Self-consistent effective medium approximation for hopping transport on a lattice with random traps

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A self-consistent cluster effective medium approximation is developed for hopping transport on a lattice with random traps which allows for transitions between nearest neighbors. The particle kinetics and the partial populations of centers with a specified escape probability are investigated. An estimate of the error of the method indicates that the results are exact in almost all limiting cases.

I. INTRODUCTION

There is much interest today in incoherent migration of quasiparticles in disordered systems, which occurs in the most diverse physical systems. Examples include exciton migration in molecular crystals, amorphous solids, and biological systems (e.g., in the photosynthetic apparatus of plants); sensitized luminescence and photochemistry; electron conduction in nonintrinsic semiconductors; spin diffusion, etc.

The master equation[1] provides a basis for the rigorous description of incoherent (Markov) hopping processes; moreover, the analogy with the close coupling problem in the quantum theory of disordered systems permits the application of the well-developed Green function formalism.[2–8,9]

The case of symmetric transition probabilities, which corresponds to structural disorder, is the best understood. For example, transfer of electron excitations between impurity molecules in a solution was considered in Ref. 2, where hops were considered between arbitrarily distant centers. The self-consistent medium approximation was also developed in Refs. 3–5 (cf. also Ref. 6) to handle the random bonding problem between nearest neighbors in a lattice. The extension of this approximation to clusters was considered in Ref. 7.

Much less work has been done for the general case of a finite (nonzero) spread in the energy levels, for which the hopping probabilities are asymmetric ($w_{jk} \neq w_{kj}$) in the indices of the centers between which the hopping occurs. For instance, self-consistent two- and three-center effective medium approximations were developed in Ref. 8, where Mott's equation $\sigma \propto \exp[-(T_0/T)^{1/4}]$ was derived for the electric conductivity in the low-temperature limit. However, detailed analytic investigations of the general problem are very difficult.

Random walks in systems containing traps are an important special case in which the transition probabilities are asymmetric. In his pioneering work,[10] Smoluchowski analyzed the case of continuous diffusion accompanied by irreversible trapping by particle sinks of low concentration. Two- and three-center effective medium approximations with allowance for jumps between all centers were developed in Ref. 9 for incoherent transport of electronic excitations in solutions containing traps (sinks) of finite concentration. The precise decrease $n \propto \exp[-\mathrm{const}\cdot t^{d/(d+2)}]$ in the concentration of free particles for large times was derived in Refs. 11 and 12 (cf. also Ref. 13) for continuous diffusion with particle sinks in a space of dimension d. Steady-state irreversible chemical reactions with external sources were considered in Ref. 14. The kinetics of reversible reactions was considered in the many-body formulation in Ref. 15 (trapping corresponds to the case when one of the reagents is "frozen"). It was shown there that the relaxation to the equilibrium populations for large times is slow, $\propto (Dt)^{d/2}$.

Our purpose in this paper is to study random walks in lattices with random traps analytically in as much detail as possible. We introduce the model in Sec. 2 and give the basic definitions and a quick derivation of the fundamental perturbation-series formula (15) for scattering by the clusters. In Sec. 3 we develop the self-consistent effective medium approximation for calculating the particle kinetics in the random trap model. Section 4 deals with the calculations of the partial Green functions. In Sec. 5, we study the generalized diffusion coefficient and the total population of traps having a specified escape probability. Finally, in Sec. 6 we estimate the error in the self-consistent effective medium approximation.

2. FORMULATION AND FUNDAMENTAL EQUATIONS

We consider a particle which hops along a d-dimensional lattice containing traps of concentration c. The microscopic spatial distribution of the traps is completely uncorrelated and random, but the macroscopic distribution is uniform.

We will assume that the particle can only jump between adjacent centers and that the hopping probability w_0 (per unit time) is the same for hops into a trap and for hops between nontrapping centers. In addition we assume that for a fixed trap, the probabilities w_t for a particle to leave the trap and enter any of its z nearest neighbors are all the same; the w_t for the different traps take random values (i.e., the depth of the traps is a random variable) whose distribution function $\rho_1(w_t)$ is normalized to unity. The total distribution density for the hopping probabilities is thus given by

$$\rho(w) = (1-c)\,\delta(w-w_0) + c\rho_1(w_t)\,\delta(w-w_t). \qquad (1)$$

By the nature of the problem, w_t is $< w_0$, i.e., a particle is less likely to escape from a trap than to make some other kind of hop; however, this fact will play little role in the

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solution of the problem. Neither the trap concentrations nor the spread in the transition probabilities will be assumed to be small.

The rate equations

$$\frac{dP_{ji}}{dt}=\sum_{k(j)} w_{jk}P_{ki}-\sum_{l(j)} w_{lj}P_{ji} \tag{2}$$

for the populations of the centers describe the incoherent migration of a particle over the lattice. The sum over $k\,(j)$ in (2) includes the nearest neighbors j-th center. We emphasize that the order of the subscripts in (2) differs from the order used in Refs. 3–5—in our case, $P_{ji}(t)$ is the probability of finding a particle in center j at time t if the particle was initially located in center i, and w_{jk} is the hopping probability from center k to center j. This order is more convenient in our case, for which the transition probabilities are not symmetric, $w_{jk}\neq w_{kj}$. We observe that in this model, the hopping probability in fact depends only on the second subscript: $w_{jk}\equiv w_k$, i.e., on the energy of the trapping center from which the particle escapes.

The Green's function for this problem is determined by Eq. (2) for an infinite lattice with the initial conditions

$$P_{ji}(t=0)=\delta_{ji}. \tag{3}$$

The initial populations $P_j'(t=0)$ of the centers are arbitrary, and the $P_j(t)$ satisfy the familiar equation

$$P_j'(t)=\sum_i P_{ji}(t)P_i'(t=0).$$

We clearly have

$$P_j'(t)=P_{j0}(t)$$

in the special case when the particle is initially located at the center $i=0$.

This problem is mathematically equivalent to calculating the currents in an electric circuit whose nodes (centers) form a regular lattice. The adjacent centers are all connected by identical resistors R ($R=1$, say); in addition, all the centers are connected by random capacitors C to a common zero potential (Fig. 1).

