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Theoretical studies of energy transfer in disordered condensed media

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In this paper we consider energy transfer among impurity molecules in disordered systems. We use the result of Gochanour, Andersen, and Fayer [J. Chem. Phys. **70**, 4254 (1979)] for the generalized diffusion coefficient $D(t)$ in terms of the decay function $\Phi(t)$, in conjunction with separate calculations of $\Phi(t)$ in the pair approximation to compute $D(t)$. Both multipolar and exchange interactions and both short and long time limits are considered. Comparisons to earlier work are made.

I. INTRODUCTION

Time-dependent energy transfer among impurity molecules in condensed media has recently been of considerable interest both experimentally and theoretically,¹⁻¹² since time-dependent studies provide valuable insight in understanding the various mechanisms of the migration of excitation among impurity molecules. Although we refer throughout this work to energy transfer in mixed crystals in the continuum approximation and to liquids, the theory accounts well also for problems of energy and charge transport in amorphous crystals.¹³⁻¹⁵

Important examples of energy transport are the electronic^{11,12} and vibrational energy transfer⁶ and the spin migration.¹⁶ In these problems, at high temperatures, it is generally agreed that phonon assisted hopping processes dominate,^{1,2,17,18} and that the limit of incoherent migration described by a master equation prevails.

Most theoretical works in the field of energy transfer under the presence of disorder address the calculation of the mean squared displacement of the electronic excitation $\langle R^2(t) \rangle$ which defines a diffusion coefficient $D(t)$,^{5,7-10} or the evaluation of $\Phi(t)$ the probability of the excitation remaining on the initially excited molecule at time t .^{1-5,19-23}

The attempts to solve the problem of the mean squared displacement have been mainly pursued by considering the corresponding Green's function and its self-energy.⁷⁻⁹ These approaches have dealt with various time regimes, mostly in the framework of the pair approximation. Another way to obtain the mean squared displacement is the continuous time random walk theory, which originated from related problems of charge transport in amorphous semiconductors.^{10,13} In this paper we discuss the connection between both approaches and the general problem of incoherent transport in disordered systems.

The function $\Phi(t)$ has been evaluated numerically over the whole time domain,²⁰ but analytically only for short times,¹⁹⁻²³ using approximations mostly within the pair

assumption. The exact relation between $\Phi(t)$ and $\langle R^2(t) \rangle$ is still unknown. Such a relation is of extreme importance, since it provides the connection between the measured energy decay data and the fundamental problem of energy migration.

An approximate and direct relation between $\Phi(t)$ and $\langle R^2(t) \rangle$ has been recently suggested by Gochanour, Andersen, and Fayer [GAF].⁸ In this work we use the GAF relation between the mean squared displacement and the decay law $\Phi(t)$ to evaluate $\langle R^2(t) \rangle$ from known forms for $\Phi(t)$, which are found from independent calculations. These calculations are in the time domain, and thus more transparent than a self-consistent evaluation of the Laplace transform of $\Phi(t)$, as suggested by GAF. Our approach enables us to compare the results obtained by both methods and assess their consistency within this approximation.

Since the expressions for $\Phi(t)$ are known for multipolar and exchange interactions in arbitrary dimensions,^{22,23} we present results for $\langle R^2(t) \rangle$ and $D(t)$ for these cases, which are valid within this approximation, in both the short and long time domain.

In Sec. II we present the general formalism and the expressions for diffusion coefficients used in the subsequent sections. A universal property of the Laplace transform of $\Phi(t)$, valid for all decay laws encountered, allows us to evaluate directly the first term in the short time limit expansion of $\langle R^2(t) \rangle$ and $D(t)$. In Sec. III we consider multipolar interactions for which we calculate additional terms of the short time expansions of $\langle R^2(t) \rangle$ and $D(t)$. The calculations use forms of $\Phi(t)$ with and without backtransfer. We also evaluate the long time diffusion constant.

In Sec. IV we discuss the case of exchange interactions, for which the short and long time expressions for $D(t)$ and $\langle R^2(t) \rangle$ are given. The long time diffusion coefficient in this case has a very strong dependence on dimension and concentration; in particular, in one dimension, $D(t)$ may go to zero for low concentrations.

Section V contains conclusions and recapitulation of results.

II. GENERAL FORMALISM

In order to specify our notation and define the problem, we start from the standard master equation ap-

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proach.^{7-9,24,25} One considers a lattice, in which a certain fraction p of sites is occupied randomly by impurity molecules. The excitation is assumed to migrate among the impurities only; the host molecules do not participate in the energy transfer process.

