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Long-range hopping in substitutionally disordered solids

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A theoretical approach for studying charge-carrier and energy diffusion due to long-range hopping in substitutionally disordered solids is presented. Unlike some earlier theories, which invoke a pair approximation to treat back-transfer processes, the current theory makes use of the exact solution to an appropriate single-defect problem—one in which long-range jumps into, out of, and between both the defect site and all other active sites in the lattice are explicitly included. From this exact solution a new long-range effective-medium theory is constructed to describe the configurationally averaged transport properties of the disordered system.

I. INTRODUCTION

The purpose of this paper is to discuss a new and conceptually simple approach to the problem of long-range, diffusive transport in substitutionally disordered condensed phases. It is intended to apply to those circumstances where the transport process takes place as a result of variable-range hopping among a set of active sites distributed randomly in some fixed concentration over a regular lattice. This is not a new subject. Indeed, both this problem and a related one, wherein the active sites are distributed randomly in a continuum, have been the subject of considerable interest.[1–36] Consequently, a diverse array of theoretical approaches have been advanced which make use of most of the normal elements of standard transport theory: master equations, diagramatic expansions, continuous-time random walks, coherent-potential-approximations, Padé approximants, effective-medium theories, cumulant expansions, etc. Existing approaches have met with reasonable success in some parameter regimes, notably the short-time low-concentration limit.[7,8,12,14] Nonetheless, the complicated nature of many of the existing approaches, the essential similarity of many of the approximations involved, and the relative dearth of exact results for the long-range problem all suggest that there may still be room for alternative approaches, particularly when they can provide insight into situations where earlier theories have proven inadequate or inappropriate.

The treatment presented here is very similar in spirit to the kind of self-consistent approaches that have been used to study transport in systems with finite (e.g., nearest-neighbor) interactions.[27–31] Such treatments, often referred to as "effective-medium" or "coherent-potential" theories are based upon the idea of finding a translationally invariant effective medium, one for which the perturbation due to embedded "defects" self-consistently vanishes when averaged over a probability distribution associated with the defect configuration. The success of such approaches for short-ranged systems arises from the fact that it is a relatively simple exercise to solve (exactly) the problem of a short-range defect embedded in a short-range effective medium.[36] When all active sites in the lattice are connected by long-ranged transistion rates, then both the averaged effective medium and the defect which one wants to embed become long range as well. As a result, the single-defect problem becomes considerably more complicated, and the construction of a useful effective medium less straightforward. Additional approximation procedures usually become necessary, and it is these which have basically distinguished the different effective-medium theories that have been implemented thus far.[1,2,12,13]

The most notable shortcoming associated with existing treatments of the long-range problem is the way in which back transfer to an initially occupied site is treated. As observed earlier,[8] some sort of pair approximation is usually invoked: Back transfer to and from one other active site in the lattice is first treated more or less exactly, and then the relative position of the two sites is subsequently averaged over. Transfer between other sites in the medium are either neglected or treated in a similar low-order approximation. While this procedure leads to a reasonable description at short times and low concentrations, it becomes increasingly problematic at long times when back-transfer processes dominate the diffusion.

It is precisely the manner in which back transfer is treated that the current approach differs from earlier treatments. In particular, the present theory has as its foundation an exact solution to a particular single-defect problem[37] in which long-range jumps between all other active sites in the effective medium are treated exactly. As a result, new expressions are obtained for the frequency-dependent diffusion constant, the memory kernels that describe transport in the disordered medium, and other characteristic features of the transport process. These expressions recover the essential features of earlier theories over comparable parameter regimes and, due to the more detailed treatment of back transfer used in the present approach, offer the possibility of providing increased accuracy in the long-time, high-concentration limit as well.

The paper is laid out as follows. In Sec. II we introduce the basic master equation describing long-range diffusive transport in a disordered solid. The average solutions to this equation are then discussed, and a for-

mal equation is introduced for the purpose of analyzing the behavior of a single active site embedded in a partially averaged effective medium. This equation is solved exactly and used to obtain a self-consistent condition obeyed by quantities chosen to characterize the effective medium. In Sec. III the self-consistent condition is analyzed in detail and related to expressions and approximate procedures that have, in appropriate limits, been implemented in previous theories. In Sec. IV expressions for the frequency-dependent diffusion coefficient arising from the theory are analyzed in detail for several important physical cases. The theory is then explicitly implemented in a study of the zero-frequency diffusion constant for systems in which the hopping rate falls off exponentially with distance. In the limit in which the hopping rates fall off over distances which are very small compared to a lattice spacing, the functional dependence of the diffusion constant on the concentration of active sites is shown to approach a limiting curve resembling that associated with nearest-neighbor site percolation. The last section contains a summary.

II. FORMUALTION OF THE EFFECTIVE MEDIUM

The dynamical behavior of a particle executing random hops among the fractionally occupied active sites of a d-dimensional hypercubic lattice can be described by the master equation

$$\frac{dp_{\mathbf{n}}}{dt}=\sum_{\mathbf{m}} W_{\mathbf{nm}}p_{\mathbf{m}}(t)-W_{\mathbf{mn}}p_{\mathbf{n}}(t) \tag{1}$$

for the probability $p_{\mathbf{n}}(t)$ of finding the transport particle at the $\mathbf{n}$th site of the lattice at time t. Here $\mathbf{n}=(n_1,n_2,\ldots,n_d)$ is a lattice vector, and $W_{\mathbf{nm}}$ is the jump rate from the $\mathbf{m}$th to the $\mathbf{n}$th site. We assume that $W_{\mathbf{nm}}$ can be factored into three parts

$$W_{\mathbf{nm}}=c_{\mathbf{n}}b_{\mathbf{m}}w_{\mathbf{n}-\mathbf{m}} \ . \tag{2}$$

The first two depend only on the sites to and from which the particle hops, respectively, and the third part is a function only of the displacement of the jump. In most treatments this displacement-dependent factor $w_{\mathbf{n}}=w(\mathbf{n})$ is taken to be either of exponential,[38] $w_{\mathbf{n}-\mathbf{m}}\sim\exp(-\mu|\mathbf{m}-\mathbf{n}|)$ or of multipolar[39] $w_{\mathbf{n}-\mathbf{m}}\sim|\mathbf{n}-\mathbf{m}|^{-s}$ form but is, at any rate, assumed to fall off with sufficient rapidity at large separations so that its second "moment" $\zeta=\sum_{\mathbf{n}}\mathbf{n}^2w_{\mathbf{n}}$ exists. For convenience we assume that the $w_{\mathbf{n}}$ are normalized to unity so that $\sum_{\mathbf{n}}w_{\mathbf{n}}=1$. We also define $w_0=0$. The site-dependent parts $c_{\mathbf{n}}$ and $b_{\mathbf{m}}$ are random variables that are zero if the relevant site is inactive. Inactive sites occur with probability $q=1-p$. Active sites occur in fractional concentration p, and for these sites $c_{\mathbf{n}}$ and $b_{\mathbf{m}}$ can be drawn from distributions $\sigma(c)$ and $\sigma(b)$ that reflect the difficulty of leaving or entering a given active site.