There is a probability c that the capacitors C will take random values C_t characterized by the distribution function $\rho_1(C_t)$; the rest of the time (with probability $1-c$), C takes the fixed value C_0. The Kirchhoff equations for the charge Q_{ji} at the j-th node lead to an equation of the form (2) with

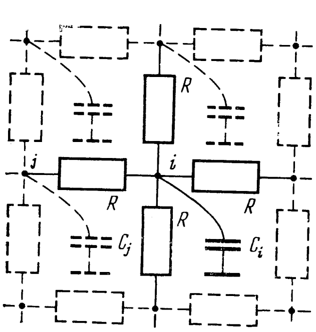

FIG. 1. Network of electrical resistors and capacitors described by Eq. (2).

$$w_k=(RC_k)^{-1},\quad P_{ji}=Q_{ji}. \tag{4}$$

We note that Kirkpatrick[16] used a similar analogy with an electric circuit to develop a self-consistent effective medium approximation for the random binding problem in the percolation limit. His method was generalized in Refs. 3–5 to calculate the frequency-dependent diffusion coefficient and electric conductivity. Unlike our model however, in the percolation limit for the bonding model all the capacitors C are identical and the resistors R are random; moreover, $R=\infty$ with a finite probability.

For definiteness we will refer to the problem as a random walk of a particle in a system with random traps.

In what follows we will briefly derive the fundamental formulas (15), (16) by drawing heavily on the analogy with the multiple scattering formalism in the quantum theory of disordered systems.[17] We note that although the homomorphic coherent potential approximation[18] is the formal quantum analogy of the effective medium approximation for the random bonding problem,[3–5] there is no complete analog for systems with asymmetric transition probabilities.

We thus introduce the transition probability matrix

$$W_{jk}=(1-\delta_{jk})\,w_k-\delta_{jk}zw_j \tag{5}$$

in terms of which we can rewrite the rate equations (2) as

$$dP/dt=WP, \tag{6}$$

where $P=\|P_{ji}\|$ is the matrix for the populations of the centers. If we take the Laplace transform

$$\tilde f(\varepsilon)=\hat{\mathscr{L}}f(t)=\int_0^\infty \exp(-\varepsilon t)f(t)\,dt,$$

of (6) and use the initial conditions (3), we get

$$[\varepsilon-W]\tilde P=I, \tag{7}$$

where $I_{ji}=\delta_{ji}$ is the unit matrix. We will henceforth denote the Laplace transform of any function f by $\tilde f=\tilde f(\varepsilon)$. Equation (7) has the formal solution

$$\tilde P=[\varepsilon-W]^{-1}. \tag{8}$$

In order to derive the self-consistent cluster effective medium approximation, we will consider the effective ordered transition probability $\tilde w^{\rm eff}(\varepsilon)$, which in general depends on ε.[1)] The corresponding transition probability matrix is given by

$$\tilde W_{jk}^{\rm eff}=(1-\delta_{jk})\,\tilde w^{\rm eff}-\delta_{jk}z\tilde w^{\rm eff}. \tag{9}$$

The identity

$$W=\tilde W^{\rm eff}+\Delta\tilde W, \tag{10}$$

expresses the true transition probability matrix W in terms of $\tilde W^{\rm eff}$, where

$$\Delta\tilde W_{jk}=(1-\delta_{jk})\,(w_k-\tilde w^{\rm eff})-\delta_{jk}z\,(w_j-\tilde w^{\rm eff}) \tag{11}$$

is the complete perturbation matrix and is given by the sum of the perturbation matrices $\Delta\tilde W_m$ corresponding to the individual perturbing clusters:

$$\Delta\tilde W=\sum_m \Delta\tilde W_m.$$

The specific form of the perturbing clusters and the corresponding matrices $\Delta\tilde{W}_m$ for the random trap model will be described below.

The Dyson equation

$$\tilde{P}=\tilde{P}^{\text{eff}}+\tilde{P}^{\text{eff}}\Delta\tilde{W}\tilde{P}, \tag{12}$$

where

$$\tilde{P}^{\text{eff}}=[\varepsilon-\tilde{W}^{\text{eff}}]^{-1} \tag{13}$$

is the Green's function for the effective system, follows readily from (8) and (10). Inversion of (12) leads to the perturbation expansion

$$\tilde{P}_{ji}=\tilde{P}_{ji}^{\text{eff}}+\sum_m(\tilde{P}^{\text{eff}}\Delta\tilde{W}_m\tilde{P}^{\text{eff}})_{ji}+\sum_{m,n}(\tilde{P}^{\text{eff}}\Delta\tilde{W}_n\tilde{P}^{\text{eff}}\Delta\tilde{W}_m\tilde{P}^{\text{eff}})_{ji}+\dots \tag{14}$$

in the "scattering amplitudes" for scattering of the particle by the perturbing clusters.

If we combine terms in (14) describing successive scatterings by the same cluster, we get the expansion

$$\tilde{P}_{ji}=\tilde{P}_{ji}^{\text{eff}}+\sum_m(\tilde{P}^{\text{eff}}\tilde{t}_m\tilde{P}^{\text{eff}})_{ji}+\sum_{\substack{m,n\\ m\neq n}}(\tilde{P}^{\text{eff}}\tilde{t}_n\tilde{P}^{\text{eff}}\tilde{t}_m\tilde{P}^{\text{eff}})_{ji}+\dots, \tag{15}$$

where the matrix $\tilde{t}$ is given by the series

$$\tilde{t}_m=\Delta\tilde{W}_m+\Delta\tilde{W}_m\tilde{P}^{\text{eff}}\Delta\tilde{W}_m+\Delta\tilde{W}_m\tilde{P}^{\text{eff}}\Delta\tilde{W}_m\tilde{P}^{\text{eff}}\Delta\tilde{W}_m+\dots. \tag{16}$$

The sums in (15) are over distinct indices $n, m,\dots$, because all of the subsequent scatterings by a single cluster are already contained in the sum in (16), so that the indices $n, m,\dots$ of adjacent matrices $\tilde{t}$ appearing in (16) cannot coincide.

3. SELF-CONSISTENT EFFECTIVE MEDIUM APPROXIMATION FOR THE RANDOM TRAP MODEL

Figure 2 shows a perturbing cluster for a three-dimensional cubic lattice in the random trap model. The only relevant properties of the effective medium are the true probabilities for a transition from the center m to a nearest neighbor. The perturbing cluster involves both correlated transition probabilities and the probabilities for transitions between different, uncorrelated clusters. The cluster may or may not be a trap; in this respect, all the centers in the lattice are equivalent. The original system is reproduced by gluing the clusters together into a mosaic.