We define $P_n(t)$ as the probability of finding the excitation on the n th impurity; the excitation transfer, assuming the lifetime of the excitation to be infinite, is then governed by a master equation:

$$\frac{d}{dt} P_n(t) = \sum_{m \neq n} [w_{mn} P_m(t) - w_{nm} P_n(t)] . \quad (2.1)$$

In Eq. (2.1) the sum extends over all impurities, and, for simplicity, the transition rates w_{mn} are assumed to be a function of the interimpurity distance r_{mn} only. The distances r_{mn} depend on the configuration. As specified in the Introduction, only the high temperature limit is considered, for which

$$w_{nm} = w_{mn} . \quad (2.2)$$

The inclusion of the intramolecular lifetime τ_D leads to a simple factor which multiplies the $P_n(t)$:

$$\tilde{P}_n(t) = e^{-t/\tau_D} P_n(t) \quad (\text{all } t) . \quad (2.3)$$

Thus, in the following we will consider only the $P_n(t)$. Assuming that the excitation was on site $n=0$ at $t=0$, one finds formally

$$P_n(t) = [\exp(t\mathbf{V})]_{n0} , \quad (2.4)$$

where

$$V_{mn} = (1 - \delta_{nm}) w_{mn} - \delta_{mn} \sum_{q \neq n} w_{nq} . \quad (2.5)$$

Being interested in the configurational average of $P_n(t)$ we obtain

$$\langle P_n(t) \rangle = \langle \exp(t\mathbf{V}) \rangle_{n0} . \quad (2.6a)$$

For $n=0$ we define

$$\langle P_{n0}(t) \rangle \equiv \Phi(t) . \quad (2.6b)$$

Equations (2.6) have the Laplace transform representations

$$\begin{aligned} \langle P_n(u) \rangle &= \mathcal{L}[\langle P_n(t) \rangle] = \int_0^\infty dt e^{-ut} \langle P_n(t) \rangle \\ &= \langle (u - \mathbf{V})^{-1} \rangle_{n0} , \end{aligned} \quad (2.7a)$$

$$\langle P_{n0}(u) \rangle = \mathcal{L}[\Phi(t)] \equiv \Phi(u) . \quad (2.7b)$$

As shown recently by Klafter and Silbey^{24,25} for general classes of interactions \mathbf{V} , the configurational average in Eq. (2.6a) may be performed exactly and leads to a general solution in terms of the self-energy matrix $\Sigma(u)[SE]$:

$$\langle P_n(u) \rangle = [u - \Sigma(u)]_{n0}^{-1} , \quad (2.8)$$

with

$$\Sigma(u) = \langle V \rangle + \langle \delta \mathbf{V} [u - (1 - Q)\mathbf{V}]^{-1} \delta \mathbf{V} \rangle , \quad (2.9)$$

where Q is the configurational averaging operator and $\delta \mathbf{V} = \mathbf{V} - Q\mathbf{V}$. Operating with Q restores, as shown in Ref. 24, the translational invariance of the lattice, so that in the \mathbf{k} representation (2.8) simplifies to

$$\langle P_{\mathbf{k}}(u) \rangle = [u - \bar{\Sigma}(\mathbf{k}, u)]^{-1} . \quad (2.10)$$

In the framework of energy transfer on disordered systems two fruitful approaches of dealing with the general form (2.10) have evolved. The first is the continuous time random walk of Scher and Lax [for the connection to Eq. (2.10) see Ref. 25; applications are in Refs. 13 and 26]. The second approach is by GAF,⁸ makes extensive use of the particular structure of \mathbf{V} [Eq. (2.5)], and determines several approximate forms for $\bar{\Sigma}(\mathbf{k}, u)$ using a diagrammatic expansion technique.

GAF obtain $\bar{\Sigma}(\mathbf{k}, u)$ in the form [Eq. (66) of Ref. 8]

$$\bar{\Sigma}(\mathbf{k}, u) = -p\rho \Sigma(\mathbf{k}=0, u) + p\rho \Sigma(\mathbf{k}, u) , \quad (2.11)$$

where ρ is the density of lattice points, and since p is the probability of a site being occupied by an impurity, $p\rho$ is the density of impurities.