To proceed, we consider the configurationally averaged system described by the averaged probabilities $P_{\mathbf{n}}(t)=\langle p_{\mathbf{n}}(t)\rangle$, in which angular brackets are used to denote averages over the ensemble of allowed configurations. As demonstrated explicitly by Klafter and Silbey,[6] the linearity of Eq. (1) ensures that the ensemble-averted probabilities obey a translationally invariant generalized master equation[6,34,35] (GME) of the form

$$\frac{dP_{\mathbf{n}}}{dt}=\int_0^t dt'\sum_{\mathbf{m}}[M_{\mathbf{n}-\mathbf{m}}(t-t')P_{\mathbf{m}}(t') -M_{\mathbf{m}-\mathbf{n}}(t-t')P_{\mathbf{n}}(t')] \ . \tag{3}$$

It is to be emphasized that the memory functions $M_{\mathbf{n}}(t)$ appearing in Eq. (3) completely determine the nature of transport in the configurationally averaged system. Indeed, along with the averaged Green's functions $G_{\mathbf{n}}(t)$ they serve to *define* the effective-medium that we seek. The Green's functions or propagators $G_{\mathbf{n}}(t)$ are the solutions to Eq. (3) corresponding to localized initial conditions. Specifically, the quantity $G_{\mathbf{n},\mathbf{m}}(t)=G_{\mathbf{n}-\mathbf{m}}(t)$ is the averaged probability of finding the particle at site $\mathbf{n}$ at time t if it was initially at site $\mathbf{m}$ at $t=0$. Introducing Laplace transforms over time with Laplace ("frequency") variable ε, and denoting the Laplace transform of $G_{\mathbf{n}}(t)$ by $g_{\mathbf{n}}(\varepsilon)$, we obtain from Eq. (3) the following equations obeyed by the Green's functions:

$$\varepsilon g_{\mathbf{n}}(\varepsilon)-\delta_{\mathbf{n},0}=-\Gamma(\varepsilon)g_{\mathbf{n}}(\varepsilon) +\sum_{\mathbf{m}}M_{\mathbf{n}-\mathbf{m}}(\varepsilon)g_{\mathbf{m}}(\varepsilon) \ . \tag{4}$$

In Eq. (4), $M_{\mathbf{n}}(\varepsilon)$ is the Laplace transform of $M_{\mathbf{n}}(t)$, and the quantity $\Gamma(\varepsilon)\equiv\sum_{\mathbf{m}}M_{\mathbf{m}}(\varepsilon)$ is the frequency-dependent "exit rate" out of active sites in the effective medium.

To calculate the memory functions we now proceed essentially as in effective-medium solutions to the short-range problem.[27–31] That is, we first imagine "embedding" some particular active site in the effective medium described by Eqs. (3) and (4). Translational invariance of the effective medium allows us to take the position of this active site to be the origin. We therefore seek equations which govern the evolution of the partially averaged system in the presence of this particular active site. We observe that for any particular realization of the disordered medium, a transport particle at a given active site is sensitive to its environment only through the total rate at which it can leave that particular site. In other words, one can characterize any active site in the real disordered system by the total rate with which hops away from that site occur. For some particular active site at the origin this exit rate, which we will denote by γ, can be written as the sum of the rates for hopping to all the other active sites in its environment, i.e.,

$$\gamma=\sum_{\mathbf{n}}W_{\mathbf{n},0}=\sum_{\mathbf{n}}c_0b_{\mathbf{n}}w_{\mathbf{n}} \ . \tag{5}$$

It is the quantity γ, therefore, which we seek to preserve in our equations of motion. Thus, introducing Lapace-transformed probabilities $P_{\mathbf{n}}(\varepsilon)$, we introduce the following equation describing the evolution of the active site plus effective medium:

$$\varepsilon P_n(\varepsilon)-P_n(0)=-\Gamma(\varepsilon)P_n(\varepsilon)+\sum_m M_{n-m}(\varepsilon)P_m(\varepsilon) +\Gamma(\varepsilon)\Delta(\varepsilon)P_0(\varepsilon)\delta_{n,0} -\Delta(\varepsilon)M_n(\varepsilon)P_0(\varepsilon) , \quad (6)$$

where

$$\Delta(\varepsilon)=[\Gamma(\varepsilon)-\gamma]/\Gamma(\varepsilon) . \quad (7)$$

Except for the last two terms, Eq. (6) is simply the Laplace transform of the GME appearing in Eq. (3). The last two terms in Eq. (6) arise from the fact that we have specified the origin as an active site from which particles jump with exit rate γ (and not Γ) to all other sites in the effective medium. The second-to-last term describes the way in which probability transfer away from the origin changes and arises only when $\mathbf{n}=\mathbf{0}$. The last term describes the way in which probability transfer from the origin to the $\mathbf{n}$th site changes due to the fact that the total rate from the origin occurs with rate γ. It should be noted that the particular balance we have chosen between forward and backward jumps, while not a unique choice, is largely determined by the requirement to conserve the total probability of finding the particle somewhere in the system. At any rate, these last two terms modify the jump rate from the origin to every other site, making the origin a local defect in the otherwise translationally invariant effective lattice.