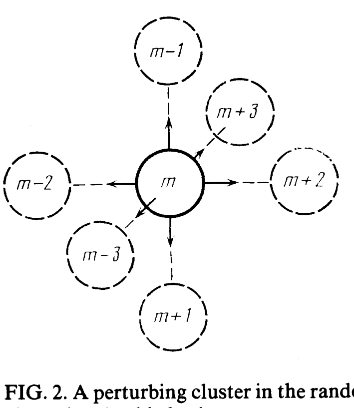

FIG. 2. A perturbing cluster in the random trap model for a simple three-dimensional cubic lattice.

The perturbation matrix $\Delta\tilde{W}_m$ has exactly $z+1$ nonzero elements, all in the m-th column:

$$\Delta\tilde{W}_m=\Delta\tilde{w}_m M_m(z), \tag{17}$$

where

$$\Delta\tilde{w}_m=w_m-\tilde{w}^{\text{eff}},$$

$$[M_m(z)]_{nk}=\begin{cases}1; & n=m\pm1;\dots;m\pm z/2; \quad k=m\\ -z; & n=m; \quad k=m.\\ 0; & k\neq m\end{cases} \tag{18}$$

The transition probabilities of the form $w_{m,n}$ $n=m\pm1,\dots, m\pm z/2$, belong to adjacent clusters and are not included in the perturbation (17).

A straightforward calculation using the symmetry properties of the ordered Green's function for the effective medium shows that the only nonzero elements in the product $\tilde{P}^{\text{eff}}\Delta\tilde{W}_m$ lie in the mth column:

$$(\tilde{P}^{\text{eff}}\Delta\tilde{W}_m)_{nk}=\Delta\tilde{w}_m\begin{cases}\tilde{\tau}_2; & k=m; \quad n=m\pm1;\dots;m\pm z/2\\ \tilde{\tau}_1; & k=n=m,\\ 0; & k\neq m\end{cases} \tag{19}$$

where

$$\tilde{\tau}_1=z(\tilde{P}^{\text{eff}}_{m,m+1}-\tilde{P}^{\text{eff}}_{m,m}), \quad \tilde{\tau}_2=\sum_{l(m)}\tilde{P}^{\text{eff}}_{m+1,l}-z\tilde{P}^{\text{eff}}_{m+1,m}.$$

The general term in series (16) is thus given by

$$\Delta\tilde{W}_m[\tilde{P}^{\text{eff}}\Delta\tilde{W}_m]^k=\Delta\tilde{w}_m^{k+1}\tilde{\tau}_1^k M_m(z) \tag{20}$$

and the entire $\tilde{t}$-matrix takes the form

$$\tilde{t}_m=\tilde{F}_m(z)M_m(z),$$
$$\tilde{F}_m(z)=\Delta\tilde{w}_m[1+z\Delta\tilde{w}_m(\tilde{P}^{\text{eff}}_{m,m}-\tilde{P}^{\text{eff}}_{m,m+1})]^{-1}. \tag{21}$$

It is important to note that it would be incorrect to evaluate $\tilde{t}_m$ by using the relation

$$\tilde{t}_m=\Delta\tilde{W}_m[1-\tilde{P}^{\text{eff}}\Delta\tilde{W}_m]^{-1} \tag{22}$$

which follows by formally summing the series in (16); in this case, one gets an erroneous expression in which all the elements of the $(z+1)x(z+1)$ matrix $\tilde{t}_m$ are nonzero.

We will need some formulas which relate the populations of adjacent centers in the effective medium. By the definition of the Green's function for an ordered system, we have the formulas

$$\sum_{j'(j)}\tilde{P}^{\text{eff}}_{j'i}=\tilde{P}^{\text{eff}}_{ji}(z+\varepsilon/\tilde{w}^{\text{eff}}), \tag{23}$$

$$\tilde{P}^{\text{eff}}_{j'j}=(1+\varepsilon/z\tilde{w}^{\text{eff}})\tilde{P}^{\text{eff}}_{jj}-1/z\tilde{w}^{\text{eff}}, \tag{24}$$

where the primed subscript $j'=j'(j)$ labels the nearest neighbors of the center j.

The formula

$$\tilde{P}^{\text{eff}}_{jj}=\int_{-\pi}^{\pi}\prod_{i=1}^{d}dk_i\left[\varepsilon+z\tilde{w}^{\text{eff}}-2\tilde{w}^{\text{eff}}\sum_{i=1}^{d}\cos k_i\right]^{-1}, \tag{25}$$

gives the diagonal elements of the Green's function on a d-

dimensional cubic lattice; for $d=1$, the integral can be expressed in terms of elementary functions:

$$\tilde{P}_{jj}^{\mathrm{eff}}=[\varepsilon(\varepsilon+4\tilde{w}^{\mathrm{eff}})]^{-1/2}. \quad (26)$$

Using (24), we can rewrite the quantity $\tilde{F}_m$ in expression (21) for the $\tilde{t}$-matrix as

$$\tilde{F}_m(z)=\tilde{w}^{\mathrm{eff}}\Delta\tilde{w}_m[w_m-\varepsilon\tilde{P}_{11}^{\mathrm{eff}}\Delta\tilde{w}_m]^{-1}. \quad (27)$$

We now return to the series (15); using (21), we can write its general term in the form

$$(\tilde{P}^{\mathrm{eff}}\tilde{t}_n\tilde{P}^{\mathrm{eff}}\tilde{t}_m\tilde{P}^{\mathrm{eff}}\ldots\tilde{t}_k\tilde{P}^{\mathrm{eff}})_{ji}$$
$$=\tilde{F}_n(z)\tilde{F}_m(z)\ldots\tilde{F}_k(z)$$
$$\times(\tilde{P}^{\mathrm{eff}}M_n(z)\tilde{P}^{\mathrm{eff}}M_m(z)\tilde{P}^{\mathrm{eff}}\ldots M_k(z)\tilde{P}^{\mathrm{eff}})_{ji}, \quad (28)$$

where the constraints on the sums in (15) imply that the indices of the adjacent M's are distinct: $n\neq m$, etc. However, nonadjacent indices may be equal; for instance, (15) contains a term of the form (28) with $n=k$.

Thus, if we use the condition

$$\langle F(z)\rangle=0 \quad (29)$$

for the self-consistency of the effective medium approximation, all terms of the form (28) with at least one index different from all the others will vanish in the averaged series (15). Indeed, let a cluster with index n appear only once in the product $\langle\Pi_m\tilde{F}_m(z)\rangle$ in (28). Then since the different clusters are completely uncorrelated, the average value factors as

$$\langle\tilde{F}_n(z)\rangle\left\langle\prod_{\substack{m\\ m\neq n}}\tilde{F}_m(z)\right\rangle$$

and vanishes by (29). Thus in the self-consistent effective medium approximation, all paths are summed in the Green's function except for exotic paths that "intersect everywhere," i.e., which pass at least twice through each center. We note that this result is also true for the random bonding problem.

