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A. Blumen and G. Zumofen

Lehrstuhl für Theoretische Chemie, Technische Universität München, Lichtenbergstrasse 4, D 8046 Garching, West Germany, and Laboratorium für Physikalische Chemie, ETH–Zentrum, CH 8092 Zürich, Switzerland
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In this work we study the energy migration on regular lattices in the framework of a continuous time random walk (CTRW). This extends our former investigations [A. Blumen and G. Zumofen, J. Chem. Phys. **75**, 892 (1981); G. Zumofen and A. Blumen, J. Chem. Phys. **76**, 3713 (1982)] to the continuous time domain. Here the ingredient is the stepping time distribution function $\psi(t)$. We derive this function from an exact formalism, for microscopic transfer rates due to multipolar and to exchange interactions. Furthermore, we study the decay law due to trapping by randomly distributed substitutional traps, starting from an exact expression. We analyze the interplay between the temporal and the pure random-walk stochastic aspects, and their respective influence on the decay law. The analysis is rendered transparent by using the cumulants of the random variables, which also offers a means to derive handy approximate expressions for the decay laws. We exemplify the findings for a square and a simple cubic lattice for CTRW mediated by dipolar interactions, as compared to random walks with constant stepping frequency.

I. INTRODUCTION

Transport in disordered materials has been an important subject of study in recent years.[1–7] The problem arises in the fields of energy transfer,[2,3,6,8–10] of spin dynamics,[11] of conduction in amorphous materials[1,4,5,12–16] and of electron scavenging.[17–20] The disordered nature of the medium over which the transport takes place strongly influences experimentally accessible basic quantities like the exciton lifetimes, the electron-scavenger recombination rates and the ac and dc conductivities. The fundamental theoretical question in this respect is in how far models based on ordered lattices may be extended so as to be able to qualitatively describe effects due to disorder, and when such extensions break down.[21]

Growing interest in the problem of energy transfer in disordered crystals has been motivated by the advances in laser material technology[22–24] and in molecular solids.[2] In such systems the disorder is mainly substitutional; also it is agreed that at high temperatures phonon-assisted hopping dominates so that the migration is determined through incoherent processes.[2,6,9,10,25–27] The energy transfer can then be viewed as a random walk over the randomly distributed active centers in the crystal.

Applications of random-walk models have encountered considerable success in many fields, see Refs. 28 and 29 for extensive reviews. This is due to the fact that the theory of random walks on *regular lattices* has attained a high degree of maturity, which greatly facilitates the calculation of exact solutions for particular models.

For random walks on *random lattices* the situation is considerably more complex and one is forced to make use of approximating schemes. An approximation which preserves the migration aspect is the continuous time random-walk (CTRW); the idea was introduced and applied by Scher and Lax in the treatment of electronic conductivity in amorphous semiconductors[12,13]; in a somewhat simplified form[14] it lets the electron migration take place on a *regular lattice*, while the randomness of the distinct site environments of the actual crystal is only taken into account through a random distribution of stepping times. In this case the problem becomes identical to the classical one considered by Montroll and Weiss in their study of random-walks on regular lattices,[30] and the powerful methods which were developed for systems with translational symmetry[31,32] can be used. In recent years the CTRW method, besides of being employed in modeling amorphous materials, was also investigated in connection with energy transfer[25,27] and scavenging[17–20] problems.

Interestingly, some of the recent investigations[18,20] lead to results which are at variance with the basic expressions of Montroll and Weiss.[30] In order to clarify the situation and also to obtain accurate numerical values for the classical CTRW model,[30] we analyze random-walks on *regular lattices* for several classes of random distributions of stepping times. This work is our third in a series of papers in this journal which treat the energy transfer as a random walk[9,10]; we will denote Refs. 9 and 10 by I and II, respectively. In these papers we have investigated the energy decay due to trapping on different two- and three-dimensional regular lattices, and also other related quantities like the average number of distinct sites visited and the mean number of returns to the origin in n steps. There we have also considered random walks mediated by multipolar and exchange interactions, and we have taken long-range steps into account. In this work we center on nearest-neighbor random walks and include, in CTRW fashion, the effect of the microscopic transfer rates into the distribution of stepping times. We do this using our experience on the direct energy transfer from a donor to randomly distributed acceptors,[26,33–35] since such expressions are frequently encountered in applications of the CTRW to experiments.[13,18,20]

The paper is structured as follows: In Sec. II we present the decay law due to trapping for the CTRW model, with particular emphasis on the expressions which form the basis of our numerical procedure. Sec. III is devoted to the derivation of the distributions

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of stepping times which follow from positional disorder combined with the microscopic transfer rates due to Coulomb or to exchange interactions. Our general approach leads in a straightforward manner to typical[13,18,20] distributions of stepping times. In Sec. IV we consider functions related to these stepping-time distributions and compute the characteristic stochastic parameters of these functions, i.e., mean and variance, valid for different dimensions and interaction ranges. The decay law due to trapping by traps distributed at random on the regular lattice is studied analytically and numerically in Sec. V. The asymptotic behavior differs from the forms suggested by Tachiya[20] and by Shlesinger,[18] but it compares very well with the expressions of Montroll and Weiss.[30] In Sec. V we also analyze in how far the decay law in the CTRW models considered differs from the one which obtains from random walks with constant stepping frequency. We close this article with a summary of results in Sec. VI.

II. TRAPPING IN THE CTRW MODEL

As mentioned in the introduction, we consider nearest-neighbor random walks on regular Δ-dimensional lattices and let the individual steps occur at random times. The time between two consecutive steps is taken to be distributed according to a (common) density $\psi(t)$. Furthermore, we assume that traps are placed at random on the regular lattice, occupying the lattice sites with probability p. The transfer to a certain site should not depend on whether the site is a trap or not. Furthermore, we take the excitation to be quenched instantaneously at the first encounter of a trap.

For a particular realization of the random walk on the perfect (trap-free) lattice, let R_n denote the number of distinct sites visited in n steps. For the same realization of the walk let F_n denote the probability (over the ensemble of lattices doped with traps) that trapping has not occurred up to the nth step. The quantities R_n and F_n are stochastic variables, related through Eq. (II. 2. 1a) [Eq. (2. 1a) of Ref. II]:

$$F_n = (1-p)^{R_{n-1}} , \tag{2.1}$$

where we assume the origin of the walk not to be a trap, else see Ref. II. The measurable survival probability at time t is then the average of Eq. (2. 1) with respect to all possible realizations of the random-walk in *space* and *time*:

$$\Phi(t) = \langle\langle F_n \rangle\rangle = \sum_{n=0}^{\infty} \langle (1-p)^{R_{n-1}} \rangle \phi_n(t) . \tag{2.2}$$

In Eq. (2. 2) the symbol $\langle\ \rangle$ denotes average with respect to the realizations of the random-walk on the *lattice*, whereas $\langle\langle\ \rangle\rangle$ includes also the *temporal* behavior. The quantity $\phi_n(t)$ in Eq. (2. 2) is the probability density for having performed exactly n steps in time t.

In Ref. II we have derived the special case of Eq. (2. 2) which holds for a fixed stepping frequency, Eq. (II. 2. 2a):

$$\langle F_n \rangle = \langle (1-p)^{R_{n-1}} \rangle . \tag{2.3}$$

Evidently Eq. (2. 2) follows from Eq. (2. 3) using the distribution $\phi_n(t)$. This is a consequence of our assumption that the spatial and temporal probability densities are uncorrelated, so that the two averages factorize:

$$\langle\langle F_n \rangle\rangle = \sum_{n=0}^{\infty} \langle F_n \rangle \phi_n(t) . \tag{2.4}$$

In previous articles[10,36-38] we have studied, based on Eq. (2. 3), the trapping behavior for several one-, two-, and three-dimensional lattices. Changes in the dimensionality influence strongly the decay law and its approximations through the cumulants of the distribution R_n.[10,36-40]

The new aspect which emerges due to the CTRW is the probability density $\phi_n(t)$ in Eq. (2. 2). This quantity is readily related to the stepping time distribution $\psi(t)$[12-14,20,30,41]; namely, one has for the probability density $\psi_n(t)$ for the occurrence of the nth step at time t, Eqs. (V. 2) and (V. 3) of Ref. 30:

$$\psi_0(t) = \delta(t) , \tag{2.5}$$

$$\psi_n(t) = \int_0^t \psi(t') \psi_{n-1}(t-t')\, dt' . \tag{2.6}$$

Denoting by $\Psi(t)$ the probability that the walker remains fixed in the time interval $[0, t)$ one has:

$$\Psi(t) = 1 - \int_0^t \psi(t')\, dt' = \int_t^{\infty} \psi(t')\, dt' , \tag{2.7}$$

and furthermore [Eq. (2. 8) of Ref. 41]

$$\phi_n(t) = \int_0^t \psi_n(t') \Psi(t-t')\, dt' , \tag{2.8}$$

as is intuitively evident. We now set $f(u)$ for the Laplace transform of $f(t)$, i.e., $f(u) \equiv \mathcal{L}[f(t)]$, $f(t) \equiv \mathcal{L}^{-1}[f(u)]$. From Eqs. (2. 5) and (2. 6) follows:

$$\psi_n(u) = \psi(u)\, \psi_{n-1}(u) = [\psi(u)]^n , \tag{2.9}$$

whereas from Eq. (2. 7) one has

$$\psi(t) = -(d/dt)\Psi(t) , \tag{2.10}$$

and thus, by partial integration,

$$\psi(u) = -\int_0^{\infty} e^{-ut} \dot{\Psi}(t)\, dt = 1 - u\, \Psi(u) . \tag{2.11}$$

Finally, from Eq. (2. 8),

$$\phi_n(u) = \psi_n(u) \Psi(u) = [\psi(u)]^n [1 - \psi(u)]/u . \tag{2.12}$$

Equation (2. 12) connects thus in a simple manner the Laplace transforms of $\phi_n(t)$ and $\psi(t)$. From $\psi(u)$ the distribution densities $\phi_n(t)$ needed in Eq. (2. 2) can be evaluated through the inverse Laplace transform of the right-hand side of Eq. (2. 12).