We now consider the GAF result in the *pair approximation*. In this paper, we mean by pair approximation (or two-body approximation in the terminology of GAF) the diagrammatic expansion of GAF where the SE in Eqs. (2.10) and (2.11) is represented by a sum of irreducible graphs in its lowest (i.e., second order) approximation. This pair approximation allows for repeated transfers between sites 1 and 2 (for example) and by the $\Phi(u)$ allows for excursions from either site to the other guest molecules. There are many procedures to find an approximate $\Phi(u)$, each leading to an approximate form for the SE *within the pair approximation*. This approximation is similar to that used by Haan and Zwanzig except that $\Phi(u)$ in each vertex is substituted here for the Haan-Zwanzig form $1/u$. Using a continuum assumption they obtain the following form for $\Sigma(\mathbf{k}, u)$, valid for all \mathbf{k} [Eq. (83) of Ref. 8]:

$$\Sigma(\mathbf{k}, u) = \int d\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r}) \frac{w(\mathbf{r})}{1 + 2\Phi(u)w(\mathbf{r})} . \quad (2.12)$$

One should note that in Ref. 8, Eq. (83) was obtained by topological considerations only and is thus, in principle, independent of dimension. Limitations on the applicability of Eq. (2.12) to lower dimensions arise only from the assumption of the thermodynamic limit and the continuum approximation.

We can now define a generalized diffusion coefficient $D(\mathbf{k}, u)$ by noticing that Eq. (2.10) is a diffusion equation in $\mathbf{k}-u$ space^{7,27}:

$$\langle P_{\mathbf{k}}(u) \rangle \equiv [u + \mathbf{k}^2 D(\mathbf{k}, u)]^{-1} . \quad (2.13)$$

For $\Sigma(\mathbf{k}, u)$ given by Eq. (2.12) one has

$$D(\mathbf{k}, u) = \frac{\rho p}{k^2} \int d\mathbf{r} [1 - \exp(i\mathbf{k} \cdot \mathbf{r})] \frac{w(\mathbf{r})}{1 + 2\Phi(u)w(\mathbf{r})} . \quad (2.14)$$

The $\mathbf{k}=0$ limit of the generalized diffusion coefficient is of interest, since it determines the migration of the excitation at large distances. Since we assumed $w(\mathbf{r})$ to depend only on the relative distance r , we have the following directly from Eq. (2.14):

$$D(u) \equiv \lim_{\mathbf{k} \rightarrow 0} D(\mathbf{k}, u) = \frac{V_{\Delta} \rho p}{2} \int_0^\infty dr \frac{r^{\Delta+1} w(r)}{1 + 2\Phi(u)w(r)} , \quad (2.15)$$

where V_{Δ} is the volume of a unit sphere in a Δ -dimen-

sional space, and b is a cutoff parameter of the order of d , the next-neighbor distance. Throughout this work we take $b=0$ (see the discussion in Refs. 7 and 22).

It should be emphasized that Eqs. (2.14) and (2.15) provide a *direct* relation between the two functions $\Phi(u)$ and $D(u)$ [or $\Phi(t)$ and $D(t)$ in the time domain], functions that have been generally studied separately.

A simple way to obtain the relation between $D(u)$ and $\langle R^2(u) \rangle$, the Laplace transform of the mean squared displacement $\langle R^2(t) \rangle$, is to observe that

$$\begin{aligned} \langle R^2(u) \rangle &= \mathcal{L}[\langle R^2(t) \rangle] = \mathcal{L} \left[\sum_n r_n^2 \langle P_n(t) \rangle \right] \\ &= \sum_n r_n^2 \langle P_n(u) \rangle = -\nabla_{\mathbf{k}}^2 \langle P_{\mathbf{k}}(u) \rangle \big|_{\mathbf{k}=0}. \end{aligned} \quad (2.16)$$

Under the assumption that $D(\mathbf{k}, u)$ is a well-behaved function of \mathbf{k} , one obtains the following immediately from Eq. (2.13):

$$\lim_{\mathbf{k} \rightarrow 0} \nabla_{\mathbf{k}}^2 \langle P_{\mathbf{k}}(u) \rangle = -2\Delta D(u)/u^2 \quad (2.17)$$

and

$$\langle R^2(u) \rangle = 2\Delta D(u)/u^2. \quad (2.18)$$

The time-dependent diffusion coefficient $D(t)$ is defined as

$$D(t) \equiv \frac{1}{2\Delta} \frac{d}{dt} \langle R^2(t) \rangle. \quad (2.19)$$

One should note that $D(u)$ is *not* the Laplace transform of $D(t)$, as is easily seen from Eqs. (2.18) and (2.19):

$$\mathcal{L}[D(t)] = \frac{u}{2\Delta} \langle R^2(u) \rangle = \frac{D(u)}{u}. \quad (2.20)$$

However, if $D(t)$ is a constant, $D(u)$ equals the same constant $D(t) = D = D(u)$.