We will discuss the error in the effective medium approximation in detail in Sec. 6; here we will content ourselves with a few observations. First, it is clear from the above discussion that the approximation is exact to first order in the concentration c as $c\to0$ or in $1-c$ as $c\to1$, while for intermediate c it gives a reasonably good interpolatation. Furthermore, since the approximation fully treats all trajectories containing up to three scattering centers, at least the three leading terms in the expansion of the generalized diffusion coefficient are exact for small times. For large times, it is clear that the neglected paths which intersect everywhere may contribute significantly; this will be the case, e.g., for percolation problems when the particle has a finite probability of being localized in an isolated conducting cluster. This extreme case occurs in the random bonding problem. However, since all jump probabilities to adjacent traps are identical in the random trap model, regions of preferential localization cannot form in this case. Nevertheless, the error in the effective medium approximation should also be appreciable in the extreme case of irreversible trapping.

4. CALCULATION OF THE PARTIAL GREEN'S FUNCTION

In addition to the kinetic properties, partial quantities such as the total population of traps with energies in a specified range are also of interest. We will therefore calculate the elements $P_{ji}(w_j)$ of the partial Green's function which depend on the unaveraged escape probabilities from a finite center j.

In order to do this we return to the original disordered system. All the hopping probabilities except those involving escape from center j will be replaced by an effective probability $\tilde{w}^{\mathrm{eff}}$. Let $\langle\tilde{P}_{kl}\rangle$ be an arbitrary element of the averaged Green's function connecting any two centers k, l with $k\neq j$, $l\neq j$; then $\langle P_{kl}\rangle$ is given by series (15), in which the averaging is over all the random transition probabilities w_i with $i\neq j$. If we require as before that $\tilde{w}^{\mathrm{eff}}$ be determined by the self-consistency condition (20), the only nonzero corrections will come from trajectories which pass through each center w_i ($i\neq j$) at least twice:

$$\langle\tilde{P}_{kl}\rangle=\tilde{P}_{kl}^{\mathrm{eff}}+(\tilde{P}^{\mathrm{eff}}\tilde{t}_j\tilde{P}^{\mathrm{eff}})_{kl}+O(\tilde{t}^3). \quad (30)$$

In other words, the only contributions neglected in (30) are those from the paths that self-intersect everywhere except at the single center j.

The definition of the Green's function for our model system now implies that the two elements $\tilde{P}_{ji}(w_j)$ and $\tilde{P}_{j'i}$ are related by

$$\tilde{P}_{ji}(w_j)=\frac{\tilde{w}^{\mathrm{eff}}}{\varepsilon+zw_j}\sum_{j'(j)}\tilde{P}_{j'i}. \quad (31)$$

(We recall that $\tilde{P}_{j'i}$ is the matrix element for a nearest neighbor j' of center j and is given by the effective medium approximation, so that Eq. (30) holds for $\tilde{P}_{j'i}$.) Equation (23), follows from (31) if we take $w_j=\tilde{w}^{\mathrm{eff}}$.

If we substitute (30) into (31), use the explicit form (21) for the $\tilde{t}$-matrix, and recall Eq. (23), we get the expression

$$\tilde{P}_{ji}(w_j)=\tilde{P}_{ji}^{\mathrm{eff}}\tilde{w}^{\mathrm{eff}}[w_j-\varepsilon\tilde{P}_{11}^{\mathrm{eff}}(w_j-\tilde{w}^{\mathrm{eff}})]^{-1}. \quad (32)$$

for the partial population of the j-th center. The density of the total population of the centers with a specified escape probability w is given by

$$\tilde{P}(w)=\sum_{j,i}\langle\tilde{P}_{ji}(w_j)\delta(w_j-w)\rangle P_{ii}(t=0).$$

Substituting (32) and using the normalization condition

$$\sum_j\langle\tilde{P}_{ji}\rangle=\sum_j\tilde{P}_{ji}^{\mathrm{eff}}=\varepsilon^{-1},$$

we get the final expression

$$P(w)=\frac{\rho(w)}{\varepsilon}\tilde{w}^{\mathrm{eff}}[w-\varepsilon\tilde{P}_{11}^{\mathrm{eff}}\cdot(w-\tilde{w}^{\mathrm{eff}})]^{-1} \quad (33)$$

for $P(w)$.

5. ANALYSIS OF THE KINETIC PROPERTIES AND PARTIAL POPULATIONS

We now turn to a specific calculation; for convenience, we use Eq. (27) and again rewrite the self-consistency condition (29), this time in the form

$$\left\langle\frac{w-\tilde{w}^{\mathrm{eff}}}{w-\varepsilon\tilde{P}_{11}^{\mathrm{eff}}(w-\tilde{w}^{\mathrm{eff}})}\right\rangle=0. \quad (34)$$

The equations

$$D(t)=\frac{l^2}{t}\hat{\mathscr{L}}^{-1}[\varepsilon^{-2}\tilde{w}^{\text{eff}}(\varepsilon)], \tag{35}$$

$$\sigma(\omega)=\frac{ne^2}{kT}l^2\tilde{w}^{\text{eff}}(\varepsilon)\,|_{\varepsilon=i\omega}, \tag{36}$$

relate the generalized time-dependent diffusion coefficient and the frequency-dependent electric conductivity to the effective transition probability given by (34). Here n is the carrier concentration and l is the distance between the centers (we take henceforth take $l=1$).

We first examine the case of small times t, which corresponds to $\varepsilon\to\infty$. If we substitute the expansion for P_{ii}^{eff} into (34), solve the resulting algebraic equation, and take the inverse Laplace transform, we get the expansion

$$D(t\to 0)=\langle w\rangle-z[\langle w^2\rangle-\langle w\rangle^2]t+\ldots \tag{37}$$

for the generalized diffusion coefficient $D(t)$ as $t\to 0$ for a z-connected lattice of arbitrary dimension d. The interpretation of (37) is clear—at the initial time $t=0$, the rate of particle migration is determined only by the probability of the first hop; in disordered systems, $D(t)$ then decreases with time.