Before proceeding, let us discuss Eq. (2. 2). We note that apart from the explicit form for $\langle F_n \rangle$ similar expressions were given by Tachiya, Eq. (4. 1) of Ref. 20, and by Weiss and Rubin, Eq. (8. 5) of Ref. 29. Equation (2. 2) connects the randomness in space and the randomness in time only through the number of steps n. Approximations to Eq. (2. 2) follow now readily along the lines of Ref. II: the average in Eq. (2. 3) can be performed by rewriting it as a cumulant average:

$$\langle F_n\rangle = e^{\lambda}\langle e^{-\lambda R_n}\rangle = e^{\lambda}\exp\left[\sum_{j=1}^{\infty}\kappa_{j,n}(-\lambda)^j/j!\right], \qquad (2.13)$$

with $\lambda = -\ln(1-p)$ and where $\kappa_{j,n}$ are the cumulants of the distribution of R_n. Restricting the sum in Eq. (2.13) to the first cumulant $\kappa_{1,n} = \langle R_n\rangle \equiv S_n$ leads to the Rosenstock approximation,[39] whereas inclusion of the second cumulant $\kappa_{2,n} = \langle R_n^2\rangle - \langle R_n\rangle^2 \equiv \sigma_n^2$ is a correction along the lines of Weiss' work,[40] see Ref. II for details.

In three dimensions one has asymptotically $S_n = a_1 n + O(\sqrt{n})$, see for instance Ref. I. This result may be used for example to obtain the somewhat crude approximation:

$$\Phi(t) \simeq \sum_{n=0}^{\infty}\exp(-\lambda a_1 n)\,\phi_n(t), \qquad (\Delta = 3) \qquad (2.14)$$

from which, with Eq. (2.12) it follows:

$$\Phi(u) = \frac{[1-\psi(u)]}{u[1-e^{-\lambda a_1}\psi(u)]}, \qquad (2.15)$$

which, in this approximation, allows to determine $\Phi(t)$ as the inverse Laplace transform of Eq. (2.15). One can even go a step further and simply set $S_n = n$, i.e., $a_1 = 1$ in Eq. (2.15). One must then, however, be aware that the random-walk aspect of the basic problem is completely lost: Eq. (2.2) with $\langle F_n\rangle = e^{-\lambda n}$ is a pure decay process in continuous time. This, on the other hand, allows one to study the influence of the pure continuous time aspect of the decay and to unravel the effects of time randomness from those of spatial randomness on the trapping law (see Sec. V).

III. STEPPING TIME DENSITIES $\psi(t)$

As already noted, the extension of the random walk with fixed stepping frequency to a continuous-time domain, the CTRW, is achieved through the introduction of a stepping time density $\psi(t)$. In Sec. II it was shown that this continuous time extension is readily incorporated into the equation giving the decay law due to trapping, Eq. (2.2). The connection between the probability densities $\phi_n(t)$ and $\psi(t)$ is expressed through the simple relation for their Laplace transforms, Eq. (2.12). Thus the CTRW-trapping problem on a given lattice is fully specified, if the stepping time densities $\psi(t)$ are given.

In this section we discuss several forms in use for $\psi(t)$, and we present their derivation from models related to the direct energy transfer.[33–35] One should remark here, however, that in general the expressions $\psi(t)$ may be chosen fairly arbitrarily[1,4,12–14,17–20,41]; the choice is mostly motivated by the wish to describe in an approximate, fairly simple way the random walk on a random lattice, *vide supra*. Thus the forms $\psi(t)$ are the ingredients of the CTRW model and are not, in general, directly related to an underlying physical situation.

A noteworthy exception is the case of an ideal regular lattice. Denoting by $w(\mathbf{r})$ the direct transfer rate to a site at distance $\mathbf{r}$, the total transfer rate from any site is given through $\tau_1^{-1} = \sum_{\mathbf{r}}' w(\mathbf{r})$, which for a regular lattice is independent of the particular site considered. Hence,

$$\Psi(t) = \exp\left[-t\sum_{\mathbf{r}}' w(\mathbf{r})\right] = \exp(-t/\tau_1), \qquad (3.1)$$

and from Eq. (2.10),

$$\psi(t) = \tau_1^{-1}\exp(-t/\tau_1). \qquad (3.2)$$

From Eq. (3.2) it follows:

$$\psi(u) = (1+u\tau_1)^{-1}, \qquad (3.3)$$

and with Eq. (2.12),

$$\phi_n(u) = \tau_1(1+u\tau_1)^{-n-1}, \qquad (3.4)$$

giving for $\phi_n(t)$ a Poisson distribution [e.g., Eq. (29.3.10) of Ref. 42]:

$$\phi_n(t) = \frac{1}{n!}(t/\tau_1)^n\exp(-t/\tau_1). \qquad (3.5)$$

Another way to obtain Eq. (3.5) uses general expressions. Let us set as generating function for $\phi_n(t)$,

$$\phi(t;z) \equiv \sum_{n=0}^{\infty} z^n\,\phi_n(t), \qquad (3.6)$$

and therefore

$$\phi(u;z) \equiv \sum_{n=0}^{\infty} z^n\phi_n(u), \qquad (3.7)$$

from which, together with Eq. (2.12), one has the general expression

$$\phi(u;z) = \frac{1-\psi(u)}{u[1-z\psi(u)]}. \qquad (3.8)$$

Specialized to the ideally regular lattice, with Eq. (3.3) it follows:

$$\phi(u;z) = [u+(1-z)/\tau_1]^{-1}. \qquad (3.9)$$

Thus

$$\phi(t;z) = \exp[-(1-z)t/\tau_1] = \sum_{n=0}^{\infty}\frac{z^n}{n!}\exp(-t/\tau_1)(t/\tau_1)^n, \qquad (3.10)$$

and Eq. (3.5) follows by comparing Eqs. (3.6) and (3.10).

The generating function $\phi(t;z)$ [Eq. (3.6)] is very handy for computing the moments of the distribution of $\phi_n(t)$, and we will make use of it later. Here we remark only that the $\phi_n(t)$ are indeed properly normalized: from Eq. (3.8) one has $\phi(u;1) = u^{-1}$, i.e., $\phi(t;1) = 1$.

We return now to our main task of this section to derive the transfer law $\Psi(t)$ for a disordered lattice. As noted in the Introduction, the systems usually encountered in the study of energy transport in defective media are substitutionally disordered. We consider a system in which active molecules occupy the lattice sites in a random, noncorrelated way with probability $\tilde{p}$; then the probability of a site being occupied by an inert molecule is $1-\tilde{p}$. Equation (3.1) thus reads for a particular site

$$\tilde{\Psi}(t) = \exp\left[-t\sum_{\mathbf{r}}'\zeta(\mathbf{r})w(\mathbf{r})\right], \qquad (3.11)$$

where the $\zeta(\mathbf{r})$ are random variables, which take only the

values 1 and 0 with probability $\tilde{p}$ and $1-\tilde{p}$, respectively, depending on whether the site at distance r is occupied or not. The configurational average of Eq. (3.11) is (see Ref. 33 for other derivations):

$$\Psi(t) \equiv \langle \tilde{\Psi}(t) \rangle_{\{\zeta(\mathbf{r})\}} = \left\langle \prod_{\mathbf{r}}{}' \exp[-t\zeta(\mathbf{r})w(\mathbf{r})] \right\rangle_{\{\zeta(\mathbf{r})\}}$$

$$= \prod_{\mathbf{r}}{}' \langle \exp[-t\zeta(\mathbf{r})w(\mathbf{r})] \rangle_{\zeta(\mathbf{r})}$$

$$= \prod_{\mathbf{r}}{}' [(1-\tilde{p}) + \tilde{p}\exp(-tw(\mathbf{r}))] . \quad (3.12)$$

In Eq. (3.12) use was made of the fact that the $\zeta(\mathbf{r})$ are uncorrelated.

Equation (3.12) is exact. It is valid for all times and all concentrations of active molecules and it explicitly includes the structure of the underlying lattice.[33] An approximation to Eq. (3.12) obtains if the lattice structure is disregarded and if the concentration of active molecules is small (continuum approximation). Then Eq. (3.12) can be approximated through

$$\Psi(t) = \exp\left(-\tilde{p}\rho \int \{1-\exp[-tw(\mathbf{r})]\} d\mathbf{r}\right), \quad (3.13)$$

see, for example, Eq. (13) of Ref. 35. In Eq. (3.13) $\tilde{p}\rho$ is the concentration of active molecules.

Interestingly, the approximate expression (3.13) occurs frequently in many fields, see Eq. (8.16) of Ref. 1. According to Lax this result was known to Markoff and may have been known to Laplace.[1] In the theory of energy transfer Eq. (3.13) was rendered popular by the work of Förster[43] and of Galanin,[44] see Eq. (3) of Ref. 44. These authors analyzed dipolar interactions, in which the dependence of $w(\mathbf{r})$ on r is proportional to $1/r^6$. The analysis of Eq. (3.13) for general multipolar interactions:

$$w(\mathbf{r}) \propto r^{-s} \quad (s = 6, 8, 10, \ldots) , \quad (3.14)$$

and for exchange interactions,

$$w(\mathbf{r}) \propto e^{-\gamma r} \quad (3.15)$$

was performed in the energy transfer field by Inokuti and Hirayama.[45] We note that identical expressions for $\Psi(t)$, calculated by inserting Eq. (3.14) or Eq. (3.15) into Eq. (3.13) were later obtained in Refs 13, 25, 46, and 47 in the field of conductivity in disordered systems and for the electron scavenging problem.

A comparison of expression (3.13) with the exact result, Eq. (3.12) was presented in Ref. 33 for multipolar and in Ref. 34 for exchange interactions, and a summary of results can be found in Ref. 35. Briefly, Eq. (3.13) for multipolar interactions has the form:

$$\Psi_m(t) = \exp(-At^{\Delta/s}) \quad (3.16)$$

[Eq. (15) of Ref. 35], where Δ is the dimensionality of the lattice considered, and A is time independent. For transfer due to exchange one finds

$$\Psi_x(t) = \exp[-Bg_\Delta(Ct)] \quad (3.17)$$

[Eq. (16) of Ref. 35], where B and C do not depend on time and $g_\Delta(x)$ is an analytical function of x, whose properties are discussed in the Appendix of Ref. 34. [For very large values of Ct one has $g_\Delta(Ct) \simeq \ln^\Delta(Ct)$.]

In the following we will make use of the stepping time densities $\psi(t)$ which follow from Eqs. (3.16) and (3.17) to determine decay laws related to these CTRW. From Eq. (2.10) one has

$$\psi_m(t) = \frac{A\Delta}{s} t^{\Delta/s-1} \exp(-At^{\Delta/s}) , \quad (3.18)$$

$$\psi_x(t) = \frac{B\Delta}{t} g_{\Delta-1}(Ct) \exp[-Bg_\Delta(Ct)] , \quad (3.19)$$

where we used the relation

$$x\frac{d}{dx} g_\Delta(x) = \Delta g_{\Delta-1}(x) \quad (3.20)$$

[Eq. (A5) of Ref. 34]. We note that Eq. (3.18) is identical to the function $\psi(t)$ of Shlesinger, Eq. (25) of Ref. 18, whereas Eq. (3.17) is akin to the $P(t)$ of Tachiya, Eq. (2.6) of Ref. 20, where $\Delta = 3$ and $g_3(x)$ is replaced by $\ln^3(x)$.