In the following we discuss different approximations to $\Phi(u)$ that can be used in obtaining $D(u)$ from (2.15), where

$$\Phi(u) = \int_0^\infty e^{-ut} \Phi(t) dt. \quad (2.21)$$

There are various approaches to calculate $\Phi(t)$ in the pair approximation. These approaches mainly differ in the way backtransfer from the other molecules is accounted for. The simplest $\Phi(t)$ is obtained by ignoring backtransfer to the initial site.^{1-5,22,28} $\Phi(t)$ in this case is the averaged solution of a master equation $[\dot{\Phi}(t) \equiv \langle \dot{P}_{n_0}(t) \rangle]$ that follows from Eq. (2.1) by omitting the first term on its right-hand side. Upon performing the configurational average one obtains exactly^{5,22,28}

$$\Phi(t) = \prod_{n=1}^N (1 - p \{1 - \exp[-tw(r_n)]\}), \quad (2.22)$$

where the product extends over all lattice sites with the exception of the origin $n=0$.

For isotropic multipolar interactions the transfer rate at distance r is given by^{1,2,18}

$$w(r) = \frac{1}{\tau} \left(\frac{d}{r} \right)^s, \quad (2.23)$$

where d is the next-neighbor distance and τ^{-1} is the transfer rate between two molecules at distance d . This form is mathematically equivalent to defining $w(r)$ in terms of the lifetime τ_D and an effective radius R_0 , since $d^s/\tau = R_0^s/\tau_D$; use of the form (2.23) implies for electronic energy transfer that the phonon relaxation time is very short on the time scale of τ .

Inserting Eq. (2.23) into Eq. (2.22) leads to the following result for times longer than τ and not too high concentrations^{1,4,22}:

$$\Phi(t) = \exp[-V_\Delta p \rho d^\Delta \Gamma(1 - \Delta/s)(t/\tau)^{\Delta/s}], \quad (2.24)$$

where $\Gamma(x)$ is the gamma function.

In the case of isotropic exchange interactions^{2,18}

$$w(r) = \frac{1}{\tau} \exp[\gamma(d - r)], \quad (2.25)$$

where τ and d have the same meaning as in Eq. (2.23). For not too high concentrations and for times longer than τ , Eq. (2.22) results in^{4,23}

$$\Phi(t) = \exp \left[-V_\Delta p \gamma^{-\Delta} g_\Delta \left(\frac{t}{\tau} e^{\gamma d} \right) \right], \quad (2.26)$$

where (See Blumen,²³ Appendix A)

$$g_\Delta(u) \equiv \Delta \int_0^\infty dx x^{\Delta-1} [1 - \exp(-ue^{-x})] \quad (\Delta \neq 0). \quad (2.27)$$

The above derivations of $\Phi(t)$ disregarded backtransfer completely. An attempt to account for backtransfer effects, at least for very short times, has been made by Huber *et al.*¹⁹ They assume only repeated hops of the excitation within all pairs consisting of the initially excited molecule and the other molecules. This assumption results in a modification of Eq. (2.22) to include backtransfer^{19,23}

$$\Phi^{\text{BT}}(t) = \prod_{n=1}^N \left(1 - \frac{p}{2} \{1 - \exp[-2tw(r_n)]\} \right), \quad (2.28)$$

namely, one has only to perform the simple transformation $p \rightarrow p/2$, $t \rightarrow 2t$ in Eq. (2.22) in order to obtain the effect of backtransfer under the above mentioned pair assumption from the results without backtransfer. Equations (2.24) and (2.26) are then modified to be

$$\Phi^{\text{BT}}(t) = \exp[-V_\Delta \rho (p/2) d^\Delta \Gamma(1 - \Delta/s)(2t/\tau)^{\Delta/s}] \quad (2.29)$$

and

$$\Phi^{\text{BT}}(t) = \exp \left[-V_\Delta \rho (p/2) \gamma^{-\Delta} g_\Delta \left(\frac{2t}{\tau} e^{\gamma d} \right) \right], \quad (2.30)$$

respectively. A better treatment of the pair approximation, without invoking repeated hops between the same molecules, has been recently developed by Lyo and applied to multipolar interactions.²¹ We defer its discussion to Sec. III.