We next consider large times $t\to\infty$ for the case of reversible trapping (nonzero transition probabilities). Expanding the diagonal element of the Green function of the effective medium for $\varepsilon\to 0$, we find from (34) and (35) that

$$D(t\to\infty)=\left\langle\frac{1}{w}\right\rangle^{-1}+\frac{1}{(\pi t)^{1/2}}\left\langle\frac{1}{w}\right\rangle^{-1/2}\times\left[\left\langle\frac{1}{w^2}\right\rangle\left\langle\frac{1}{w}\right\rangle^{-2}-1\right]-\ldots \tag{38}$$

for $d=1$,

$$D(t\to\infty)=\left\langle\frac{1}{w}\right\rangle^{-1}+G_2\frac{1}{t}\left[\gamma+\ln\left(\left\langle\frac{1}{w}\right\rangle^{-1}t\right)\right]\times\left[\left\langle\frac{1}{w^2}\right\rangle\left\langle\frac{1}{w}\right\rangle^{-2}-1\right]-\ldots \tag{39}$$

for $d=2$, and

$$D(t\to\infty)=\left\langle\frac{1}{w}\right\rangle^{-1}+G_3\frac{1}{t}\left[\left\langle\frac{1}{w^2}\right\rangle\left\langle\frac{1}{w}\right\rangle^{-2}-1\right]-\ldots \tag{40}$$

for $d=3$, where $\gamma\approx 0.5772$ is Euler's constant,

$$G_2=\begin{cases}(4\pi)^{-1} & \text{for a square lattice}\\ 3^{-1/2}(4\pi)^{-1} & \text{for a triangular lattice}\\ 3^{1/2}(4\pi)^{-1} & \text{for a tetragonal lattice}\end{cases} \tag{41}$$

$$G_3=\frac{\sqrt{6}}{192\pi^3}\Gamma\left(\frac{1}{24}\right)\Gamma\left(\frac{5}{24}\right)\Gamma\left(\frac{7}{24}\right)\Gamma\left(\frac{11}{24}\right)\approx 0.2527\ldots, \tag{42a}$$

$$G_3=\frac{1}{32\pi^3}\left[\Gamma\left(\frac{1}{4}\right)\right]^4\approx 0.1742\ldots, \tag{42b}$$

$$G_3=\frac{3}{(4\pi)^4 2^{8/3}}\left[\Gamma\left(\frac{1}{3}\right)\right]^6\approx 0.1121,\ldots. \tag{42c}$$

Here Eqs. (42a-c) are valid for simple cubic, bcc, and fcc lattices, respectively (cf., e.g., Ref. 6).

According to the results in Sec. 6 below, the first (and possibly also the second) terms in the expansions (38)–(40) are exact. We note that the analogy with electrical circuits in Sec. 2 yields a simple proof that the leading terms are exact. Consider, e.g., the case when $t\to\infty$. In this limit the charge in the system in Fig. 1 approaches an equilibrium distribution, the currents across the resistors R tend to zero, and the voltages across the capacitors C_i all approach the same limiting value. Since the system clearly acts as a circuit of parallel capacitors to a dc current, the total capacitance of the system is $\Sigma_i C_i$ and the effective capacitance per capacitor is given by

$$C^{\text{eff}}=\lim_{N\to\infty}\frac{1}{N}\sum_{i=1}^{N}C_i=\langle C_i\rangle.$$

The leading terms in the expansions (38)–(40) now follow if we recall the correspondence (4). The above proof also shows that the principal terms in (38)–(40) are also valid for arbitrary correlations between the spatial positions and energy levels (escape probabilities w) of the different traps.

It is noteworthy that the expression for $D(t\to\infty)$ is independent of d and z. We also note that a case of physical interest occurs for systems with deep traps such that $c\langle w_t^{-1}\rangle\gg(1-c)w_0^{-1}$—in this case, $D(t\to\infty)$ depends only on the concentration and depth of the traps and is completely independent of the properties of the medium in which the particle diffuses.

We can derive an expression for $D(t)$ valid for all t if the traps are shallow and of the same depth. Indeed, let the distribution density of the transition probabilities be of the form

$$\rho(w)=(1-c)\delta(w-w_0)+c\delta(w-w_t), \tag{43}$$

with $\Sigma=1-w_t/w_0\ll 1$. Up to terms quadratic in Σ we then find in the one-dimensional case $d=1$ that

$$\tilde{w}^{\text{eff}}=w_0\left\{1-c\Sigma+c(1-c)\Sigma^2\left[\left(1+\frac{4w_0}{\varepsilon}\right)^{-1/2}-1\right]+O(\Sigma^3)\right\}.$$

Taking inverse Laplace transforms, we then find the exact formula

$$D(t)=w_0\left\{1-c\Sigma+c(1-c)\Sigma^2\left[F\left(\frac{1}{2};2;-4w_0t\right)-1\right]+O(\Sigma^3)\right\}, \tag{44}$$

where F is the confluent hypergeometric function.

We can derive an analytic formula for $d=3$ by using the approximation

$$\tilde{P}_{ii}^{\text{eff}}=2\{\varepsilon+6\tilde{w}^{\text{eff}}+[\varepsilon(\varepsilon+12\tilde{w}^{\text{eff}})]^{1/2}\}^{-1}, \tag{45}$$

which corresponds to a semicircular state density. Proceedings as above, we find that

$$D(t)=w_0\{1-c\Sigma+c(1-c)\Sigma^2\{(3w_0t)^{-1}[1-\exp(-6w_0t)\times(I_1(6w_0t)+I_0(6w_0t))]-1\}+O(\Sigma^3)\}, \tag{46}$$

where $I_\nu(x)$ is the modified Bessel function. According to Eqs. (44) and (46), $D(t)$ decays smoothly and monotonically with time.

The frequency-dependent electric conductivity can be analyzed similarly; we will give an expression for $\sigma(\omega)$ for systems of arbitrary dimension with sparse trapping centers all of the same depth. To first order in c, we have

$$\sigma(\omega)=\frac{ne^2}{kT}w_0\left\{1+c\frac{w_t-w_0}{w_t+(w_0-w_t)\varepsilon\tilde{P}_{ii}^{\text{eff}}}\bigg|_{\varepsilon=i\omega}+\dots\right\} \tag{47}$$

for all frequencies ω. According to (47), $\sigma(\omega)$ is smooth and increases monotonically with ω as the latter increases from $w_0[1-c(w_0/w_t-1)]$ to $w_0[1-c(1-w_t/w_0)]$.

In order to consider the case when the transition probabilities vanish, we first refine our terminology. Assume that a particle has entered a trap with a zero escape probability. Then we will say that the particle has been irreversibly trapped if it remains a physically distinct entity which can be treated as before, i.e., if it gives a constant contribution to the meansquare displacement and the total normalization of the probability is correspondingly unchanged. If however the particle falls into an infinitely deep trap and disappears, we will refer to the trap as a particle sink.