The densities $\psi_m(t)$ and $\psi_x(t)$ are relatively well behaved. Defining the moments of $\psi(t)$ through

$$\tau_n \equiv \int_0^\infty dt\, t^n \psi(t) = n \int_0^\infty dt\, t^{n-1} \Psi(t) , \quad (3.21)$$

we remark that all moments of $\Psi_m(t)$ [and, *a fortiori*, of $\psi_m(t)$], $(\Delta < s)$, exist:

$$\tau_n = n \int_0^\infty dt\, t^{n-1} \exp(-At^{\Delta/s}) ,$$

$$= A^{-ns/\Delta} \Gamma(ns/\Delta)\, ns/\Delta . \quad (3.22)$$

In Eq. (3.22), $\Gamma(x)$ denotes the Euler gamma function, Eq. (6.1.1) of Ref. 42. Also for $\Delta > 1$ all moments of $\Psi_x(t)$ exist. We show it by considering the behavior of $\Psi_x(t)$ for very large t:

$$n \int^\infty dt\, t^{n-1} \Psi_x(t) \simeq n \int^\infty dt\, t^{n-1} \exp[-B\ln^\Delta(Ct)]$$

$$= nC^{-n} \int^\infty dx \exp(-Bx^\Delta + nx) , \quad (3.23)$$

which is convergent. For $\Delta = 1$ the integral may diverge, see Ref. 26 for details. Therefore the densities $\psi(t)$ given by Eqs. (3.18) and (3.19) are considerably less pathological than some of the stepping probabilities employed in other CTRW treatments, for which already the first moments do not exist.[12,14] For long times one expects therefore that the decay laws due to the CTRW will parallel those which obtain for a simple random walk with constant stepping frequency.[30,41] In particular, for three-dimensional lattices and a low density of traps the decay law should be nearly exponential. This is in line with the results of Montroll and Weiss[30] and in disagreement with recent claims that the long-time behavior of the decay law should be nonexponential, Eq. (4.22) of Ref. 20 and Eq. (26) of Ref. 18. In the following we will show both analytically and numerically that the early result of Montroll and Weiss is the right one.

In the next section we continue our study of the densities $\psi(t)$ by analyzing the moments of $\phi_n(t)$ with respect

to n. In this section we derived $\Psi(t)$ as an ensemble averaged quantity over a substitutionally disordered crystal, Eqs. (3.11) ff. We emphasize again that Eq. (3.13) holds only for low densities of active molecules, i.e., for a *high degree of disorder*; this, of course runs counterparallel to letting the CTRW take place on a *highly ordered* crystal. We tend thus not to put too much weight on the *a priori* determination of the CTRW model from a physically underlying disordered structure, but simply to view the CTRW as a versatile mathematical tool on its own, to be used for approximating purposes.

IV. THE FUNCTIONS $\phi_n(t)$

In the preceding section we have determined that multipolar and exchange interactions lead to the stepping time probabilities $\psi_m(t)$ [Eq. (3.18)] and $\psi_x(t)$ [Eq. (3.19)] for a substitutionally disordered crystal. In order to obtain the decay law due to trapping, Eq. (2.2):

$$\Phi(t) = \sum_{n=0}^{\infty} \langle (1-p)^{R_n - 1} \rangle \phi_n(t) \ , \tag{2.2}$$

we need the functions $\phi_n(t)$, which are related to $\psi(t)$ via Eq. (2.12). Before analyzing the decay laws in Sec. V, we first clarify in this section the main stochastic aspects related to the quantities $\phi_n(t)$.

The connection between $\phi_n(t)$ and $\psi(t)$ is given in Eq. (2.12) by means of their Laplace transforms $\phi_n(u)$ and $\psi(u)$. To obtain $\phi_n(t)$ from $\psi(t)$ involves both a Laplace transform and an inverse Laplace transform; thus, in general, $\phi_n(t)$ is not readily expressible analytically as a function of $\psi(t)$. However, a noteworthy exception is the exponential density $\psi(t)$, Eq. (3.1), which leads to the Poisson distributions, Eq. (3.5). Moreover, we are not necessarily interested in $\phi_n(t)$ *per se* but rather, as in Eq. (2.2), in weighted sums over n of the functions $\phi_n(t)$. In fact we may even view a complete table of $\phi_n(t)$ for n and t as overdetailed and quite redundant.

Stochastic variables whose definition closely resembles the structure of Eq. (2.2), and which lead to a more compact description of the functions $\phi_n(t)$ are the cumulants with respect to the variable n. We remark that the cumulants $X_j(t)$ are defined through the relation

$$\sum_{n=0}^{\infty} e^{-cn} \phi_n(t) \equiv \exp\left[\sum_{j=1}^{\infty} \frac{(-c)^j}{j!} X_j(t) \right] . \tag{4.1}$$

Here we follow the notation of our previous work, Ref. II, Eqs. (II.2.6), and of Ref. 42, Eq. (26.1.13).

At first glance one may view the change from $\phi_n(t)$ to $X_j(t)$ as purely formal, since these functions are exactly related through Eq. (4.1) and since both quantities have two variables. In fact, this is not so, simply because in our cases only the first few cumulants will be important at long times, whereas for the same time regime a description of the decay law through the $\phi_n(t)$ involves many n values.

To calculate the cumulants $X_j(t)$ we make use of the moments $M_j(t)$, defined through

$$M_j(t) \equiv \sum_{n=0}^{\infty} n^j \phi_n(t) \ , \tag{4.2}$$

since cumulants of order j can be expressed through the moments of order less or equal to j [see for instance Eqs. (II.2.6)]. The moments $M_j(t)$ may be obtained from $\phi(t;z)$, Eq. (3.6), through repeated differentiation with respect to z:

$$M_j(t) = \left(z \frac{\partial}{\partial z} \right)^j \phi(t;z) \Big|_{z=1} , \tag{4.3}$$

from which the Laplace-transformed quantities follow:

$$M_j(u) = \left(z \frac{\partial}{\partial z} \right)^j \phi(u;z) \Big|_{z=1} . \tag{4.4}$$

From Eq. (3.8) one obtains the derivatives of $\phi(u;z)$ as

$$\frac{\partial^k}{\partial z^k} \phi(u;z) \Big|_{z=1} = \frac{k!}{u} \left[\frac{\psi(u)}{1-\psi(u)} \right]^k . \tag{4.5}$$

Thus one has for the first four moments,

$$M_1(u) = \phi'(u;1) = \frac{\psi(u)}{u[1-\psi(u)]} \ , \tag{4.6a}$$

$$M_2(u) = \phi''(u;1) + \phi'(u;1) = \frac{\psi(u)[1+\psi(u)]}{u[1-\psi(u)]^2} \ , \tag{4.6b}$$

$$M_3(u) = \phi'''(u;1) + 3\phi''(u;1) + \phi'(u;1) = \frac{\psi(u)[1+4\psi(u)+\psi^2(u)]}{u[1-\psi(u)]^3} \ , \tag{4.6c}$$

and

$$M_4(u) = \phi^{IV}(u;1) + 6\phi'''(u;1) + 7\phi''(u;1) + \phi'(u;1) = \frac{\psi(u)[1+11\psi(u)+11\psi^2(u)+\psi^3(u)]}{u[1-\psi(u)]^4} \ . \tag{4.6d}$$

We expand now $\psi(u)$, relying on the fact that in our cases $\psi(u)$ and all moments of $\psi(t)$ with respect to t exist[48]:

$$\psi(u) = \int_0^{\infty} dt \ e^{-ut} \psi(t) = \sum_{j=0}^{\infty} \frac{(-u)^j \tau_j}{j!} \ . \tag{4.7}$$

Here the τ_j are defined as in Eq. (3.21). Inserting Eq. (4.7) into Eqs. (4.6), expanding in powers of u [u is taken to be small, since we are interested in the long time behavior of $M_j(t)$] and reverting to the time domain, we obtain the following asymptotic expressions for the moments $M_j(t)$, valid for long times t:

$$M_j(t) = \sum_{k=0}^{j} \mu_{jk} (t/\tau_1)^k = \sum_{k=0}^{j} \mu_{jk} \tilde{t}^k \ . \tag{4.8}$$

Here the coefficients μ_{jk} are constants. For $j \leq 4$ the coefficients are listed in Appendix A; for illustrative purposes we present the asymptotic behavior of the first two moments:

$$M_1(t) = \tilde{t} + \tau_2/(2\tau_1^2) - 1 \ , \tag{4.9a}$$

$$M_2(t) = \tilde{t}^2 + (2\tau_2/\tau_1^2 - 3)\tilde{t} - 2\tau_3/(3\tau_1^3) + 3\tau_2^2/(2\tau_1^4) - 3\tau_2/(2\tau_1^2) + 1 \ . \tag{4.9b}$$

In Eqs. (4.8) and (4.9) we have scaled the time t in units of τ_1, by defining $\tilde{t} \equiv t/\tau_1$. The value of τ_1 is a natural time unit, being the average time spent between steps; indeed, as will become evident in the following, $\tilde{t}$ correlates directly to the average number of

steps taken during the time t, if t is large. Thus, we will make repeated use of $\tilde{t}$ from now on.

From Eqs. (II.2.6), which relate the cumulants to the moments, and Eq. (4.8) we have calculated the asymptotic behavior of the cumulants $X_j(t)$ for large t. We find that the cumulants have the structure

$$X_j(t) = \xi_{j1}(t/\tau_1) + \xi_{j0} = \xi_{j1}\tilde{t} + \xi_{j0} \ , \tag{4.10}$$

with constant coefficients ξ_{j1} and ξ_{j0}. Again for $j \leq 4$ these coefficients are listed in Appendix A. For instance, one has asymptotically,

$$X_1(t) = \tilde{t} + \tau_2/(2\tau_1^2) - 1 = M_1(t) \ , \tag{4.11a}$$

$$X_2(t) = (\tau_2/\tau_1^2 - 1)\tilde{t} - 2\tau_3/(3\tau_1^3) + 5\tau_2^2/(4\tau_1^4) - \tau_2/(2\tau_1^2) \ . \tag{4.11b}$$

Remembering now that the cumulants may be viewed as the exponents of approximate decay laws, [see Eq. (4.1) and the following discussion] we remark the noteworthy form of Eq. (4.10). This equation implies, namely, under the assumed approximations for the description of the random walk and for "well-behaved" distributions $\psi(t)$, that the decay law should be quasi-exponential for long times. This result is, of course, in line with Eq. (V.19) of Ref. 30 by Montroll and Weiss for random walks on three-dimensional lattices, when the first two moments of $\psi(t)$ exist. In Sec. V we will encounter many examples of nonexponential decay laws; from Eq. (4.10) it should, however, be evident that the nonexponential behavior cannot be solely due to the continuous time aspect of the CTRW problem. As long as the moments of $\psi(t)$ exist, the reasons for nonexponential decay arise from the R_n distributions created by the random walk (i.e., nonlinear dependence of $\langle R_n \rangle$ on n, large variances) and from the interplay between the spacial and the temporal stochastic behavior. The only time regime where the distribution $\psi(t)$ may lead per se to nonexponential decays is that *before* the asymptotic regime, i.e., for relatively short times.