Equation (6) is intended to represent the set of equations obeyed by a partially averaged effective medium containing an active site with exit rate γ. As such, it *defines* the single-defect problem which we wish to use in constructing an effective-medium theory. That is, a final average (over γ) of the solutions to Eq. (6) should be expected to self-consistently reproduce the actual solutions for the effective medium. Of course, as in short-range theories, in order to carry this program through we need to solve the coupled set of equations represented by Eq. (6) in terms of the formal solutions to the effective medium. Fortunately, as shown by Kenkre and Wong[37] in a different context, this can be done exactly by using a variation of a technique due to Montroll.[36(a)] The first step is to formally represent the solution to Eq. (6) in terms of the Green's functions for the effective medium. This leads to the Dyson equations[36]

$$P_n(\varepsilon)=g_n(\varepsilon)-\sum_{m,s} g_{n-m}(\varepsilon)V_{m,s}(\varepsilon)P_s(\varepsilon) \quad (8)$$

in which we have assumed that the particle is placed initially at the active site at the origin, so that $P_n(0)=\delta_{n,0}$. The relevant perturbation terms can be identified from the last two terms on the right-hand side of Eq. (6).

$$V_{m,s}(\varepsilon)=\delta_{s,0}\Delta(\varepsilon)[\Gamma(\varepsilon)\delta_{m,0}-M_m(\varepsilon)] . \quad (9)$$

Substitution of Eq. (9) into Eq. (8) yields a more explicit relation

$$P_n(\varepsilon)=g_n(\varepsilon)+g_n(\varepsilon)\Delta(\varepsilon)\Gamma(\varepsilon)P_0(\varepsilon) -\sum_m \Delta(\varepsilon)g_{n-m}(\varepsilon)M_m(\varepsilon)P_0(\varepsilon) . \quad (10)$$

Equation (10) is an exact consequence of Eq. (6). Now using the GME [Eq. (4)] obeyed by the Green's functions, the sum appearing in Eq. (10) can be written

$$\sum_m g_{n-m}M_m=[(\varepsilon+\Gamma)g_n-\delta_{n,0}] . \quad (11)$$

By writing equation Eq. (10) for the case $\mathbf{n}=\mathbf{0}$, and using the corresponding result from Eq. (11), a closed equation for P_0 results, namely,

$$P_0=g_0+g_0(\Gamma-\gamma)P_0 -[(\Gamma-\gamma)/\Gamma][(\varepsilon+\Gamma)g_0-1]P_0 . \quad (12)$$

This is readily solved to give [37]

$$P_0=\frac{g_0\Gamma}{\gamma+(\Gamma-\gamma)\varepsilon g_0} . \quad (13)$$

Equation (13) can be substituted back into, e.g., Eq. (10) to obtain the remaining probabilities. It is worth emphasizing again that Eq. (13) is the exact solution to the problem of a long-range defect embedded in a long-range system, and includes back transfer processes between all sites. The random variable in the solution is γ, which is governed by a distribution $\rho(\gamma)$ that depends upon the entire set of random variables $\{c_0,b_m\}$ [see Eq. (2)]. Self-consistency is now achieved by requiring that the average of P_0 over the distribution $\rho(\gamma)$ coincide with the dynamical solution of the effective medium for the same initial conditions, i.e., we set

$$\langle P_0\rangle=g_0 . \quad (14)$$

The resulting effective medium is then characterized by Eq. (3), in which the detailed structure of the memory functions have yet to be examined, and the quantity $\Gamma(\varepsilon)$ is determined upon applying the self-consistency condition to Eq. (13). That is, the self-consistent value of $\Gamma(\varepsilon)$ is the one which satisfies the equation

$$\left\langle \frac{\Gamma(\varepsilon)-\gamma}{\gamma+[\Gamma(\varepsilon)-\gamma]\varepsilon g_0(\varepsilon)} \right\rangle=0 . \quad (15)$$

[From this point onward, angular brackets will denote averages over the exit rate distribution function $\rho(\gamma)$.] To close Eq. (15) we can combine it with the usual spectral representation for the self-propagator g_0 as an integral over the Brillouin zone of the reciprocal lattice, i.e.,

$$g_0(\varepsilon)=(2\pi)^{-d}\int d\mathbf{k}\, g^{\mathbf{k}}(\varepsilon) =(2\pi)^{-d}\int d\mathbf{k}[\varepsilon+\Gamma(\varepsilon)-M^{\mathbf{k}}(\varepsilon)]^{-1} \quad (16)$$

in which $M^{\mathbf{k}}$ and $g^{\mathbf{k}}$ denote the discrete Fourier transforms of M_n and g_n, respectively. For example,

$$M^{\mathbf{k}}(\varepsilon)=\sum_n M_n(\varepsilon)\exp(-i\mathbf{k}\cdot\mathbf{n}) . \quad (17)$$

III. SOLUTIONS TO THE SELF-CONSISTENT CONDITION

A. The frequency-dependent exit rate Γ

Equation (15) has a very simple form similar to the self-consistent condition obtained in the short-range problem.[27–31] This simplicity does not come without a price. In particular, much of the complex structure of the theory is hidden in the fact that the multisite distribution function $\rho(\gamma)$ over which averages must be performed is considerably more complex than the single-site distribution functions which appear in other theories. By definition, the quantity $\rho(\gamma)d\gamma$ represents the probability for the total hopping rate out of a randomly chosen active site to lie between γ and $\gamma+d\gamma$. Naturally, this total rate depends upon the positions of all the other active sites in the disordered medium as well as on the distributions $\sigma(c)$ and $\sigma(b)$. For convenience in what follows, we will focus on the situation where the functions c_n and b_n reflect no energetic site disorder aside from the random occupation of the lattice sites. Specifically, we will assume that the variables b_n are dimensionless and have density $\sigma(b)=p\delta(b-1)+(1-p)\delta(b)$, and that the variables c_n (which have units of frequency) are distributed according to the density $\sigma(c)=p\delta(c-\Lambda)+(1-p)\delta(c)$, where Λ represents the exit rate for leaving a site in the pure crystal ($p=1$). For the active site at the origin we take $c_0=\Lambda$, so that $\gamma=\sum_n \Lambda b_n w_n$.