We will examine irreversible trapping first by considering three classes of hopping probability distributions $\rho(w)$ which correspond to different limiting behaviors $D(t\to\infty)$ (cf. the random bonding problem in Ref. 6):

$$\text{a) } \rho(w)\to\rho(0)=\text{const} \quad \text{for} \quad w\to 0, \tag{48}$$

$$\text{b) } \rho(w)\sim w^{-\alpha},\ 0<\alpha<1 \quad \text{for} \quad w\to 0, \tag{49}$$

$$\text{c) } \rho(w)=c\delta(w)+(1-c)\rho_2(w), \tag{50}$$

where

$$\rho_2(w=0)=0, \qquad \int_0^\infty \rho_2(w)\,dw=1.$$

For the first two distributions, the infinitely deep traps are of zero measure ($c=0$), while their concentration is >0 for the distribution (50).

The self-consistency condition (34) and the expansions of the diagonal elements of the Green function of the effective medium for $\varepsilon\to 0$ (i.e., $t\to\infty$) yield the following limiting expressions:

class a)

$$D(t\to\infty)=\text{const}/\rho(0)\ln t \tag{51}$$

for systems of arbitrary dimension;

class b)

$$D(t\to\infty)=\text{const}[\alpha(1-\alpha)]^{2/(2-\alpha)}\left[\Gamma\left(\frac{4-3\alpha}{2-\alpha}\right)\right]^{-1}t^{-\alpha/(2-\alpha)} \tag{52}$$

for $d=1$ and

$$D(t\to\infty)=\text{const}\frac{\alpha(1-\alpha)}{\Gamma(2-\alpha)}t^{-\alpha} \tag{53}$$

for $d=3$; for $d=2$, logarithmic corrections must be added to (53). In Eqs. (51)–(53), const denotes a constant of order unity which depends only on the detailed form of the distribution $\rho(w)$.

For systems with a distribution of type c) D decays as 1/t for large t, which corresponds to a finite meansquare particle displacement

$$D(t\to\infty)=[(1-c^2)/4c^2]t^{-1} \tag{54}$$

and

$$D(t\to\infty)=\Omega t^{-1} \tag{55}$$

for $d=1$ and $d>1$, respectively, where Ω is defined by

$$\varepsilon\tilde{P}_{11}^{\text{eff}}(\tilde{w}^{\text{eff}}=\Omega\varepsilon)\,|_{\varepsilon\to 0}=c.$$

The higher-order terms in the expansion can be found similarly; they turn out to depend essentially on the form of $\rho_2(w)$. According to the results in Sec. 6, the error in the leading terms in the expansions (54) and (55) is of the same order in $1/t$ as $D(t\to\infty)$ itself.

An analytic expression for $\tilde{w}^{\text{eff}}$ valid for all ε can easily be derived for the special case when the distribution (50) is binary, i.e., when

$$\rho(w)=c\delta(w)+(1-c)\delta(w-W). \tag{56}$$

For $d=1$, we find

$$\tilde{w}^{\text{eff}}=W\left\{1+2c^2\frac{W}{\varepsilon}-c\left[1+4\frac{W}{\varepsilon}+4c^2\frac{W^2}{\varepsilon^2}\right]^{1/2}\right\}. \tag{57}$$

Using the approximation (45), we find similarly for a three-dimensional cubic lattice that

$$\tilde{w}^{\text{eff}}=\frac{1}{2}\varepsilon\left(3c+\frac{\varepsilon}{W}\right)^{-2}\left\{6c+\frac{\varepsilon}{W}(2-c)\right.$$
$$\left.-c^{1/2}\left[36c^2+4\frac{\varepsilon}{W}(3c-1)+\frac{\varepsilon^2}{W^2}(c+4)\right]^{1/2}\right\}. \tag{58}$$

We will need these formulas to analyze random walks of particles in systems with sinks.

We next find the partial populations for a one-dimensional system with traps of finite depth in the limit $t\to\infty$. If we use the exact expression (26) for the Green's function in Eq. (33), we get an expansion for the partial population $\tilde{P}(w)$ as $\varepsilon\to 0$ which can be inverted term-by-term to give the expansion

$$P(w)=\rho(w)\left\{\frac{1}{w}\left\langle\frac{1}{w}\right\rangle^{-1}\right.$$
$$+\frac{1}{2\sqrt{\pi t}}\left\langle\frac{1}{w}\right\rangle^{1/2}\left[\frac{1}{w}\left\langle\frac{1}{w^2}\right\rangle\left\langle\frac{1}{w}\right\rangle^{-3}\right.$$
$$\left.\left.-\frac{1}{w^2}\left\langle\frac{1}{w}\right\rangle^{-2}\right]-\dots\right\} \tag{59}$$

in the t-representation.

The first term corresponds to the Boltzmann distribution to which the system relaxes for $t\to\infty$. The second term is the kinetic correction; it is proportional to $1/\sqrt{t}$ and shows that the equilibrium populations are approached slowly, $\propto t^{-1/2}$ (Ref. 19). For $d=2$ and 3 we can use a similar procedure to find the expansions of the partial populations in ε-space:

$$\tilde{P}(w)=\rho(w)\left\{\frac{1}{\varepsilon}\frac{1}{w}\left\langle\frac{1}{w}\right\rangle^{-1}\right.$$
$$+G_2\ln\left(\frac{1}{\varepsilon}\left\langle\frac{1}{w}\right\rangle^{-1}\right)\left\langle\frac{1}{w}\right\rangle$$
$$\left.\times\left[\frac{1}{w}\left\langle\frac{1}{w^2}\right\rangle\left\langle\frac{1}{w}\right\rangle^{-3}-\frac{1}{w^2}\left\langle\frac{1}{w}\right\rangle^{-2}\right]-\dots\right\}, \tag{60}$$

$$\tilde{P}(w)=\rho(w)\left\{\frac{1}{\varepsilon}\frac{1}{w}\left\langle\frac{1}{w}\right\rangle^{-1}+G_3\left\langle\frac{1}{w}\right\rangle\left[\frac{1}{w}\left\langle\frac{1}{w^2}\right\rangle\left\langle\frac{1}{w}\right\rangle^{-3}-\frac{1}{w^2}\left\langle\frac{1}{w}\right\rangle^{-2}\right]-\ldots\right\}. \quad (61)$$

As before, the leading terms give the Boltzmann distribution in the limit $\varepsilon\to 0$; however, the kinetic corrections in this case can no longer be found by inverting (60), (61) term by term, which would require knowing the explicit form of $\tilde{P}(w)$ for arbitrary ε.