Before considering in the next section explicit decay laws due to trapping, we wish to exemplify the results obtained in this section with the help of special cases. The simplest case involves the exponential stepping time density $\psi(t)$, Eq. (3.2), which leads to the Poisson distributions for $\phi_n(t)$, Eq. (3.5). In this case the moments τ_j are found to be $\tau_j = \Gamma(n+1) = n!$; as follows from Eq. (3.21) and the definition of the gamma function. One has therefore for all j in Eq. (4.10), $\xi_{j1} = 1$ and $\xi_{j0} = 0$. This result may, of course, be obtained directly from the definition of the cumulants $X_j(t)$, Eq. (4.1). Using the generating function of the Poisson distribution [Eq. (3.10)] and setting $z = e^{-c}$ it follows:

$$\sum_{n=0}^{\infty} e^{-cn}\phi_n(t) = [\exp(e^{-c} - 1)\tilde{t}] = \exp\left[\sum_{j=1}^{\infty} \frac{(-c)^j}{j!}\,\tilde{t}\right] \ , \tag{4.12}$$

from which identification with Eq. (4.1) leads to $X_j(t) = \tilde{t} = t/\tau_1$. We remark that this result is not only valid in the asymptotic limit, but is true for all times.

For general stepping time densities $\psi(t)$, the ξ_{j1} and ξ_{j0} show a complex behavior. We exemplify the situation for multipolar interactions, and take for $\psi(t)$ the form Eq. (3.18), which was derived in Sec. III for a substitutionally disordered lattice. The advantage rests in the fact that all the moments τ_j of this distribution are fairly simple; they are given by Eq. (3.22). Of practical interest in the study of energy transfer are the cases $s = 6$, 8, and 10 for the transfer rates $w(\mathbf{r}) \sim r^{-s}$, Eq. (3.14); these values of s correspond to dipolar, dipolar–quadrupolar, and quadrupolar interactions, respectively.

Table I presents the asymptotic behavior of $M_1(t) = X_1(t) \sim \tilde{t} + \xi_{10}$ and of $X_2(t) \sim \xi_{21}\tilde{t} + \xi_{20}$ for large $\tilde{t}$. We have tabulated ξ_{10}, ξ_{21}, and ξ_{20}, both for three- and for two-dimensional cases ($\Delta = 3$ and $\Delta = 2$). As may readily be seen, the effect of lower dimensionality and of shorter interaction ranges (larger s) consists in a considerable increase in ξ_{21}, i.e., an increase in the variance $X_2(t)$. At this point we remark that the variance plays an important role in determining the decay law, *vide infra*, thus pronounced effects may be expected for low values of Δ/s.[10,36-40]

In order to further quantify the range of $\tilde{t}$ values for which the asymptotic forms given by Table I are a good approximation, we present in Table II the temporal be-

TABLE I. Asymptotic forms for the mean $X_1(t) \propto \tilde{t} + \xi_{10}$ and the variance $X_2(t) \propto \xi_{21}\tilde{t} + \xi_{20}$ of the distributions $\phi_n(t)$ for multipolar interactions, $w(\mathbf{r}) \propto r^{-s}$. Here $\tilde{t} = t/\tau_1$. The stepping time probability density is given by Eq. (3.18). Both two- and three-dimensional probabilities ($\Delta = 2$ and $\Delta = 3$) are considered.

Δ	s	ξ_{10}	ξ_{21}	ξ_{20}
2	6	9	19	−630
	8	34	69	−17 010
	10	125	251	−425 250
3	6	2	5	−18
	8	5.648	12.295	−201.8
	10	14.122	29.243	−1 918.1

TABLE II. Exact results for the mean $X_1(\tilde{t})$ and the variance $X_2(\tilde{t})$ of the distributions $\phi_n(t)$ for multipolar interactions. All parameters are as in Table I.

	$\Delta = 3$, $s = 6$		$\Delta = 2$, $s = 6$		$\Delta = 2$, $s = 10$	
$\tilde{t}$	$X_1(\tilde{t})$	$X_2(\tilde{t})$	$X_1(\tilde{t})$	$X_2(\tilde{t})$	$X_1(\tilde{t})$	$X_2(\tilde{t})$
0.1	0.51	0.64	1.16	2.06	3.59	13.34
0.2	0.75	1.03	1.59	3.20	4.66	20.49
0.3	0.96	1.39	1.93	4.23	5.47	26.78
0.5	1.31	2.07	2.49	6.14	6.76	38.25
0.7	1.62	2.74	2.96	7.97	7.83	48.97
1.0	2.05	3.75	3.59	10.66	9.20	64.34
2.0	3.31	7.16	5.35	19.54	12.83	113.1
3.0	4.47	10.75	6.88	28.61	15.78	160.9
5.0	6.65	18.39	9.61	47.60	20.80	256.8
7.0	8.76	26.51	12.13	67.68	25.18	354.6
10.0	11.85	39.34	15.70	99.61	31.10	505.7
20.0	21.95	85.32	26.80	218.4	48.12	1047.6
30.0	31.98	133.6	37.39	351.0	63.17	1641.1
50.0	52.00	232.4	58.03	643.6	90.61	2956.4
70.0	72.00	332.0	78.35	960.1	116.18	4414.1
100.0	102.00	482.4	108.62	1462.8	152.65	6818.4

havior of $X_1(\tilde{t})$ and $X_2(\tilde{t})$ as a function of $\tilde{t} = t/\tau_1$, for Δ/s equal to 1/2, 1/3, and 1/5, which correspond to $\Delta = 3$, $s = 6$, $\Delta = 2$, $s = 6$, and $\Delta = 2$, $s = 10$, respectively.

Here we have calculated $X_1(\tilde{t})$ and $X_2(\tilde{t})$ from $M_1(\tilde{t})$ and $M_2(\tilde{t})$ which are obtained by Laplace inverting $M_1(u)$ and $M_2(u)$, Eqs. (4.6a) and (4.6b). The distributions $\psi(u)$ appearing in these equations were computed through the asymptotic expansion Eq. (4.7), in the case of small u, whereas for large u the series expansion

$$\psi(u) = -\sum_{j=1}^{\infty} (-A/u^{\Delta/s})^j \Gamma(1 + j\Delta/s)/j! \qquad (4.13)$$

has been employed. We have achieved the Laplace inversion numerically through an improved method of Durbin[49,50] and we have executed the calculations on a CDC Cyber 174 64 bits computer, partly with double-precision accuracy.

As may be seen from Table II, the asymptotic behavior of both $X_1(\tilde{t})$ and $X_2(\tilde{t})$ is in all cases almost linear in $\tilde{t}$, for $\tilde{t}$ large. This substantiates the basic analysis of this section. For the case $\Delta = 3$, $s = 6$ the asymptotic representation $X_1(\tilde{t}) = \tilde{t} + 2$ is already satisfactory for $t \gtrsim 5$, the relative error being then below 5%. The same accuracy is achieved for $\Delta = 2$ and $s = 6$ with $X_1(\tilde{t}) = \tilde{t} + 9$ for $t \gtrsim 30$, i.e., at significantly longer times. For $\Delta = 2$ and $s = 10$ the asymptotic form $X_1(t) = t + 125$ deviates even at $\tilde{t} = 100$ by a factor 1.5 from the exact result. This exemplifies the fact that for lower Δ/s values the asymptotic regime is reached only at considerably longer times.

Similar results hold for exchange interactions in two and in three dimensions, where we take for $\psi(t)$ the form Eq. (3.19). Of practical interest in the study of energy transfer is the regime $3 \lesssim \gamma d \lesssim 10$, with γ as in Eq. (3.15) and where d is the nearest-neighbor lattice spacing.[26] The numerical findings parallel the multipolar case: both $X_1(\tilde{t})$ and $X_2(\tilde{t})$ show asymptotically a linear dependence on $\tilde{t}$. Moreover, as for multipolar interactions, the asymptotic regime is reached at smaller values of $\tilde{t}$ if the dimensionality is higher (larger Δ) and if the interaction is longer ranged (smaller values of γd).

After these remarks concerning $\phi_n(t)$ and their corresponding cumulants $X_n(t)$ we turn now to the analysis of the decay laws due to trapping.

V. DECAY LAWS DUE TO TRAPPING

This section is devoted to the analysis of the decay laws due to trapping of the excitation, when the energy performs a nearest-neighbor random walk over a regular lattice in continuous time, i.e., the stepping times occur randomly, according to a given distribution $\psi(t)$. It is certainly by now evident that the particular forms of the decay laws considered arise from two different stochastic processes: the random sampling of newly visited sites as a result of the random walk in *space*, and the random stepping distribution in *time*. In Eq. (2.2) these two aspects are symbolized by R_n and by $\phi_n(t)$ and are connected through the number of steps n. In order to get a feeling for these different aspects, we start our description of decay laws by considering first the temporal and the spacial problems distinctly, and show subsequently their interplay.

Let us start with the time-dependent problem first, and take the simplest case, that of an exponential distribution $\psi(t) = \tau_1^{-1} \exp(-t/\tau_1) = \tau_1^{-1} e^{-\tilde{t}}$ of stepping times. As shown in Sec. III, the $\phi_n(t)$ are then distributed according to a Poisson law. Since at this stage we disregard the random-walk aspect, we set $R_n = n + 1$, which corresponds to visiting at every step n a new site. From Sec. II the corresponding decay law is, Eqs. (2.2) and (3.10):

$$\Phi(t) = \sum_{n=0}^{\infty} (1-p)^n \phi_n(t) = \exp(-pt/\tau_1) = e^{-p\tilde{t}} . \qquad (5.1)$$

As above, p is the probability for each site on the lattice to be a trap. The decay given by Eq. (5.1) is exponential, since no randomness in R_n occurs, and since under the assumed $\psi(t)$ n correlates linearly with t, $n = t/\tau_1$, at all times.