With this simplification, the first point worth noting is that $\psi(\tau)$, the Laplace transform of the distribution function $\rho(\gamma)$, is a well-known quantity in the literature associated with dispersive transport.[3–6,8] Letting τ denote the Laplace variable conjugate to γ, we have

$$\psi(\tau)=\int_0^\infty e^{-\gamma\tau}\rho(\gamma)d\gamma=\langle e^{-\gamma\tau}\rangle \ . \tag{18}$$

Thus, $\psi(\tau)$ gives the configurationally averaged probability that a particle has not left by time τ the active site on which it was placed at $\tau=0$. Since

$$\gamma=\sum_n \Lambda b_n w_n=\sum_n W_n$$

is the sum of N independently distributed random variables (N being the number of sites in the lattice), the distribution $\rho(\gamma)$ will be the N-fold convolution of the corresponding single-variable distribution functions, and the Laplace transform of $\rho(\gamma)$ will be the product of their Laplace transforms. Thus,

$$\psi(\tau)=\prod_n[(1-p)+p\exp(-\omega_n\tau)] \ , \tag{19}$$

in which we have introduced the pure-crystal jump rates

$$\omega_n=\Lambda w_n \ . \tag{20}$$

The factors in the product appearing in Eq. (19) are just the Laplace transforms of the distributions

$$\rho(W_n)=p\delta(W_n-\omega_n)+(1-p)\delta(W_n)$$

which follow from the distributions for the b_n. Equation (19) has been obtained by other means previously.[3–6] It is worth noting that the function $\psi(\tau)$ or its Laplace transform appear at some point in most treatments of the long-range transport problem. Often, however, it appears as an approximation[8] to the diagonal element of the Green's function g_0 (see, e.g., the discussion in Sec. IV B). While this is an adequate approximation at short times (before any back transfer occurs) it becomes progressively worse at long times when the effects of back transfer dominate the decay of g_0. In fact, as we shall now show, the self-consistency condition (15) implies a more fundamental relationship between $G_0(t)$ and $\psi(t)$, one which is most easily expressed in terms of the Laplace transforms $g_0(\varepsilon)$ and $\Psi(\varepsilon)$. To see this we first reexpress Eq. (15) as

$$\langle(\Gamma-\gamma)/(\Gamma+\alpha\gamma)\rangle=0 \ , \tag{21}$$

where we have introduced the quantity $\alpha=(1-\varepsilon g_0)/(\varepsilon g_0)$. We now rewrite the left-hand side of Eq. (21) using the integral identity

$$(\Gamma-\gamma)/(\Gamma+\alpha\gamma)=\int_0^\infty d\tau(\Gamma-\gamma)\exp[-(\Gamma+\alpha\gamma)\tau] \ . \tag{22}$$

With Eq. (22) substituted into Eq. (21) the averages can be expressed in terms of the function $\psi(\tau)$ defined in Eq. (18). The self-consistent condition then takes the form

$$\int_0^\infty \exp(-\Gamma\tau)\{\Gamma\psi(\alpha\tau)+d[\psi(\alpha\tau)]/d(\alpha\tau)\}d\tau=0 \ . \tag{23}$$

Equation (23) is now in the form of a Laplace transform. By using the usual theorems regarding the Laplace transform of a derivative it reduces (after some slight manipulation) to a much simpler expression, namely,

$$u\Psi(u)=\varepsilon g_0(\varepsilon) \ , \tag{24}$$

where

$$u=\Gamma(\varepsilon)/\alpha(\varepsilon) \ . \tag{25}$$

In Eq. (24) the function $\Psi(\varepsilon)$ is the Laplace transform of $\psi(\tau)$. Equation (24) is completely equivalent to the self-consistent condition (15). Nonetheless, expressed in this way it seems somewhat surprising since it appears to equate the decay of probability *without* back transfer (as represented by Ψ) to the corresponding decay *with* back transfer (as represented by g_0). However, because of the argument u on the left-hand side, Eq. (24) has a simple (and quite reasonable) physical interpretation. To see this, we rewrite $\Psi(\varepsilon)$ as

$$\Psi(\varepsilon)=[\varepsilon+\Sigma(\varepsilon)]^{-1} \ , \tag{26}$$

where $\Sigma(\varepsilon)$ is the Laplace transform of a kernel which describes irreversible decay from an initially occupied active site. We can write a similar expression for $g_0(\varepsilon)$, namely,

$$g_0(\varepsilon)=[\varepsilon+\Gamma(\varepsilon)-\Gamma_B(\varepsilon)]^{-1} \ , \tag{27}$$

where $\Gamma(\varepsilon)$ and $\Gamma_B(\varepsilon)$ correspond to the gain and loss terms in the GME. Equation (27) is exact provided we identify

$$\Gamma_B(\varepsilon)=\sum_n M_n(\varepsilon)g_n(\varepsilon)/g_0(\varepsilon) \ . \tag{28}$$

With these we can reexpress the variable u appearing in Eq. (24) in the form

$$u=\Gamma/\alpha=\Gamma\varepsilon/(\Gamma-\Gamma_B) . \tag{29}$$

In Eq. (29) we have used the definition of

$$\alpha=[1-\varepsilon g_0(\varepsilon)]/\varepsilon g_0(\varepsilon)$$

along with Eq. (27). Replacing ε with u [as given by Eq. (29)] in Eq. (26) and substituting the result into the self-consistent relation expressed by Eq. (24) we obtain a simple expression relating Σ and Γ, namely,

$$\Gamma(\varepsilon)=\Sigma(u) . \tag{30}$$

One intuitively expects the kernels describing transfer away from an initially occupied site with and without back transfer to be closely related. Equation (30) suggests that they are essentially identical except for a (self-consistent) scaling of the arguments. Of course, for large ε (corresponding to very short times before back transfer is important), Γ_B can be neglected. In this limit Eq. (29) shows that u is essentially equal to ε. Moreover in the opposite limit in which ε goes to zero, α diverges, and so u goes to zero linearly in ε as well. Thus, u and ε behave very similarly, suggesting that at least for the purposes of calculating $\Gamma(\varepsilon)$, we can, to reasonable approximation, replace u and ε in the argument of Σ. This gives $\Gamma(\varepsilon)\simeq\Sigma(\varepsilon)$, which allows Eq. (26) to be written

$$\Psi(\varepsilon)\simeq[\varepsilon+\Gamma(\varepsilon)]^{-1} . \tag{31}$$

Thus, this simple approximation to the self-consistent condition expressed by Eqs. (15) and (24) is equivalent to insisting that the kernel describing loss of excitation from an active site be given by a single function, independent of the form of the back-transfer kernel Γ_B. This approximate form also allows us to obtain from Eq. (31) an explicit (but approximate) expression for $\Gamma(\varepsilon)$, namely,

$$\Gamma(\varepsilon)\simeq\Sigma(\varepsilon)=[1-\varepsilon\Psi(\varepsilon)]/\Psi(\varepsilon) . \tag{32}$$

Equation (32) may be used with the exact expression for $\psi(t)$ given in Eq. (19) to investigate the frequency-dependent jumping rate $\Gamma(\varepsilon)$. The error in this approximation will be most noticeable for small but nonzero ε, where it can be shown that $u/\varepsilon\to\Gamma g_0(0)$, instead of approaching unity. Nonetheless, it is also possible to show that the full self-consistent condition and the approximate one embodied by Eq. (32) lead to the same zero-frequency limit for dynamical quantities such as the diffusion constant. Thus both the very-short and very-long-time limits of the self-consistent theory are correctly treated by this approximation.