In order to derive an analytic expression we consider a three-dimensional system with shallow traps (43) of identical depths. Substitution of (45) into (33) yields the Laplace transform $\tilde{P}(w)$, which up to terms quadratic in Σ is given by

$$\tilde{P}(w)=\rho(w)\frac{w^{\text{eff}}}{w}\left\{\frac{1}{\varepsilon}+\frac{2(w-w^{\text{eff}})}{w(\varepsilon+6w_0+[\varepsilon(\varepsilon+12w_0)]^{1/2})}+O(\Sigma^2)\right\}.$$

Taking inverse Laplace transforms, we get the expression

$$P(w)=\rho(w)\frac{w^{\text{eff}}}{w}\left\{1+\left(1-\frac{w^{\text{eff}}}{w}\right)(3w_0t)^{-1}\times\exp(-6w_0t)I_1(6w_0t)+O(\Sigma^2)\right\} \quad (61)$$

for the total population of all the centers with a specified escape probability w. Expression (62) is valid for all t, and the time-independent transition probability w^{eff} is given by the first two terms in (46).

Recalling the expansion of the modified Bessel function for large arguments, we get the result

$$P(w)=\rho(w)\frac{w^{\text{eff}}}{w}\left\{1+\frac{1}{6(3\pi)^{1/2}}\left(1-\frac{w^{\text{eff}}}{w}\right)\frac{1}{(w_0t)^{3/2}}-O((w_0t)^{-5/2})\right\} \quad (63)$$

for the kinetic corrections that describe how the populations relax to equilibrium. Again, the relaxation is quite slow, $\propto t^{-3/2}$. We note that similar kinetic corrections of the form $\propto(Dt)^{-3/2}$ were found for the related many-body problem in Ref. 15, where the kinetics of diffusion-controlled reactions was studied.

Similar calculations can also be carried out for the one-dimensional case. The partial population is given by the expression

$$P(w)=\rho(w)\frac{w^{\text{eff}}}{w}\left\{1+\left(1-\frac{w^{\text{eff}}}{w}\right)\times\exp(-2w_0t)I_0(2w_0t)+O(\Sigma^2)\right\}, \quad (64)$$

which is valid for all t [the terminology is the same as in (62)]. Of course, the two leading terms in (64) coincide with the more general expression (59) as $t\to\infty$. Equation (64) is exact.

We next examine the case of particle sinks; for simplicity, we will consider the binary distribution (56). Equation (32) implies the simple relation

$$\tilde{P}(w=0)=\rho(w=0)/\varepsilon^2\tilde{P}_{11}^{\text{eff}}, \quad (65)$$

for the density function describing the total population of the centers with escape probability $w=0$ (i.e., the distribution density for the fraction of particles trapped by the sinks). Here $\tilde{P}_{11}^{\text{eff}}$ is given by Eqs. (26) and (45) for $d=1$ and 3, respectively, and $\tilde{w}^{\text{eff}}$ is given by Eqs. (57), (58).

The mean square displacement of the "surviving" particles is given by the obvious relation

$$\langle\tilde{R}^2(\varepsilon)\rangle=\sum_{j,i}\langle(1-\delta_{w_j;0})\tilde{P}_{ji}(w_j)R_{ji}^2P_{ii}(t=0)\rangle, \quad (66)$$

where R_{ji} is the distance between centers i and j. Using (32), we can recast (66) as

$$\langle\tilde{R}^2(\varepsilon)\rangle=\frac{2d}{\varepsilon^2}\tilde{w}^{\text{eff}\,2}[W-\varepsilon\tilde{P}_{11}^{\text{eff}}(W-\tilde{w}^{\text{eff}})]^{-1}, \quad (67)$$

where the terminology is the same as in (65).

Expressions (65) and (67) are quite complicated; however, numerical methods are available for calculating the inverse Laplace transforms needed to analyze the population kinetics and generalized diffusion coefficient in systems with sinks. Numerical methods can also be employed to analyze more general situations for complicated hopping distribution functions $\rho(w)$ for arbitrary ε and trap concentrations G.

6. ERROR BOUNDS FOR THE SELF-CONSISTENT EFFECTIVE MEDIUM APPROXIMATION

We now examine the accuracy of the method in greater detail by returning to the averaged series expansion for the Green's function (15). When condition (29) is used to determine the effective medium parameter, all corrections in (15) that include scattering by three or fewer clusters will vanish. If we denote the first nonvanishing terms by X and Y, we see that they are fourth-order in $\tilde{t}$ and are given by the formulas

$$X=\langle\tilde{P}^{\text{eff}}\tilde{t}_j\tilde{P}^{\text{eff}}\tilde{t}_n\tilde{P}^{\text{eff}}\tilde{t}_j\tilde{P}^{\text{eff}}\tilde{t}_n\tilde{P}^{\text{eff}}\rangle_{ji};\quad n\neq j,$$
$$Y=\langle\tilde{P}^{\text{eff}}\tilde{t}_m\tilde{P}^{\text{eff}}\tilde{t}_n\tilde{P}^{\text{eff}}\tilde{t}_m\tilde{P}^{\text{eff}}\tilde{t}_n\tilde{P}^{\text{eff}}\rangle_{ji};\quad m\neq j;\quad m\neq n.$$

If we use the explicit form (21) of the $\tilde{t}$-matrices and apply Eqs. (23), (24) to expand the products, we get

$$X=\frac{\varepsilon^3(\varepsilon\tilde{P}_{11}^{\text{eff}}-1)}{\tilde{w}^{\text{eff}\,4}}\tilde{P}_{jn}^{\text{eff}\,3}\tilde{P}_{ni}^{\text{eff}}\langle F_j^2\rangle\langle F_k^2\rangle;\quad n\neq j, \quad (68)$$

$$Y=\frac{\varepsilon^4}{\tilde{w}^{\text{eff}\,4}}\tilde{P}_{jm}^{\text{eff}}\tilde{P}_{mn}^{\text{eff}\,3}\tilde{P}_{ni}^{\text{eff}}\langle F_m^2\rangle\langle F_n^2\rangle;\quad m\neq j;\quad m\neq n. \quad (69)$$

We first analyze the leading terms in the four-center corrections (68), (69). Let $t\to 0$ and recall that we have

$$\tilde{w}^{\text{eff}}=O(1),\quad \langle F_m^2\rangle=O(1),\quad \tilde{P}_{ij}^{\text{eff}}=O(\varepsilon^{-1-|i-j|}),$$

in the limit as $\varepsilon\to\infty$. We then find that

$$X\sim\varepsilon^{-2-|n-i|-3|n-j|}\leq\varepsilon^{-5},\quad n\neq j. \quad (70)$$

The correction Y is also of order five in ε^{-1}, while the other (neglected) terms are of higher order. For $t\to 0$ (or equivalently, $\varepsilon\to\infty$), they thus contribute to the fourth term in the expansion for the averaged Green's function $\langle G\rangle$ and to the third term in the expansion for the generalized diffusion coefficient $D(t)$. This result is also valid for irreversible trapping.