In Sec. IV we have pointed out that a useful description of the decay law $\Phi(t)$ involves the cumulants, e.g., Eq. (4.1). In the simple case which we now consider all cumulants equal $\tilde{t} = t/\tau_1$, see the discussion following Eq. (4.12). One has therefore, similar to Eqs. (2.13) and (4.12):

$$\Phi(t) = \exp\left[\sum_{j=1}^{\infty} \tilde{t}(-\lambda)^j/j!\right] \qquad (5.2)$$

with $\lambda = -\ln(1-p)$. Evidently, a description in terms of cumulants is reasonable, if one succeeds to mimic the decay behavior only with the few first terms in the sum of the right-hand side of Eq. (5.2). In the following we will affix an index N to the letter Φ in order to denote the approximation by which only the first N cumulants are explicitly accounted for; here, for instance,

$$\Phi_N(t) \equiv \exp\left[\sum_{j=1}^{N} \tilde{t}(-\lambda)^j/j!\right] . \qquad (5.3)$$

As an example we have plotted in Figs. 1(a) and 1(b) the decay law $\Phi(t)$ as a function of time over four orders of magnitude, and we chose for p the values 0.03, 0.1, 0.2, and 0.5. Also we have drawn approximate forms $\Phi_N(t)$, with N between 1 and 4. We remark that for $p = 0.1$, $\Phi_2(t)$ is already an excellent approximation in the range $10^{-4} \leq \Phi(t) \leq 1$ considered, whereas in the same range for $p = 0.5$ one has to use at least $\Phi_4(t)$ to achieve the same accuracy. In the following we will encounter this effect repeatedly: larger concentrations p force one to use higher cumulants for an accurate approximation of $\Phi(t)$.

We turn now our attention to more complex cases, and consider the effect of the random walk. As is well known, see for instance Refs. I and II, the behavior of R_n gets more pathological for *lower* dimensions. A simpler case is therefore a random walk on a three-dimensional lattice: In Fig. 2(a) we have plotted the decay law due to trapping of a random walker on a simple-cubic lattice, when the individual steps occur only to nearest neighbors at fixed time intervals. Here we have simulated a series of random walks, of the order of 1000, on the given lattice and obtained the distribution of random variables R_n. The numerical procedure em-

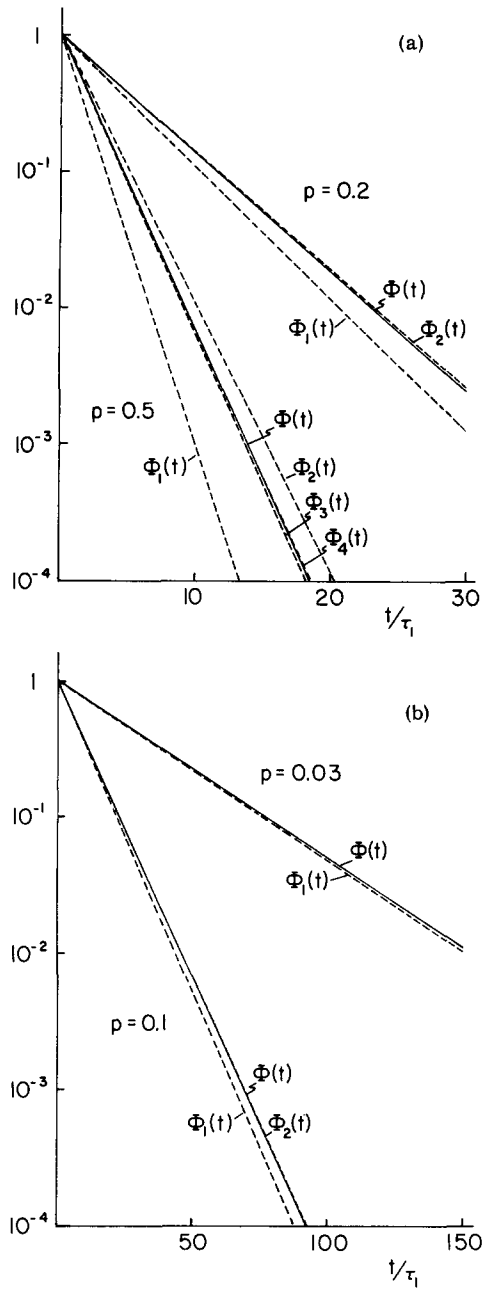

FIG. 1. (a) Decay due to trapping for an exponential stepping density, Eq. (3.2). The probabilities of trapping at each step are $p=0.2$ and $p=0.5$. $\Phi(t)$ (full line) denotes the exact decay, whereas $\Phi_N(t)$ (broken lines) are approximate forms [Eq. (5.3)] which involve the cumulants. (b) Decay due to trapping for an exponential stepping density. Here the probabilities of trapping at each step are $p=0.03$ and $p=0.1$. The symbols are as in Fig. 1(a).

ployed was explained in detail in Refs. I and II and will not be repeated here. One can find there and in Refs. 36–38 other examples for decay laws on different lattice types. Plotted is the exact decay Φ_n as a function of the number of steps n and the approximate decay laws $\Phi_{1,n}$ and $\Phi_{2,n}$, see Eq. (2.13):

$$\Phi_{1,n} = \exp[-\lambda(S_n - 1)]\,, \tag{5.4a}$$

$$\Phi_{2,n} = \Phi_{1,n}\exp(\lambda^2\sigma_n^2/2)\,, \tag{5.4b}$$

with $S_n = \langle R_n\rangle$ and $\sigma_n^2 = \langle R_n^2\rangle - \langle R_n\rangle^2$. From Fig. 2(a) we remark that in the range plotted the approximation $\Phi_{2,n}$ is very good for the concentrations considered, $p=0.1$ and 0.5. For lower concentrations even $\Phi_{1,n}$, the Rosenstock approximation, becomes quite accurate, see Refs. 10, 36, and 37 for details. Although not always very reliable, the approximate form $\Phi_{1,n}$, Eq. (5.4a) is particularly appealing, since it involves only S_n, the *average* number of distinct sites visited in n steps. The quantity S_n was extensively studied in the theory of random-walks,[28–32] and for it both analytical and numerical expressions exist, whereas for the determina-

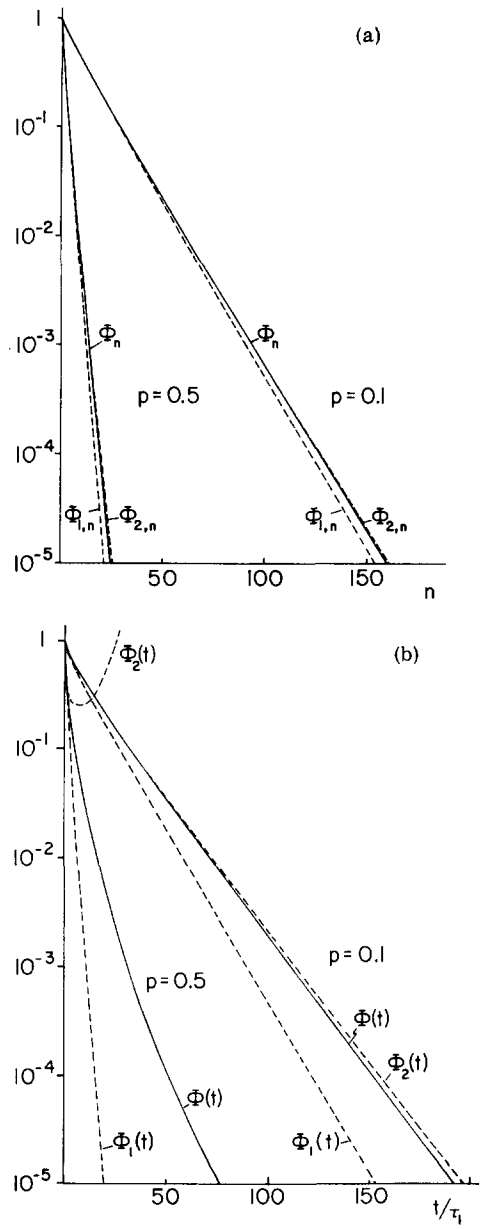

FIG. 2. (a) Decay law due to trapping in a nearest-neighbor random walk on a simple cubic lattice, for a fixed stepping frequency. Φ_n (full line) is the exact decay and $\Phi_{N,n}$ (broken lines) are approximate forms [Eq. (2.13)] involving the cumulants. The probabilities that a site is a trap are $p=0.1$ and $p=0.5$. (b) Decay law due to trapping for a CTRW on a simple cubic lattice for the dipolar stepping time density, Eq. (3.18) with $s=6$, $\Delta=3$. The cumulants are those of Eq. (5.7) and the symbols are as in Fig. 1. The probabilities that a site is a trap are $p=0.1$ and $p=0.5$.

tion of the higher moments of R_n considerably more effort is needed.[9,10] Thus, from the tabulated values of S_n (see for instance Refs. I and II) one obtains readily analytical expressions for $\Phi_{1,n}$. These expressions are in excellent agreement with the $\Phi_{1,n}$ curves of Fig. 2(a).

We are now ready to consider the case of a random-walk in continuous time (CTRW): we again let the walk take place over a simple cubic lattice and allow steps to nearest neighbors only; however we introduce a distribution of stepping times $\psi(t)$ and choose the dipolar interaction ($s = 6$, $\Delta = 3$) in Eq. (3.18). The results are plotted in Fig. 2(b). Here we have simulated 1000 to 3000 random-walks where the time intervals were discretized in units of τ_1. We have computed $R(t)$, the number of distinct sites visited in time t, for each walk and from it $(1-p)^{R(t)-1}$, and we have taken the averages $\langle R(t)\rangle$, $\langle R^2(t)\rangle$, and $\langle (1-p)^{R(t)-1}\rangle$ to determine cumulant approximations and the exact form of the decay function. We have applied two different random-number generators, without any significant change in the results.

The results are summarized in Fig. 2(b), where $\Phi(t)$ denotes the results obtained from the simulation, and $\Phi_1(t)$ and $\Phi_2(t)$ are the curves corresponding to the first two cumulants. Of course, because both the temporal and the spacial effects are involved, the decay $\Phi(t)$ is given by Eq. (2.2). Denoting by $\rho_n(x)$ the distribution of the R_n values for the random walk with constant stepping frequency, Eq. (2.2) may also be written as

$$\Phi(t) = e^{\lambda} \sum_n \int dx\, e^{-\lambda x} \rho_n(x) \phi_n(t)$$

$$= e^{\lambda} \int dx\, e^{-\lambda x} \Omega(x;t) , \qquad (5.5)$$

with

$$\Omega(x;t) \equiv \sum_n \rho_n(x) \phi_n(t) . \qquad (5.6)$$

Equation (5.5) allows the cumulant expansion

$$\Phi(t) = e^{\lambda} \exp\left[\sum_{j=1}^{\infty} \frac{(-\lambda)^j}{j!} Y_j(t) \right] , \qquad (5.7)$$

where the cumulants $Y_j(t)$ correspond to the distribution $\Omega(x;t)$. Equation (5.7) incorporates both Eq. (2.13) and Eq. (4.1). The curves labeled $\Phi_1(t)$ and $\Phi_2(t)$ in Fig. 2(b) correspond to restricting the sum in Eq. (5.7) to $j = 1$ and to $j = 1, 2$, respectively.