B. The memory kernels M_n

We now use the expressions for $\Gamma(\varepsilon)$ developed in the last section to obtain useful expressions for the memory kernels. We start by using Eq. (26) [which defines $\Sigma(\varepsilon)$] at argument u, along with Eq. (30) (which is just another expression of the self-consistent condition) to obtain

$$u\Psi(u)-1=-\Gamma(\varepsilon)\Psi(u) . \tag{33}$$

The left-hand side of (33) is the Laplace transform of the time derivative of $\psi(t)$. Using Eq. (19) we find

$$\frac{d\psi}{dt}=-\sum_n\frac{p\omega_n\exp(-\omega_n t)\psi(t)}{[q+p\exp(-\omega_n t)]} . \tag{34}$$

Multiplying Eq. (34) by $\exp(-ut)$ and integrating, we obtain

$$u\Psi(u)-1=-\sum_n\omega_n\phi_n(u) , \tag{35}$$

where

$$\phi_n(u)=\int_0^\infty dt\frac{p\exp[-(u+\omega_n)t]\psi(t)}{q+p\exp(-\omega_n t)} . \tag{36}$$

Upon comparison of Eq. (35) and Eq. (33) we obtain the following expression for $\Gamma(\varepsilon)$:

$$\Gamma(\varepsilon)=\sum_n M_n(\varepsilon)=\sum_n\omega_n\phi_n(u)/\Psi(u) . \tag{37}$$

A sum over lattice sites is contained in the right-hand side of both equalities in Eq. (37). Equating corresponding terms in each sum we obtain the desired result for the memory functions

$$M_n(\varepsilon)=\omega_n\phi_n(u)/\Psi(u) . \tag{38}$$

In addition, the functions $\phi_n(u)$ can be expressed explicitly in terms of the concentration and the Laplace transform of $\psi(t)$. Expanding the denominator of Eq. (36) in a geometric series and performing the integration we obtain

$$\phi_n(u)=-\sum_{j=1}^{\infty}(-p/q)^j\Psi(u+j\omega_n) , \tag{39}$$

so that

$$M_n(\varepsilon)=-\sum_{j=1}^{\infty}(-p/q)^j\Psi(u+j\omega_n)\omega_n/\Psi(u) , \tag{40}$$

which is a functional of $\Psi(\varepsilon)$ over an extended range of its argument. We should point out that Eqs. (38)–(40) completely close the self-consistent equations we have derived and provide an implicit iterative scheme for determining the dynamical properties of the effective medium. For example, since $\Psi(\varepsilon)$ is known exactly through a Laplace transformation of Eq. (19), one can use it with the initial guess $u=\varepsilon$ in Eqs. (38)–(40) to calculate an initial approximation to the memory functions, which may be then used to determine $g_0(\varepsilon)$ and $\Gamma(\varepsilon)$. These can be used to evaluate a new approximation to u from Eq. (24), and the whole process repeated until it converges. In the present paper we do not explicitly follow this procedure except in the limit $\varepsilon=u=0$, for which no iteration is necessary. In addition, we derive in the next section some analytical results which follow from the theory in important limits.

IV. DIFFUSION IN THE EFFECTIVE MEDIUM

Transport in a disordered medium can be characterized by the behavior of the average mean-squared dis-

placement

$$\langle r^2(t)\rangle=\sum_{\mathbf{n}}\mathbf{n}^2P_{\mathbf{n}}(t)$$

of the transport particle as a function of time (note that all distances are measured in units of the lattice constant). Equivalently, one can focus on the time- or frequency-dependent diffusion coefficients,

$$D(t)=(2d)^{-1}\frac{d}{dt}\langle r^2\rangle \tag{41}$$

and

$$D(\varepsilon)=\int_0^\infty dt\,\varepsilon e^{-\varepsilon t}D(t)\ , \tag{42}$$

respectively. These latter quantities are defined so that if transport is ultimately diffusive, i.e., if asymptotically the mean-square displacement grows linearly with time, then the linear growth will be characterized either by the infinite-time limit of $D(t)$ or the zero-frequency limit of $D(\varepsilon)$.

We now obtain expressions for these quantities from the theory developed in Secs. II and III. We first observe that in the translationally invariant effective medium the diffusion coefficients are readily obtained in terms of the memory functions. For a particle initially localized at the origin

$$\langle r^2(t)\rangle=\sum_{\mathbf{n}}\mathbf{n}^2G_{\mathbf{n}}(t)=-\{\nabla_{\mathbf{k}}^2G^{\mathbf{k}}\}_{\mathbf{k}=0}\ , \tag{43}$$

where $\nabla_{\mathbf{k}}^2$ denotes the Laplacian operator in reciprocal space and $G^{\mathbf{k}}(t)$ is implicitly defined in terms of its Laplace transform in Eq. (16). A straightforward calculation based upon Eqs. (41)–(43) and Eqs. (16) and (17) shows that

$$D(\varepsilon)=(2d)^{-1}\sum_{\mathbf{n}}\mathbf{n}^2M_{\mathbf{n}}(\varepsilon)\ . \tag{44}$$

Thus, from Eqs. (38) and (44) we obtain

$$D(\varepsilon)=(2d)^{-1}\sum_{\mathbf{n}}\mathbf{n}^2\omega_{\mathbf{n}}\phi_{\mathbf{n}}(u)/\Psi(u)\ . \tag{45}$$

Along with Eq. (36), this provides a direct relationship between the diffusion constant $D(\varepsilon)$ and the function $\Psi(\varepsilon)$. We now consider various limiting cases.

