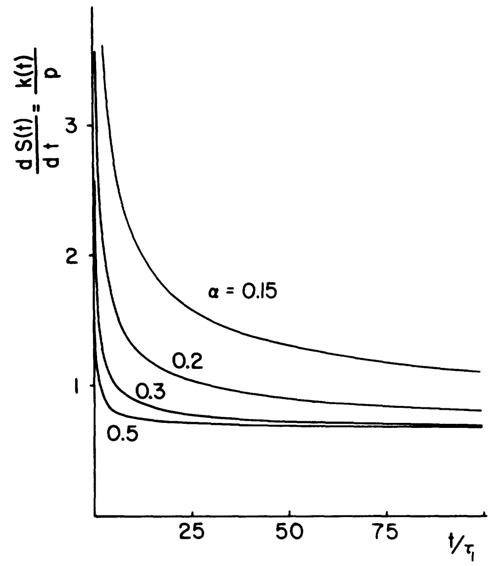

FIG. 1. Decay rate $k(t)$ due to carrier recombination in the regime of low rc concentration p. The stepping-time density $\psi(t)$ of the CTRW is given by Eq. (2); here α is, respectively, 0.5, 0.3, 0.2, and 0.15. The time is scaled in units of the mean stepping time τ_1; we plotted $k(t)/p$ vs t/τ_1.

through the reaction rate $K(t)$. We remark that other treatments of recombination in amorphous systems also admit chemical analogs, which, however, have a different character. In the multiple-trapping models it is assumed that only the mobile carriers can recombine, and that their motion is temporarily stopped by trapping. The reaction scheme is therefore

$$A \rightleftarrows A_t \,, \tag{28a}$$

$$A + B \rightarrow AB \,, \tag{28b}$$

where A_t are the carriers immobilized by trapping.[9,27] In this case the time dependence of the recombination Eq. (28b) is due to the trapping and release processes (28a).

IV. NUMERICAL RESULTS AND CONCLUSIONS

From the discussions of previous sections it becomes obvious that a purely analytical treatment of the CTRW model is restrictive, since in most cases the decay laws due to recombination could be determined only for a very low density of carriers ($p \ll 1$) and in the long-time limit. These difficulties may be overcome by the use of numerical methods, as we show in this section.

To exemplify the procedure we start from the stepping-time distribution function Eq. (2), used by Ngai and Liu (Ref. 4). One verifies readily that all moments of this $\psi(t)$ exist. From the discussion in Secs. II and III this implies a constant decay rate for longer times. Thus in a unimolecular reaction scheme the decay, Eq. (25), is exponential, whereas for a bimolecular reaction one has from Eq. (26) $N_A(t) \sim t^{-1}$ for long times. These results contrast strongly with the decay laws given in Ref. 4, Eqs. (60) and (66), which show a different time behavior.

At this point it can be argued that all analytical approaches presented are only approximate, so that for certain parameter ranges the result of Ref. 4 may hold. We can check this possibility only through numerical simulations. Before demonstrating this, we first point out the reason for the existing discrepancies. Equation (53) of Ref. 4 is recognized to be the Laplace transform of $p dS(t)/dt$, when our Eq. (15) is used, and one identifies p with $1/(V-1)$, where V is the volume of the *finite* crystal. Therefore, $F(t)$ of Ref. 4 is identical to $k(t)$, our Eq. (11). Obviously, here it makes no difference whether finite or infinite lattices are considered. Using the expansion $\psi(u) \approx 1 - u\tau_1$ in Eq. (53) of Ref. 4 leads to $k(t) \equiv F(t) \propto pa/\tau_1$, the standard result of Sec. II. This result is different from Eq. (57) of Ref. 4, which shows a complex time dependence.

We now present the decay rate $k(t)$ for short- and medium-ranged times, $0 \le t/\tau_1 \le 100$, where we consider a nearest-neighbor CTRW on a simple cubic lattice with a distribution $\psi(t)$ which obeys Eq. (2). We start from a very low density of rc and study the influence of the parameter α on $k(t)$. We concentrate on $k(t)$, since all moments of $\psi(t)$ exist, and thus, as shown in Sec. III, the decay rates $K(t)$ are readily related to $k(t)$. For this, we first evaluate numerically $S(t)$ from Eq. (15), using the exact analytical form of $P(\vec{0};z)$ as given by Joyce[28] and an inverse Laplace-transform procedure based on Ref. 29. In Eq. (15) $\psi(u)$, the Laplace-transform of $\psi(t)$, Eq. (2), is also needed; we evaluated $\psi(u)$ using the series expansions formulated in Ref. 14.