Comparison of Fig. 2(a) with Fig. 2(b) clearly shows the influence of the continuous time component on the decay law. Now neither $\Phi_1(t)$ nor $\Phi_2(t)$ describe the decay well for the range of concentrations ($p = 0.1$ and $p = 0.5$) considered. For lower concentrations $\Phi_2(t)$ tends to become a good approximation; however, for $p = 0.5$ it may only be used to describe a very short time regime, after which $\Phi_2(t)$ diverges to infinity. The approximation $\Phi_1(t)$ on the other hand, is quite poor and may only be used at very low concentrations $p < 0.01$, and for relatively short periods of time t. Such a behavior was encountered in our previous work on random walks with fixed stepping frequency only in cases of lower ($\Delta < 3$) dimensions.

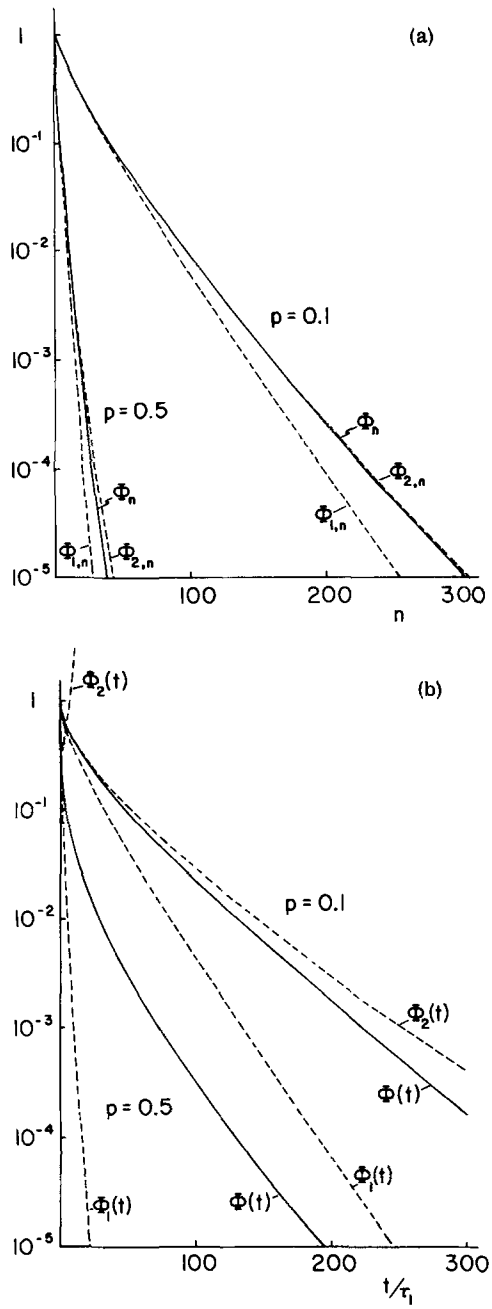

FIG. 3. (a) Decay law due to trapping in a nearest-neighbor random walk on a square lattice for a fixed stepping frequency. The symbols are as in Fig. 2(a). (b) Decay law due to trapping for a CTRW on a square lattice for the dipolar stepping time density, Eq. (3.18) with $s = 6$ and $\Delta = 2$. The symbols are as in Figs. 1 and 2(b).

To exemplify this point still further we plot in Fig. 3(a) the decay law due to a nearest-neighbor random walk at fixed time intervals on a square lattice. The meaning of the symbols is as in Fig. 2(a); we obtained Fig. 3(a) by performing the numerical simulations and the corresponding analysis in terms of cumulants as above. The main difference between the decay behavior Figs. 2(a) and 3(a) rests in the clearly nonexponential character of the decay law in two dimensions. As emphasized in Ref. II this is mainly due to the very large variance of the distribution of the R_n and less to the fact that in two dimensions $S_n = \langle R_n \rangle$ is not asymp-

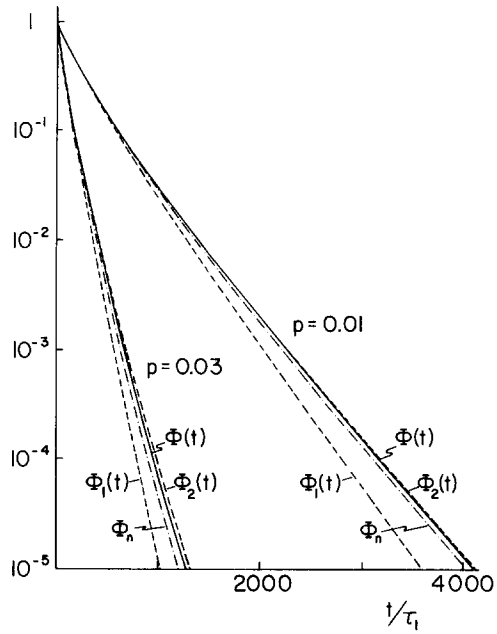

FIG. 4. Comparison of the decay laws due to trapping on a square lattice for a CTRW vs a random walk with constant stepping frequency. Here the probabilities that a site is a trap are $p = 0.01$ and $p = 0.03$. The symbols for the CTRW are as in Figs. 2(b) and 3(b); the dash-dotted line denotes Φ_n, the exact decay for the simple random walk.

totically linear in n. The effect of the variance can also be seen from Fig. 3(a), where the difference between Φ_n and $\Phi_{1,n}$ is much larger than in the three-dimensional case of Fig. 2(a).

In Fig. 3(b) we have drawn the corresponding decay laws for a random walk on the square lattice in continuous time. For ready comparison with the case of Fig. 2(b) we again choose the dipolar interaction ($s = 6$, $\Delta = 2$) with $\psi(t)$ given by Eq. (3.18). As was perhaps to be expected, the differences between $\Phi(t)$, $\Phi_1(t)$, and $\Phi_2(t)$ are even more dramatic than in three dimensions. Admittedly, we consider here really high concentrations ($p = 0.1$ and $p = 0.5$); on the other hand $\psi(t)$ for $\Delta/s = 1/3$ is quite a mild stepping time density, whose moments all exist. Here we find that neither $\Phi_1(t)$ nor $\Phi_2(t)$ reproduce $\Phi(t)$ even qualitatively.

In order not to leave the reader under the impression that $\Phi_2(t)$ is not at all useful, we continue our presentation of the decay laws in this two-dimensional case in Fig. 4. The drawing has the same parameters as in Fig. 3, apart from the fact that we consider lower values of p, $p = 0.03$, and $p = 0.01$. For $p = 0.01$ we find that $\Phi_2(t)$ offers a very reasonable description of the true decay law $\Phi(t)$, whereas $\Phi_1(t)$ is still widely off the mark. To emphasize the fact that here the decay $\Phi(t)$ is more influenced by the random walk than by the continuous time aspect, we have plotted in Fig. 4 also the exact decay Φ_n, with $n = t/\tau_1$, for a fixed stepping frequency τ_1^{-1}. As may be readily seen Φ_n is a much better approximation to $\Phi(t)$ than $\Phi_1(t)$.

It is convenient, in order to explain these findings, to use a more formal description. As previously noted, the advantage of employing approximate decay laws like $\Phi_{1,n}$, which include only the first moment S_n of R_n, rests in the relative ease with which the S_n may be obtained in simple cases. A compact way to an analytical treatment was rendered popular by the works of Montroll and Weiss.[30-32] It consists in using the generating function $\tilde{S}(z)$:

$$\tilde{S}(z) \equiv \sum_{n=0}^{\infty} z^n S_n \,, \tag{5.8}$$

where, for the lattices considered here:

$$\tilde{S}(z) = [(1-z)^2 P(0;z)]^{-1} \,, \tag{5.9}$$

and for which the function $P(0;z)$ may be expressed in terms of $K(x)$, the complete elliptic integral of the first kind, Eq. (17.3.1) of Ref. 42. Thus,[10]

$$P^{sq}(0;z) = (2/\pi)K(z^2) \,, \tag{5.10}$$

whereas $P^{sc}(0;z)$ was shown by Joyce to be expressible in terms of two elliptic integrals, Eqs. (7.10)–(7.13) of Ref. 51;

$$P^{sc}(0;z) = f_1 K(f_2) K(f_3) \,, \tag{5.11}$$

with f_1, f_2, and f_3 being algebraic functions of z (see Ref. 51 for details).

Reverting now to the CTRW description involves, as pointed out by Montroll and Weiss,[30] mainly the replacement of z through $\psi(u)$, the Laplace transform of $\psi(t)$, in some of the expressions above. We exemplify it in our notation. Being interested in $\Phi_1(t)$, we have to evaluate $Y_1(t)$ in Eq. (5.7), which is nothing else but $S(t)$:

$$\begin{aligned} S(t) \equiv Y_1(t) &= \int_0^{\infty} x\Omega(x;t)\,dx \\ &= \sum_{n=0}^{\infty} \phi_n(t) \langle R_n \rangle = \sum_{n=0}^{\infty} S_n \phi_n(t) \,, \end{aligned} \tag{5.12}$$

whose Laplace transform is

$$\begin{aligned} S(u) = \mathcal{L}[S(t)] &= \sum_{n=0}^{\infty} S_n \phi_n(u) \\ &= \{[1-\psi(u)]/u\} \sum_n [\psi(u)]^n S_n \\ &= \{[1-\psi(u)]/u\} \tilde{S}[z = \psi(u)] \,, \end{aligned} \tag{5.13}$$

where we made use of Eq. (2.12). Inserting now $\psi(u)$ in Eq. (5.9) leads to

$$S(u) = \mathcal{L}[S(t)] = \{u[1-\psi(u)]P[0;\psi(u)]\}^{-1} \,. \tag{5.14}$$

Our Eq. (5.12) differs only slightly, by a factor of $\psi(u)$, from the original Eq. (V.15b) of Ref. 30. The difference can be traced to the fact that one starts S_n at the value one, i.e., $S_0 = 1$, Eq. (III.9) of Ref. 30. Thus, it follows that $\lim_{t \to 0^+} S(t) = 1$, in accordance to this usage. One verifies now readily that the right-hand side of Eq. (5.12) indeed fulfills this requirement, since it tends to u^{-1} for u large, i.e., $\mathcal{L}^{-1}[S(u)] \to 1$ for $t \to 0^+$. On the other hand Eq. (V.15b) of Ref. 30 does not, since $\psi(u)/u = o(u^{-1})$ for u large.