A. Short-time limit

To examine the dynamical behavior at very short times we can expand $\Psi(u)$ for large ε. As we mentioned earlier, when ε is large, the quantity u is very nearly equal to ε and in this limit Eq. (19) gives

$$\Psi(\varepsilon)=\varepsilon^{-1}-\langle\gamma\rangle\varepsilon^{-2}+\langle\gamma^2\rangle\varepsilon^{-3}+O(\varepsilon^{-4})\ . \tag{46}$$

Substituting this result into Eq. (39) and (40) and retaining terms to order ε^{-1} we obtain

$$M_{\mathbf{n}}(\varepsilon)=-\sum_{j=1}^{\infty}(-p/q)^j\omega_{\mathbf{n}}[1-(j\omega_{\mathbf{n}}+\langle\gamma\rangle)\varepsilon^{-1}]\times(1+\langle\gamma\rangle\varepsilon^{-1})$$

which can be summed exactly to give

$$M_{\mathbf{n}}(\varepsilon)=p\omega_{\mathbf{n}}[1-(1-p)\omega_{\mathbf{n}}\varepsilon^{-1}]\ . \tag{47}$$

This gives for the different coefficient

$$D(\varepsilon)=(2d)^{-1}[p\Lambda\zeta+p(1-p)\Lambda^2\zeta_2\varepsilon^{-1}]+O(1/\varepsilon^2)$$
$$=pD_0(1-q\Lambda\zeta_2/\zeta\varepsilon) \tag{48}$$

in which

$$\zeta=\sum_{\mathbf{n}}\mathbf{n}^2w_{\mathbf{n}},\quad \zeta_2=\sum_{\mathbf{n}}\mathbf{n}^2w_{\mathbf{n}}^2,\quad \text{and } D_0=(2d)^{-1}\Lambda\zeta$$

is the pure-crystal diffusion constant. We see that the very-short-time limit is characterized by a diffusion constant which is reduced from the pure-crystal value by a factor corresponding to the concentration of active sites. Note that the validity of this result is not limited to small concentrations, since we have summed all powers of p to obtain Eq. (47). Indeed, in Eq. (48) the frequency dependence of $D(\varepsilon)$ vanishes in the pure-crystal limit ($p=1$), to give the exact pure-crystal result, valid for all times.

B. Low concentrations

Equation (48) is expected to hold out to times on the order of $1/p\Lambda$. For times longer than this, but still small compared to the asymptotic limit, additional approximations become necessary. In particular, it is convenient to consider low concentrations at short to intermediate times. It has been observed in earlier work that the low-concentration and short-time limits are in a certain sense complementary.[8,12,14] Using the first term of Eq. (39) in Eq. (45) we find for $p\ll 1$

$$D(\varepsilon)=(p/2d)\sum_{\mathbf{n}}\mathbf{n}^2\omega_{\mathbf{n}}[\Psi(u+\omega_{\mathbf{n}})/\Psi(u)]\ . \tag{49}$$

As in much of the earlier work, it is now convenient to use the assumed low concentration of active sites to replace the lattice sum in Eq. (49) with an integral over a dimensionless position variable $\mathbf{r}$. In this continuum approximation,[8] Eq. (49) becomes

$$D(\varepsilon)=(p/2d)\int d\mathbf{r}\ \mathbf{r}^2\omega_{\mathbf{r}}\Psi(u+\omega_{\mathbf{r}})/\Psi(u)\ . \tag{50}$$

Using Eq. (26), we can now rewrite the factor involving the function Ψ in the form

$$\Psi(u+\omega_{\mathbf{r}})/\Psi(u)=\frac{u+\Sigma(u)}{u+\omega_{\mathbf{r}}+\Sigma(u+\omega_{\mathbf{r}})}\ , \tag{51}$$

or equivalently

$$\Psi(u+\omega_{\mathbf{r}})/\Psi(u)=\frac{1}{\lambda+\omega_{\mathbf{r}}\Psi(u)}\ , \tag{52}$$

in which

$$\lambda=[u+\Sigma(u+\omega_{\mathbf{r}})]/[u+\Sigma(u)]\ .$$

Insofar as we are interested in short times, and therefore large values of u, we can replace Σ by the lowest term in a large-u expansion, namely $\Sigma(u)\simeq\langle\gamma\rangle$. This is independent of u. Hence, to leading order, $\Sigma(u)\simeq\Sigma(u+\omega_{\mathbf{r}})$ and

$\lambda \simeq 1$. Making this substitution in Eqs. (50) and (52) and employing our earlier approximation $u \simeq \varepsilon$, which is very good at short times (large u), we obtain the expression

$$D(\varepsilon)=(p/2d)\int d\mathbf{r}\,\mathbf{r}^2\omega(\mathbf{r})[1+\omega(\mathbf{r})\Psi(\varepsilon)]^{-1} . \quad (53)$$

This is very similar in form to results that have been obtained previously in this limit by different methods.[12,8] Indeed, over the parameter regime for which it is expected to be valid Eq. (53) is in essential agreement with the earlier results. For example, an analysis of Eq. (53) along the same lines as that presented by Blumen, Klafter, and Silbey in Ref. 8 reveals the same functional dependence on the basic transport parameters as earlier treatments.[7,8,12,14] This includes, among other things, the correct scaling behavior of the diffusion constant for multipole transfer rates found by Haan and Zwanzig.[14] The corresponding analysis is of sufficient similarity to that given by Blumen *et al.*, that we refer the interested reader to Ref. 8 for details. We now turn to a study of the long-time, high-concentration limits in which theories based upon a pair approximation or low-density expansion are expected to break down.

C. Long-time limit

The very-long-time behavior of the system is determined by the low-frequency properties of the expressions we have developed. In particular the zero-frequency limit of Eq. (45) yields the following expression for the diffusion constant:

$$D=\sum_{\mathbf{n}}\mathbf{n}^2\omega_{\mathbf{n}}\phi_{\mathbf{n}}(0)/\Psi(0) . \quad (54)$$

Note that Eq. (54) is an exact solution to the full self-consistent condition, and does not depend upon our earlier approximation $\varepsilon=u$. We can reexpress Eq. (54) by introducing the function

$$f(z)=\int_0^\infty dt \frac{\exp(-zt)\psi(t)}{q+p\exp(-zt)} . \quad (55)$$

Comparison with Eq. (36) then shows that $\Psi(0)=f(0)$ so that Eq. (54) can be written

$$D=p\sum_{\mathbf{n}}\mathbf{n}^2\omega_{\mathbf{n}}f(\omega_{\mathbf{n}})/f(0) . \quad (56)$$

The function $\psi(t)$ can be calculated to any desired degree of accuracy through Eq. (19); hence, so can the function $f(z)$ by numerical integration. Thus Eq. (56) provides an explicit means for calculating the diffusion constant for particular systems and is one of the main results of this paper.