Up to now, we have found different forms for $\Phi(t)$ [see Eqs. (2.24), (2.26), (2.29), and (2.30)]. Although $\Phi(u)$ is the Laplace transform of $\Phi(t)$ and thus a different function in each case, it should be noted that its asymptotic behavior for $u \rightarrow \infty$ is independent of $\Phi(t)$. This feature corresponds to the very short time limit of $\Phi(t)$. For a well behaved $\Phi(t)$, $\Phi(0)=1$ and $\Phi(t) \lesssim 1$ for t very small. Thus,

$$\Phi(u) = \int_0^\infty e^{-ut} \Phi(t) dt = \frac{1}{u} \int_0^\infty e^{-z} \Phi\left(\frac{z}{u}\right) dz \rightarrow \frac{1}{u}, \quad \text{as } u \rightarrow \infty. \quad (2.31)$$

One should note that, although $\Phi(t)$ in Eq. (2.31) represents the exact function, which is a well-behaved function of time, the same general feature characterizes all the above-mentioned approximate functions—see Secs. III and IV.

Returning to $D(u)$ in Eq. (2.15) and adopting the general short time result $\Phi(u) = 1/u$ for both multipolar and exchange interactions, we immediately rederive the Haan-Zwanzig expression for the short time diffusion coefficient. We first obtain

$$D(u) = \frac{V_\Delta \rho p}{2} \int_0^\infty dr \frac{r^{\Delta+1} w(r) u}{u + 2w(r)} \quad (2.32)$$

and the mean squared displacement [Eq. (2.18)]

$$\langle R^2(u) \rangle = \Delta V_\Delta \rho p \int_0^\infty dr \frac{r^{\Delta+1} w(r)}{u + 2w(r)}. \quad (2.33)$$

By using the inverse Laplace transform

$$\mathcal{L}^{-1} \left[\frac{1}{u(u+A)} \right] = \frac{1}{A} (1 - e^{-At}), \quad (2.34)$$

we obtain

$$\langle R^2(t) \rangle = \frac{\Delta V_\Delta \rho p}{2} \int_0^\infty dr r^{\Delta+1} (1 - e^{-2w(r)t}), \quad (2.35)$$

which is Eq. (36) of Ref. 7. The diffusion coefficient corresponding to short times is then

$$\begin{aligned} D(t) &= \frac{1}{2\Delta} \frac{d}{dt} \langle R^2(t) \rangle \\ &= \frac{V_\Delta \rho p}{2} \int_0^\infty dr r^{\Delta+1} w(r) e^{-2w(r)t}. \end{aligned} \quad (2.36)$$

For any decay law $\Phi(t)$, the Haan-Zwanzig approximation is thus the short time limit of the GAF diagrammatic result. We now concentrate on the short time behavior for multipolar and exchange interactions, and present results independent of $\Phi(t)$.

In the multipolar case

$$\begin{aligned} D(t) &= \frac{V_\Delta \rho p}{2} \frac{d^s}{\tau} \int_0^\infty r^{\Delta+1-s} \exp[-(2t/\tau)(d/r)^s] dr \\ &= \frac{V_\Delta \rho p}{2} \frac{d^{\Delta+2}}{\tau s} \left(\frac{2t}{\tau} \right)^{(\Delta+2-s)/s} \int_0^\infty dz e^{-z} z^{-(\Delta+2)/s} \\ &= \frac{V_\Delta \rho p}{2s} d^{\Delta+2} \tau^{(\Delta+2)/s} (2t)^{(\Delta+2-s)/s} \Gamma\left(1 - \frac{\Delta+2}{s}\right). \end{aligned} \quad (2.37)$$

This result was obtained in the three-dimensional case by Godzik and Jortner⁹ using a Dyson equation method. The time dependence in Eq. (2.37) ($t^{(\Delta+2-s)/s}$) agrees with the time dependence derived by extending the Haan-Zwanzig scaling argument to any Δ and s (for details see Appendix A).