Equations (5.10), (5.11), and (5.14), together with the distribution $\psi(t)$ of Eq. (3.18) which stems from the multipolar interactions, allow now the direct computa-

TABLE III. The mean number $S(t)$ of distinct sites visited during the time t for random walks on the square ($\Delta=2$) and on the simple-cubic ($\Delta=3$) lattices. Shown are the exact results for stepping time probabilities $\psi_m(t)$, Eq. (3.18), due to multipolar interactions with $s=6$, 8, and 10 in Eq. (3.14). For comparison the $S(t)$ for an exponential stepping density (exp) and for steps with constant frequency τ_1^{-1} (const) are also included.

	$\Delta=2$					$\Delta=3$				
t/τ_1	const	exp	6.	8	10	const	exp	6	8	10
0.1	1	1.10	2.00	2.73	3.70	1	1.10	1.48	1.84	2.30
0.2	1	1.20	2.33	3.20	4.39	1	1.20	1.70	2.15	2.72
0.3	1	1.29	2.58	3.56	4.89	1	1.29	1.88	2.40	3.04
0.5	1	1.47	2.98	4.12	5.67	1	1.48	2.19	2.80	3.56
0.7	1	1.65	3.31	4.58	6.30	1	1.67	2.45	3.14	4.00
1.0	2	1.91	3.73	5.15	7.09	2	1.94	2.81	3.58	4.56
2.0	2.75	2.70	4.87	6.65	9.10	2.83	2.80	3.84	4.83	6.09
3.0	3.50	3.43	5.80	7.85	10.68	3.67	3.63	4.76	5.89	7.37
5.0	4.84	4.78	7.41	9.85	13.26	5.25	5.22	6.45	7.80	9.61
7.0	6.10	6.05	8.83	11.57	15.45	6.79	6.76	8.05	9.56	11.62
10.0	7.88	7.84	10.77	13.88	18.32	9.05	9.03	10.35	12.04	14.41
20.0	13.34	13.30	16.47	20.40	26.22	16.38	16.37	17.73	19.74	22.81
30.0	18.38	18.35	21.60	26.07	32.90	23.54	23.53	24.90	27.07	30.60
50.0	27.81	27.78	31.07	36.26	44.60	37.64	37.63	38.99	41.31	45.43
70.0	36.73	36.70	39.97	45.63	55.11	51.57	51.56	52.92	55.30	59.79
100.0	49.50	49.48	52.69	58.83	69.64	72.29	72.28	73.63	76.04	80.89

tion of $S(t)$. From $S(t)$ we then obtain $\Phi_1(t)$, according to Eq. (5.7). We remark that this evaluation is *not stochastic* (different from the simulation calculations which we presented before); thus it is an additional, independent means of computing $\Phi_1(t)$. We can even use the results to check the accuracy of the simulation procedure.

We now continue by first describing the results for $S(t)$, the average number of sites visited during the time t, and return afterwards to the discussion of $\Phi_1(t)$. For both the simple cubic and the square lattice we have evaluated $S(t)$ by performing the Laplace inversion of the right-hand side of Eq. (5.14), in which Eq. (5.9) or Eq. (5.10) were, respectively, inserted. The results are displayed in Table III. For stepping time densities $\psi(t)$ we chose both the multipolar interactions, Eq. (3.18) with $s=6$, 8, and 10, and also the exponential density Eq. (3.2). A description of the method for the Laplace transformation of $\psi(t)$ and of the procedure for the inverse Laplace transformation is given in Sec. IV. For the inverse Laplace transformation values of the complete elliptic integral of the first kind $K(z)$ for complex arguments z are needed. We obtained these employing a descending Landen transformation which leads to a rapidly converging recursion formula, Eq. (17.3.29) of Ref. 42. In Table III we also present, for comparison, the values S_n which obtain for a nearest-neighbor random walk on the same lattices, with a constant stepping frequency.

As may have been expected, the differences between S_n and $S(t)$ for an *exponential* stepping time density are small, and are due to the small skewness of the distribution of S_n with respect to n. Larger differences occur between S_n and the $S(t)$ which obtain for multipolar stepping time densities: Here we find again that the differences are more accentuated for the lattice with the lower dimension and for shorter-ranged interactions, i.e., larger values of s.

To relate $S(t)$ to S_n in an approximate way one may start from Eq. (5.12), $S(t)=\sum_{n=0}^{\infty} S_n\phi_n(t)$, and replace, for t fixed, the sum by an averaged value of n, thus $S(t)\simeq S_{\langle n\rangle}$. We remark that from Eq. (4.2) one has

$$\langle n\rangle=\sum_{n=0}^{\infty} n\phi_n(t)=M_1(t)=X_1(t)\ , \tag{5.15}$$

and therefore $S(t)\simeq S_{X_1^{\wedge}(t)}$. From Tables II and III one can verify that this approximation works very well for large t. This satisfactory finding is due to the smooth asymptotic behavior of S_n for three- and two-dimensional lattices, $S_n\propto a_1 n$ and $S_n\propto \tilde{a}_1 n/\ln n$, respectively, the former being itself linear in n whereas the latter does not depart markedly from linearity on short intervals of n values. As evident from Tables I and II, $\langle n\rangle=X_1(t)$ is larger than $n=t/\tau_1$, the difference between the two values being greater for lower values of Δ/s. Thus $S_{X_1^{\wedge}(t)}$ is larger than S_{t/τ_1}, and explains the qualitative findings of Table III.

For very short times $S(t)$ mimics the behavior of the decay function $\Psi_m(t)$, Eq. (3.16). As noted before, $S(t)$ is scaled in such a way as to have $\lim_{t\to 0^+} S(t)=1$. Since this feature is perhaps not immediately evident from Table III, one should keep in mind that the slope of $dS(t)/dt$ at $t=0^+$ is infinite; this is due to the divergent behavior of the stepping time distribution $\psi_m(t)$, Eq. (3.18), at very short times, fact which arises from the continuum approximation together with the unphysical behavior of $w(\mathbf{r})\propto r^{-s}$ for very small r; for better expressions for $\Psi_m(t)$ see Ref. 33.

We return now to the discussion of $\Phi_1(t)$. As already stated, one has from Eq. (5.7), $\Phi_1(t)=e^{\lambda}\exp[-\lambda S(t)]$. With the help of the calculated $S(t)$, which are also given in Table III, we have evaluated $\Phi_1(t)$ for the two lattices considered and for dipolar interactions ($\Delta=2$, 3; $s=6$). Comparison of the computed decays $\Phi_1(t)$ with the corresponding decay laws in Figs. 2(b) and 3(b) shows both for the simple cubic and for the square lattice an ex-

cellent agreement: This supports our confidence that both the simulation routine and the Laplace-inversion technique lead to accurate results.

As noted before, one has $S_{\langle n\rangle} > S_n$ for $\langle n\rangle = X_1(t)$ and $n = t/\tau_1$. Thus the decay $\Phi_1(t)$ in the CTRW case is more rapid than the decay $\Phi_{1,n}$, which holds for a random walk with constant stepping frequency. This can also be seen by comparing Figs. 2(a) and 2(b) and Figs. 3(a) and 3(b), respectively. However, the deviation of $\Phi_{1,n}$ from $\Phi_1(t)$ is quite small as compared to the large difference between $\Phi_1(t)$ and the true decay $\Phi(t)$. This point is worth keeping in mind, since most approaches which treat trapping in the CTRW framework really consider forms related to $\Phi_1(t)$ only. This is understandably so, since to go beyond $\Phi_1(t)$ requires additional knowledge about the higher moments of the corresponding distributions; the derivation of such moments for R_n is not an easy analytical task (see the references to this problem cited in Ref. 10). With respect to $\Phi_1(t)$, at least for stepping time distributions $\psi(t)$ whose first and second moments exist, approximate analytical expressions may readily be determined using the approach of Montroll and Weiss.[30] Some claims contrary to Ref. 30 have been made [e.g., Eq. (4.22) of Ref. 20 and Eq. (26) of Ref. 18] but these are due to computational errors; in both cases an improper inverse Laplace transformation is involved, starting from Eq. (4.21) in Ref. 20 and Eqs. (17a)–(17c) in Ref. 18.

We close this section with an analysis of $\Phi_2(t)$, the approximate decay form which involves also the second cumulant $Y_2(t)$, see Eq. (5.7). Paralleling Eq. (5.12) one has

$$\begin{aligned} Y_2(t) &= \int_0^\infty x^2 \Omega(x;t)\,dx - [S(t)]^2 \\ &= \sum_{n=0}^{\infty} (S_n^2 + \sigma_n^2)\,\phi_n(t) - \sum_{n,m=0}^{\infty} S_n S_m \phi_n(t)\phi_m(t) \\ &= \sum_{n=0}^{\infty} \sigma_n^2 \phi_n(t) + \frac{1}{2} \sum_{n,m=0}^{\infty} (S_n - S_m)^2 \phi_n(t)\phi_m(t)\,, \end{aligned} \tag{5.16}$$

where in the last line we used the relation $\sum_{n=0}^{\infty} \phi_n(t) = 1$, and where $\sigma_n^2 = \langle R_n^2\rangle - \langle R_n\rangle^2 = \langle R_n^2\rangle - S_n^2$. In order to obtain an approximate expression for $Y_2(t)$ from Eq. (5.16) we observe that σ_n^2 and S_n are slowly varying functions of n on the scale of variation of $\phi_n(t)$ with n for fixed t. Then, as in the discussion preceding Eq. (5.15), we replace the first sum through $\sigma^2_{\langle n\rangle}$; furthermore $S_n - S_m \simeq (n-m)\,dS_n/dn$. Observing now that $X_2(t)$ is given by

$$\begin{aligned} X_2(t) &= \sum_{n=0}^{\infty} n^2 \phi_n(t) - \left[\sum_{n=0}^{\infty} n\phi_n(t)\right]^2 \\ &= \frac{1}{2} \sum_{n,m=0}^{\infty} (n-m)^2 \phi_n(t)\phi_m(t)\,, \end{aligned} \tag{5.17}$$

it follows:

$$Y_2(t) \simeq \sigma^2_{\langle n\rangle} + X_2(t) \left(\frac{dS_n}{dn}\right)^2 \Bigg|_{\langle n\rangle}\,, \tag{5.18}$$

with $\langle n\rangle$ being given by Eq. (5.15). The advantage of having expression (5.18) rests in the fact that in certain cases asymptotical expressions for σ_n^2 are known; therefore an approximate decay law $\Phi_2(t)$ may be readily obtained by using the information about random walks with fixed stepping frequency (S_n and σ_n^2) and computing $X_1(t)$ and $X_2(t)$ from Eqs. (4.11). Here we do not pursue this point further, but we show in Fig. 5 the astonishingly good agreement between $Y_2(t)$ and the approximate form (5.18). The drawing involves three distinct, independent simulations: a random walk with fixed stepping frequency on a square lattice, to determine S_n and σ_n^2; a CTRW on the same lattice, with $\psi(t)$ corresponding to the dipolar case, $s = 6$ in Eq. (3.18), to determine $Y_2(t)$; a temporal simulation to obtain $X_2(t)$. Plotted are $Y_2(t)$, σ_n^2 for $n = t/\tau_1$ and the approximate form (5.18), all three as a function of time. The jitter in the approximate form is mainly due to the term dS_n/dn, and can be avoided by making use of an analytical expression for S_n.