To test the ability of the theory we have developed to correctly treat the long-time limit we have used Eq. (56) to evaluate the diffusion constant for a system which has well-defined limiting cases. Specifically, we considered a three-dimensional cubic lattice with hopping rates of experimental form, $w_{\mathbf{n}}=A\exp(-\mu|\mathbf{n}|)$, for values of the concentration ranging from the filled lattice $p=1$, down to $p=10^{-2}$. One would expect that for a small enough value of the exponential constant μ, the environment seen by any given active site would not be substantially different from any other, since all sites would be "in contact" with a large number of others. Thus in this limit, the diffusion constant would be close to that associated with the average environment, so that $D \simeq pD_0$, where D_0 is the diffusion constant in the pure lattice. As the exponential fall off of the rates becomes stronger, the existence or absence of nearest neighbors becomes increasingly important. In the limit in which the next-nearest-neighbor hopping rate w_2 becomes small compared to the nearest-neighbor rate w_1 (i.e., for very large μ) there should be a very strong drop off of the diffusion constant at the concentration for which a path of nearest-active-neighbor sites fails to span the solid. That is to say, one might expect the curves to approach or at least resemble that associated with a site-percolating lattice.[28] Of course for any value of the constant μ which is not infinite, one expects there to be a finite (but exponentially small) value of the diffusion constant for all concentrations below the nearest-neighbor percolation threshold. Indeed, according to the arguments given by Ambegaokar, Halperin, and Langer,[15] the actual value at lower concentrations should scale with the hopping rate for the closest lattice neighbor for which a percolating path spans the lattice. The ability to display such a wide variation in behavior represents, therefore, a rather strong test of any long-ranged theory.

Given the simple, single-defect character of the theory that we have developed, the features discussed above are surprisingly well reproduced in the curves which appear in Figs. 1 and 2. In both of these curves we have evaluated Eq. (56) for three different values of $\mu=1$, 5, and 8; and for concentrations p between 10^{-2} and 1. In Fig. 1 we also include a curve for the case $\mu=14$, corresponding to a very strong fall off of the exponential hopping rates, along with representative numerical data (the solid trian-

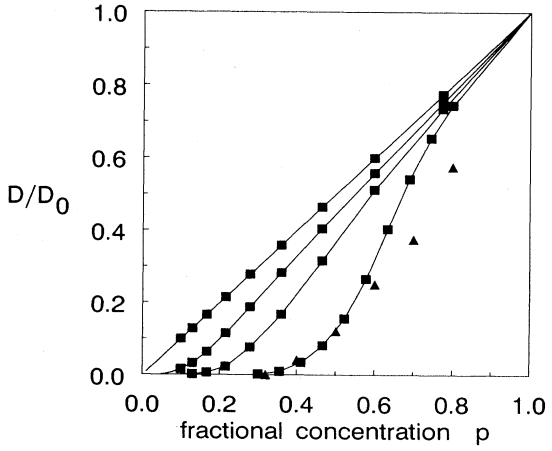

FIG. 1. Normalized diffusion constant vs the fractional concentration of active sites for a three-dimensional lattice with exponential hopping rates $w_{\mathbf{n}}=A\exp(-\mu n)$. The four curves correspond to values of the exponent $\mu=1$, 5, 8, and 14, respectively, with larger values of μ lying closer to the axis. The solid triangles indicate the diffusion constant for a site percolating lattice with nearest-neighbor hopping rates (see text).

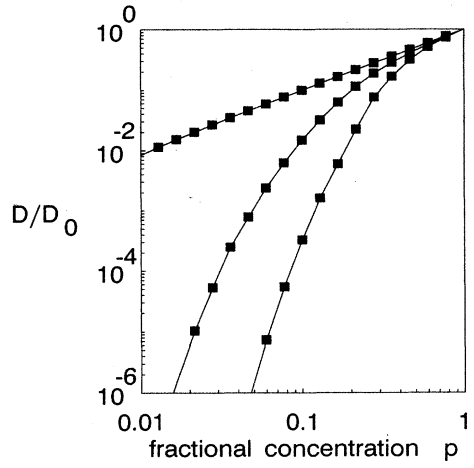

FIG. 2. Normalized diffusion constant vs the fractional concentration of active sites for a three-dimensional lattice with exponential hopping rates $w_n = A\exp(-\mu n)$. The three curves correspond to values of the exponent $\mu = 1$, 5, 8, respectively, with larger values of μ falling off more rapidly at low concentrations.

gles) for the site-percolation problem taken from the work of Kirkpatrick.[28] All curves have been normalized to the value of the diffusion constant for the filled lattice to facilitate comparison. Note that for $\mu = 1$, 5, 8, and 14, the ratio of the next-nearest-neighbor hopping rate to the nearest-neighbor hopping rate is $w_2/w_1 = \exp[-(2^{1/2}-1)\mu] = 0.66$, 0.12, 0.036, and 0.003, respectively. In Fig. 1 we plot the diffusion constant on a linear scale. Figure 2 is plotted logarithmically. In each case the squares indicate the actual concentrations where calculations were performed, and the curves are straight lines connecting the points to provide visual guides. Each point calculated required a numerical evaluation of the function $f(z)$ for a whole range of z values as in Eq. (56).