We now consider the case of shallow traps for which $\rho(w)$ is nonzero only in a narrow range δw of w values, so that

$\Sigma = \delta w/w \ll 1$. We then have

$$\langle F_m{}^2\rangle \sim \Sigma^2, \quad X \sim Y \sim \Sigma^4, \tag{71}$$

for arbitrary ε, i.e., for small spreads δw in the transition probabilities, the leading corrections are fourth order in Σ.

An estimate for the largest corrections as $t \to \infty$ for the case of nonvanishing transition probabilities (finite trap depths) shows that the corrections appear to fourth order in the expansions for $D(t)$ and $\langle G\rangle$.

Finally, for class a and class b distributions, the corrections for irreversible trapping for large times ($\varepsilon \to 0$) are of the same order as the second terms in the expansions for $\langle G\rangle$, while for class-c distributions the correction is comparable to the leading term $\langle P\rangle$.

However, the above estimates for the leading corrections are suggestive only; they do not necessarily characterize the actual error, which may be larger. We can obtain a more realistic bound in the one-dimensional case by adding all of the four-center correction terms (68), (69), say. We will not give the complicated expression for this sum (which we denote by Z) but will merely state the results.

In agreement with the above analysis, the first four (respectively, first three) terms in the expansion of $\langle G\rangle$ (respectively, D) are exact for small times. If the traps are shallow, the first four terms in the expansion are accurate to $0(\Sigma^3)$ for all times t, again in agreement with the above estimate. However, for $t \to \infty$ the error is larger than predicted by the above analysis of the leading error terms. Specifically, we have $Z = O(\varepsilon^{1/2})$ for traps of finite depth for which

$$\widetilde{w}^{\text{eff}} = O(1), \quad \langle F_m{}^2\rangle = O(1), \quad \widetilde{P}_{ji}^{\text{eff}} = O(\varepsilon^{-1/2}) \quad \text{for } \varepsilon \to 0,$$

i.e., the third terms in the expansions for $\langle G\rangle$ and D are in error. If the trapping is irreversible, the sum Z of the four-center corrections has the following order of magnitude for $\varepsilon \to 0$: class a), $Z = O(\varepsilon^{-1/2})$; class b) $Z = O(\varepsilon^{-1/2(2-\alpha)})$; class c) $Z = O(\varepsilon^{-1})$. That is, in all cases the error in the principal terms in the expansions for $\langle G\rangle$ and D is comparable to the principal terms themselves.

For multidimensional systems the error in the effective medium approximation is clearly larger than for $d = 1$.

We can summarize our results as follows. The range of trap energies and transition probability spreads for which the effective medium approximation gives exact results can be depicted as a "box" (cf. Ref. 17, where the quantum coherent potential approximation was considered). In the cross section of this box shown in Fig. 3, the two (horizontal) axes correspond to the dimensionless Laplace parameter $\varepsilon' = \varepsilon/w$ and to the spread $\Sigma = (w_{\max} - w_{\min})/w_{\min}$ in the transition probabilities. The trap concentration c is plotted along the vertical axis (normal to the plane of the figure). The first three terms of the expansion of D are exact for $\varepsilon' \to \infty$ (small times) for arbitrary Σ and c; we indicate this in Fig. 3 by the upper hatched region of thickness 3Δ. The left-hand region ($\Sigma \ll 1$) corresponds to the case of shallow traps; its thickness is 4Δ. For large times, i.e., $\varepsilon' \to 0$, the two leading terms in the expansion of D may be exact (in any case, we showed rigorously in Sec. 5 that one of them is exact); thus the thickness of the bottom hatched region is either 2Δ or Δ. The right-hand edge of the box ($\Sigma \to \infty$) corresponds to irreversible trapping

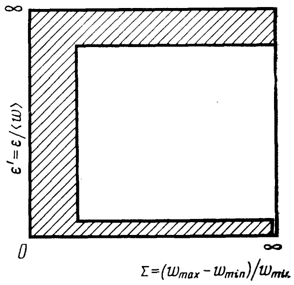

FIG. 3. Horizontal cross section of a "box" depicting the region in which the effective medium approximation gives exact results.

and is of vanishing thickness. Finally, the reader can imagine hatched "concentration" regions above and below the plane of the figure which are of thickness Δ. The effective medium approximation gives interpolated results in the interior of the box.

We can use a similar method to estimate the error in Eqs. (32), (33) for the partial populations. The first terms neglected in the sum (31) are third-order in $\tilde{t}$. Calculations using (21) yield corrections of the form

$$U = \frac{\varepsilon^3}{(\varepsilon + z w_j)\,\widetilde{w}^{\text{eff}\,2}}\, \widetilde{P}_{jk}^{\text{eff}\,3}\, \widetilde{P}_{ki}^{\text{eff}} \langle F_k{}^2\rangle F_j \big|_{w_j = w}$$

to the expression for $\tilde{P}_{ji}(w_j)$.

An analysis similar to the one above shows that for $\varepsilon \to \infty$ (small times t) the four leading terms in the expansion of $\tilde{P}_{ji}(w_j)$ are accurate to $\sim \varepsilon^{-5}$; for a system with shallow traps, the three leading terms are accurate to $\sim \Sigma^2$ for arbitrary ε; for $\varepsilon \to 0$ ($t \to \infty$), at least one (and possibly two) of the leading terms is exact. For irreversible trapping, the partial Green function G_{part} always contains an error of the same order in ε as G_{part} itself. The region in which the formulas for the partial quantities are accurate can again be depicted by suitably modifying the box in Fig. 3.

[1)]In the time representation, the effective system is described by an equation with "memory":

$$\frac{dP}{dt} = \int_0^t W^{\text{eff}}(t-\tau) P(\tau)\, d\tau.$$

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