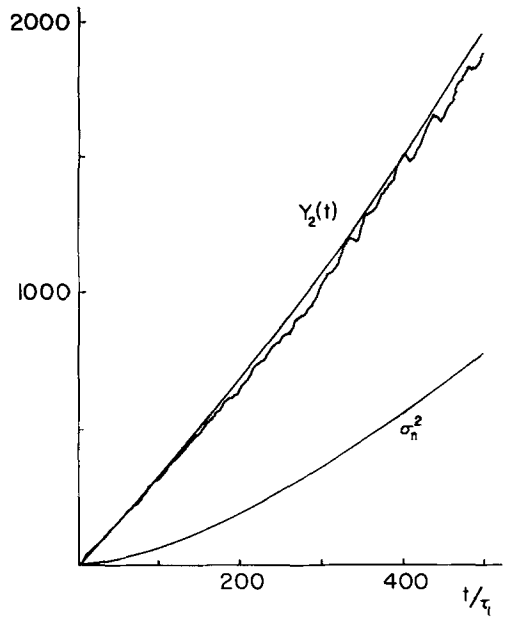

FIG. 5. Analysis of the second cumulant $Y_2(t)$—the variance—Eq. (5.16) of the decay law $\Phi(t)$. The decay is due to a CTRW on a square lattice for the dipolar stepping time density, Eq. (3.18), with $s = 6$ and $\Delta = 2$. Plotted are $Y_2(t)$, the variance σ_n^2 of the corresponding random walk with fixed stepping frequency τ_1^{-1}, and the approximate expression (bumpy line), Eq. (5.18).

We turn now to a summary of results.

VI. CONCLUSIONS

In this article we have studied the energy migration in the framework of the CTRW formalism. Much attention was paid to the trapping problem, where the energy of the system is transferred irreversibly to randomly distributed substitutional traps. The migration was modeled through a nearest-neighbor random walk on regular lattices, during which the steps occurred at random time intervals, following a common stepping time density $\psi(t)$.

Thus, the CTRW involves two stochastic processes, one due to the time development and the other due to the spatial random walk, both of which are, *prima facie*, strongly interrelated. The major conclusion

which emerges from the present work is that in the energy decay problem one can still separate the effects of these two different random processes; this simplifies, of course, the task of finding accurate expressions for the decay law.

Fundamental in this respect is the exact decay law, Eq. (2.2), which connects the two aspects only via n, the number of steps performed. In this article our analysis centered around the temporal behavior described by $\psi(t)$ and $\phi_n(t)$ on the one hand, and around the spacial behavior exemplified by R_n, the number of distinct sites visited by the random walker, on the other. We exemplified this in the last section, where we also demonstrated the interplay of both aspects by presenting a series of different decay behaviors.

Since the pure random walk at constant time intervals was our object of study in Refs. I and II, we concentrated in this article primarily on the part of the problem dealing with the time development. In Sec. III we therefore showed that many of the currently employed forms for $\psi(t)$ arise naturally from the decay forms of the *direct* energy transfer from donors to randomly distributed acceptors, when the microscopic transfer rates are due to multipolar or to exchange interactions. We pointed out, however, that some of these expressions for $\psi(t)$ are valid only at low acceptor concentrations, i.e., for strongly disordered lattices; thus their use in the CTRW formalism runs counter to the assumption of an underlying regular lattice, and can be motivated only on model-related grounds. For two- and three-dimensional lattices we found that both for multipolar and for exchange interactions all moments of the corresponding stepping time densities $\psi(t)$ exist; thus in the energy transfer case one is faced with the classical CTRW problem, as formulated by Montroll and Weiss.[30]

As in our Ref. II, we have found that one can achieve a very convenient description of the decay laws in terms of the cumulants of the corresponding random distributions. In Sec. IV we have therefore derived the cumulants connected to the continuous time given by $\psi(t)$ and in Sec. V we have used these results for the complete analysis of the CTRW-decay laws in terms of cumulants. As in Ref. II, we find that in many cases the decay law is represented very poorly by $\Phi_1(t)$, which involves only the first cumulant, whereas the inclusion of the second cumulant leads to $\Phi_2(t)$, a form which is in general very adequate. This is an incentive for additional theoretical efforts, since most of the approaches applied so far in the CTRW problem rely on forms related to $\Phi_1(t)$—like $S(t)$—to describe the energy trapping. From the results of this article it is apparent that $S(t)$ is in general not sufficient to describe the decay, $\Phi_1(t)$ being here a worse approximation to the true decay $\Phi(t)$ than was the case for the approximate form $\Phi_{1,n}$ for random walks with constant stepping frequency. This is due to the fact that the variances of the two random processes involved are large, and, as shown in Eq. (5.18), additive. These variances, however, do not follow from the elegant generating function formalism and its extension for continuous times[30] which leads to $S(t)$. In fact, even the analytical evaluation of σ_n^2 for simple random walks is complex. Of course, this does not mean that no simple analytical approximate forms can be found: In applications one can rely on equations like Eq. (5.18), to obtain approximate decay laws which are superior to $\Phi_1(t)$.

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APPENDIX

In Sec. IV we have studied the cumulants $X_j(t)$ and the moments $M_j(t)$ of the distributions $\phi_n(t)$. These quantities were defined through Eqs. (4.1) and (4.2). For stepping time densities $\psi(t)$, for which all moments τ_j exist, we find that $M_j(t)$ and $X_j(t)$ have asymptotically the form

$$M_j(t) = \sum_{k=0}^{j} \mu_{jk} \bar{t}^k \,, \tag{A1}$$

$$X_j(t) = \xi_{j1} \bar{t} + \xi_{j0} \,, \tag{A2}$$

with $\bar{t} = t/\tau_1$. We list here the values for μ_{jk} and ξ_{jk} for $j \leq 4$, obtained as described in Sec. IV. One has

$$\mu_{kk} = 1 \text{ for all } k \,,$$

and

$$\mu_{10} = \tau_2/(2\tau_1^2) - 1 \,,$$

$$\mu_{21} = 2\tau_2/\tau_1^2 - 3 \,,$$

$$\mu_{20} = -2\tau_3/(3\tau_1^3) + 3\tau_2^2/(2\tau_1^4) - 3\tau_2/(2\tau_1^2) + 1 \,,$$

$$\mu_{32} = 9\tau_2/(2\tau_1^2) - 6 \,,$$

$$\mu_{31} = -3\tau_3/\tau_1^3 + 9\tau_2^2/\tau_1^4 - 12\tau_2/\tau_1^2 + 7 \,,$$

$$\mu_{30} = 3\tau_4/(4\tau_1^4) + 4\tau_3/\tau_1^3 + 15\tau_2^3/(2\tau_1^6) - 9\tau_2^2/\tau_1^4 - 6\tau_2\tau_3/\tau_1^5 + 7\tau_2/(2\tau_1^2) - 1 \,,$$

$$\mu_{43} = 8\tau_2/\tau_1^2 - 10 \,,$$

$$\mu_{42} = -8\tau_3/\tau_1^3 + 30\tau_2^2/\tau_1^4 - 45\tau_2/\tau_1^2 + 25 \,,$$

$$\mu_{41} = 4\tau_4/\tau_1^4 + 30\tau_3/\tau_1^3 + 60\tau_2^3/\tau_1^6 - 90\tau_2^2/\tau_1^4 - 40\tau_2\tau_3/\tau_1^5 + 50\tau_2/\tau_1^2 - 15 \,,$$

$$\mu_{40} = -4\tau_5/(5\tau_1^5) - 15\tau_4/(2\tau_1^4) + 20\tau_3^2/(3\tau_1^6) - 50\tau_3/(3\tau_1^3) + 105\tau_2^4/(2\tau_1^8) - 75\tau_2^3/\tau_1^6 - 60\tau_2^2\tau_3/\tau_1^7 + 75\tau_2^2/(2\tau_1^4) + 10\tau_2\tau_4/\tau_1^6 + 60\tau_2\tau_3/\tau_1^5 - 15\tau_2/(2\tau_1^2) + 1 \,. \tag{A3}$$

Furthermore:

$$\xi_{11} = 1 \,,$$

$$\xi_{10} = \tau_2/(2\tau_1^2) - 1 \,,$$

$$\xi_{21} = \tau_2/\tau_1^2 - 1 \,,$$

$$\xi_{20} = -2\tau_3/(3\tau_1^3) + 5\tau_2^2/(4\tau_1^4) - \tau_2/(2\tau_1^2) \,,$$

$$\xi_{31} = -\tau_3/\tau_1^3 + 3\tau_2^2/\tau_1^4 - 3\tau_2/\tau_1^2 + 1 \,,$$

$$\xi_{30} = 3\tau_4/(4\tau_1^4) + 2\tau_3/\tau_1^3 + 11\tau_2^3/(2\tau_1^6) - 15\tau_2^2/(4\tau_1^4) - 5\tau_2\tau_3/\tau_1^5 + \tau_2/(2\tau_1^2) ,$$

$$\xi_{41} = \tau_4/\tau_1^4 + 6\tau_3/\tau_1^3 + 15\tau_2^3/\tau_1^6 - 18\tau_2^2/\tau_1^4 - 10\tau_2\tau_3/\tau_1^5 + 7\tau_2/\tau_1^2 - 1 ,$$

$$\xi_{40} = -4\tau_5/(5\tau_1^5) - 9\tau_4/(2\tau_1^4) + 16\tau_3^2/(3\tau_1^6) - 14\tau_3/(3\tau_1^3) + 279\tau_2^4/(8\tau_1^8) - 33\tau_2^3/\tau_1^6 - 44\tau_2^2\tau_3/\tau_1^7 + 35\tau_2^2/(4\tau_1^4) + 17\tau_2\tau_4/(2\tau_1^6) + 30\tau_2\tau_3/\tau_1^5 - \tau_2/(2\tau_1^2) . \quad \text{(A4)}$$

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