Note that for the smallest exponent, $\mu = 1$, the curves in Figs. 1 and 2 are very close to the line $D/D_0 = p$, in keeping with our previous expectations. In contrast, the curves with stronger exponential decay of the hopping rate show dramatic decreases at a point somewhat below the nearest-neighbor site-percolation threshold, $p_c \simeq 0.31$. For values of μ in the range considered, the curves tend to be greater than the actual nearest-neighbor percolation curve: This is as one would expect based upon their greater connectivity to the rest of the lattice. Also Fig. 2 clearly shows that the "transition" which seems to appear in the linear curves is not absolute; the diffusion constant actually remains nonzero for all nonzero concentrations, although it does take on very small values. Thus the effective-medium theory presented above seems to provide a quantitatively reasonable description of the long-time limit, at least for exponential hopping with exponents in the range $\mu < 14$. Indeed, the curve corresponding to $\mu = 14$ actually does a reasonable job of reproducing the critical curvature of the percolation data, although it shows significant deviations at higher concentrations. Apparently this deviation corresponds to a breakdown of the theory rather than an actual influence arising from the increasing number of non-nearest-neighbor at higher concentrations (see the discussion at the end of Sec. IV D, where the slope of the curve in the high-concentration limit is calculated explicitly). This breakdown manifests itself for values of $\mu > 14$ in values of D which fall appreciably below the percolation curve (which we would expect to represent a lower bound for the long-ranged system). Of course, a value of μ equal to 14 corresponds to a hopping rate which falls off over distances comparable to $\frac{1}{14}$ of the lattice spacing. Insofar as exponential hopping rates are associated with the overlap of electronic wave functions this is probably well below the range required for any real physical application. Moreover, for hopping rates which fall off more rapidly than this a nearest-neighbor model is probably more appropriate (and more tractable). Thus we feel, in view of the relatively low order of the effective-medium theory that we have developed, the results are quite satisfactory and suggest that the theory performs well in the limit for which it was designed, namely the case where the hopping rates have an extended range.

For the three-dimensional lattice that we have considered, the diffusion constant never vanishes except at zero active-site concentration. In the long-range problem the vanishing of the diffusion constant is a signature of anomalous diffusion, that is, a mean-square displacement $r^2(t) \sim t^\nu$ which grows with time, but with a power ν that is less than 1. From the form of Eq. (56) we see that a vanishing of the diffusion constant for a finite concentration of active sites requires the divergence of $f(0)$, or equivalently, the divergence of the relaxation function at zero frequency, $\Psi(0)$. [Note the factors in the numerator of Eq. (56) are all finite since they are evaluated at finite frequencies.] This has a simple physical interpretation. Recall that by definition $\Psi(\varepsilon)$ is the Laplace transform of $\psi(t)$ and so [cf. Eq. (18)]

$$\Psi(0) = \int_0^\infty dt \langle \exp(-\gamma t) \rangle = \langle 1/\gamma \rangle \ . \tag{57}$$

Thus, as observed earlier,[3] the diffusion coefficient is inversely proportional to the mean waiting time between jumps. For exponentially decaying hopping rates this quantity does not diverge in two and three dimensions. In one dimension it is possible for the average waiting time to diverge at low concentrations and thus give rise to anomalous diffusion.[2,8] Identical arguments can be given which predict the existence of this type of transport threshold in d-dimensions whenever the hopping rates fall off more rapidly than $\exp(-\mu n^d)$. This could be important in low-dimensional systems since recent theoretical work suggests that in some strongly dissipative systems[40] the hopping rate can fall off as $\exp(-\lambda R^2)$.

D. High concentrations

Finally we consider the limit of a small number of inactive sites. For a nearly pure material the concentration of active sites will be close to one, and we can expand in powers of the concentration q of inactive sites. Performing a Taylor series expansion of Eq. (19) about $q = 0$ and

taking Laplace transforms we obtain

$$\Psi(u)=\Psi_0(u)\left[1+q\sum_{\mathbf{n}}\omega_{\mathbf{n}}\Psi_0(u-\omega_{\mathbf{n}})\right]+O(q^2)\ , \tag{58}$$

where $\Psi_0(\varepsilon)=(\varepsilon+\Lambda)^{-1}$ is the relaxation function for a pure lattice with $q=0$. Substituting this into Eq. (33) we find

$$\Gamma(\varepsilon)=\sum_{\mathbf{n}}\omega_{\mathbf{n}}[1-q\Psi_0(u-\omega_{\mathbf{n}})/\Psi_0(u)]\ . \tag{59}$$

Then using the definition of $\Gamma(\varepsilon)$ as the sum over the memory functions we obtain

$$M_{\mathbf{n}}(\varepsilon)=\omega_{\mathbf{n}}[1-q\Psi_0(u-\omega_{\mathbf{n}})/\Psi_0(u)] \tag{60}$$

which gives for the diffusion coefficient

$$D(\varepsilon)=(2d)^{-1}\sum_{\mathbf{n}}\mathbf{n}^2\omega_{\mathbf{n}}[1-q\Psi_0(u-\omega_{\mathbf{n}})\Psi(u)]\ . \tag{61}$$

This reduces at zero frequency to

$$D(0)=D_0-qD_1\ , \tag{62}$$

where $D_0=\Lambda\xi$ and

$$D_1=(2d)^{-1}\sum_{\mathbf{n}}\mathbf{n}^2\omega_{\mathbf{n}}[\Lambda(\Lambda-\omega_{\mathbf{n}})^{-1}]\ . \tag{63}$$

Considering our earlier example of exponential hopping rates in which $\omega_{\mathbf{n}}=A\exp(-\mu\mathbf{n})$, we note that for small μ, the quantity $\Lambda-\omega_{\mathbf{n}}\simeq\Lambda$, because Λ is then the sum over many rates very close to A. Thus, in this limit $D_1\simeq D_0$. From Eq. (62) we then obtain $D(0)\simeq pD_0$ as discussed earlier. In the opposite limit in which μ is very large we can approximately neglect all but the nearest neighbors ($\mathbf{n}=1$). We then find $D_0\simeq\omega_1$, $\Lambda\simeq 2d\omega_1$, and $D_1\simeq(2d-1)^{-1}D_0$.

V. SUMMARY

We have developed a simple effective-medium theory for treating long-range transport processes in substitutionally disordered condensed phases. The theory is based upon the exact solution to the problem of a single-defect embedded in a partially averaged environment and involves a more complete description of back-transfer processes than is obtained within the pair approximation usually employed. We have explored different limits of the theory and found that it reproduces essential details of the low-concentration, short-time results obtained previously. It also yields exact results in the high-concentration limit, $p=1$. To test the usefulness of the theory for describing other features of the long-time, high-concentration behavior, we have employed it to study diffusion on a three-dimensional lattice with exponential hopping rates for active-site concentrations greater then 10^{-2}. We find that the theory produces reasonable results over physical regimes of interest, but breaks down when the hopping rates fall off over distances much smaller than the lattice spacing. It is possible that a multidefect effective-medium theory of the present type would improve the theory in this regime. Nonetheless, for exponents which are large, but not too large, the results realistically predict a quasitransition near the concentration at which a nearest-neighbor path of active sites fails to span the lattice. The theory also predicts anomalous diffusion below a critical concentration for exponential hopping rates in one-dimension, in agreement with earlier results.

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