The decay rates $k(t)$ for the low-concentration limit ($p \ll 1$) are presented in Fig. 1. Here we let the parameter α of Eq. (2) take the values $\alpha = 0.5$, 0.3, 0.2, and 0.15, and we consider the time range $0 \le t/\tau_1 \le 100$. As is evident from the figure, the dispersive regime [region of large variations of $k(t)$] is larger for lower values of α. Remarkably, however, for $\alpha = 0.5$ the decay rate reaches an almost constant value after the time $t = 10\tau_1$, where τ_1 is the mean stepping time. Even for $\alpha = 0.3$ the value of $k(t)$ does not change much for $t \gtrsim 30\tau_1$. Remembering that the values of α sometimes used to explain experimental findings range from $\alpha = 0.3$ to 0.7,[13] we infer that for very low rc concentrations

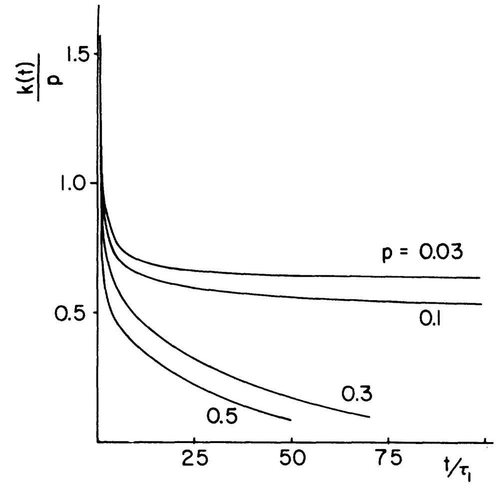

FIG. 2. Decay rate $k(t)$ for higher rc concentrations, $p=0.03$, 0.1, 0.3, and 0.5 for $\psi(t)$ given by Eq. (2) with $\alpha=0.5$. The units are as in Fig. 1.

($p \lesssim 0.001$), apart from the onset, the decay law is quasiexponential in the time regime studied. For the record, we note that all curves in Fig. 1 have the same limiting value, so that for very dispersive behavior ($\alpha<0.2$) the asymptotic domain is reached quite slowly.

In the short-time domain ($t \lesssim 10\tau_1$) we remark that $k(t)/p$ turns out to be larger than 1. This is different from the behavior encountered in random walks with fixed stepping frequencies, where one always has $k_n/p \leq 1$. The behavior found here can be traced to the large values of $\psi(t)$, Eq. (2), for very small t.[14]

As mentioned in Sec. II, only if the concentration of rc is not too high ($p \lesssim 0.01$) is the decay law discussed here determined mainly by $S(t)$. To show what happens at larger concentrations and to reinforce our findings through an independent numerical method, we have performed a series of simulation calculations. In these we have generated random walks on the simple cubic lattice by using the stepping-time distribution Eq. (2) for several values of α. In every case some 4000 realizations of the walk were created. The advantage of the simulation procedure is that one obtains the whole *distribution* of the number of distinct sites visited in time t, and not only the *mean* value $S(t)$. From this distribution we obtain directly the exact decay.[16,18]

For large p the difference between the exact decay law, Eq. (6), and the approximate form, Eq. (9), is substantial. The same is, of course, true for $k(t) \equiv -\dot{\Phi}(t)/\Phi(t)$, a fact exemplified in Fig. 2, where we plotted $k(t)/p$ vs t for $\alpha=0.5$ for several p values, $p=0.03$, 0.1, 0.3, and 0.5. We find that for small-p values the constant $k(t)$ regime is reached quite rapidly. Remarkably, however, for very large p the values of $k(t)/p$ are considerably smaller than those of the corresponding limiting curve for $p \rightarrow 0$ in Fig. 1. This is due to the fact that for larger p the higher moments of the distribution of distinct sites visited become increasingly important, so that Eq. (9) decays more rapidly than the exact recombination law, Eq. (6), *viz.*, also Refs. 16 and 18.

In conclusion, through independent analytical and numerical methods we have established that the stepping-time distribution $\psi(t)$, Eq. (2), leads to a *time-independent* rate $k(t)$ for longer times.[30] This reaffirms the fact emphasized in Refs. 12 and 24, that well-behaved stepping-time distributions give rise to normal transport. Thus in the range of parameters considered the decay law $\Phi(t)$ is quasiexponential. From the results of Sec. III the same holds for the quasiunimolecular decay due to recombination, Eq. (25), whereas in the bimolecular case $N_A(t)$ is at long times proportional to $1/t$, Eq. (26). Neither of the two laws has the structure of Eq. (1), in contrast to the forms of Ref. 4, and we concur with Scher's conclusion[1] that only pathological long-time tails for $\psi(t)$, such as Eq. (3), result in $N_A(t)$ having this structure.

For pathological $\psi(t)$ forms, care must be taken that the analysis of the recombination starts from the exact form, Eq. (6). As we have shown in this paper, Eq. (10) stemming from the cumulant expansion in time, gets poorer if the distributions $\psi(t)$ become broader. In three dimensions the distribution R_n of sites visited in n steps is sharply centered around its mean S_n; also one has to good accuracy $S_n \cong an$.[20] This leads then to a very satisfactory approximate form, Eq. (12).

In the framework of the CTRW and using chemical-reaction schemes we have presented in this work a unified picture of carrier recombination in amorphous materials. From an exact decay law we have derived several approximate expressions, valid for different stepping-time distributions for low rc concentration and longer times. Furthermore, for a definite stepping-time distribution we have assessed the limits of validity of these asymptotic expressions by numerical methods.

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