In the exchange case

$$\begin{aligned} D(t) &= (V_\Delta \rho p e^{\gamma_d}/2\tau) \int_0^\infty dr r^{\Delta+1} \exp[-\gamma r - (2t/\tau) e^{\gamma_d} e^{-\gamma}] \\ &= (V_\Delta \rho p/4t) \gamma^{-\Delta-2} (\Delta+1) \int_0^\infty dy y^\Delta \\ &\quad \times \{1 - \exp[-(2t/\tau) e^{\gamma_d} e^{-y}]\} \\ &= (V_\Delta \rho p/4t) \gamma^{-\Delta-2} g_{\Delta+1}(2t e^{\gamma_d}/\tau), \end{aligned} \quad (2.38)$$

where $g_\Delta(y)$ is defined in Eq. (2.27). The result in Eq. (2.38) reduces in the three-dimensional case to the result obtained in Ref. 9 through the Dyson equation approach.

Equations (2.37) and (2.38) represent the short time characteristic behavior of energy transfer among impurities. This behavior depends strongly on Δ and on $w(r)$, but is independent of the particular form of the decay law $\Phi(t)$, since for every decay law one has the general form $\Phi(u) = 1/u$ [Eq. (2.31)] in the short time limit. In following sections, utilizing the basic formalism derived here, we improve the short time expressions and we also study the longer time regime.

III. MULTIPOLAR INTERACTIONS

This section will be devoted to the study of the multipolar case, where the interaction is given by Eq. (2.23). Of interest are both the short and the long time limits of the diffusion coefficient $D(t)$ and of the mean squared displacement $\langle R^2(t) \rangle$. We will determine these by using forms for $\Phi(t)$ that include backtransfer in approximate ways, as well as the $\Phi(t)$ form valid if backtransfer is neglected.

In the multipolar case the generalized diffusion coefficient $D(u)$ is given by

$$\begin{aligned} D(u) &= V_\Delta \rho p (2\tau)^{-1} \int_0^\infty dr r^{\Delta+1} \frac{(d/r)^s}{1 + \frac{2\Phi(u)}{\tau} \left(\frac{d}{r}\right)^s} \\ &= V_\Delta \rho p d^{\Delta+2} \pi \left[2s \sin\left(\frac{\Delta+2}{s}\pi\right) \right]^{-1} \\ &\quad \times \tau^{-(\Delta+2)/s} [2\Phi(u)]^{[(\Delta+2)/s]-1}, \end{aligned} \quad (3.1)$$

where we used the general expression for $D(u)$ [Eq. (2.15)] and Eq. (3.241.2) of Ref. 29:

$$\int_0^\infty \frac{x^{a-1}}{1+x^b} dx = \frac{\pi}{b} \csc \frac{a\pi}{b} \quad (\text{Re } b \geq \text{Re } a > 0). \quad (3.2)$$

To obtain $D(u)$ from Eq. (3.1) we will use different forms for $\Phi(u)$; these follow from the low concentration results for $\Phi(t)$ which are given by Eq. (2.24) in the absence of backtransfer and by Eq. (2.29) when backtransfer is included.

A. Short time limit

The purpose of this subsection is to calculate in the short time limit additional terms to $D(t)$ and to present the results for the mean squared displacement $\langle R^2(t) \rangle$. A straightforward way to proceed is to evaluate the terms following $1/u$ in the asymptotic expansion of $\Phi(u)$.

We first observe that around $t=0$ the forms in the exponents of Eqs. (2.24) and (2.29) are not analytical

functions of t . (At $t=0$ even their first derivatives do not exist.) However, a representation of $\Phi(t)$ in ascending powers of t (not all of which are integers) is obtained by expanding the exponentials:

$$\Phi(t) = \exp(-At^{\Delta/s}) = \sum_{j=0}^{\infty} \frac{(-A)^j t^{j\Delta/s}}{j!}, \quad (3.3)$$

where according to Eqs. (2.24) and (2.29),

$$A = V_{\Delta} \rho p d^{\Delta} \Gamma(1 - \Delta/s) \tau^{-\Delta/s} \quad (3.4)$$

in the case without backtransfer, and

$$A = 2^{(\Delta/s)-1} V_{\Delta} \rho p d^{\Delta} \Gamma(1 - \Delta/s) \tau^{-\Delta/s} \quad (3.5)$$

in the backtransfer case.

From Eq. (3.3), $\Phi(u)$ may be evaluated by integrating term by term:

$$\begin{aligned} \Phi(u) &= \int_0^{\infty} dt e^{-ut} \Phi(t) = \sum_{j=0}^{\infty} \frac{(-A)^j}{j!} \int_0^{\infty} dt e^{-ut} t^{j\Delta/s} \\ &= \frac{1}{u} \sum_{j=0}^{\infty} \frac{(-A)^j}{j!} \Gamma(1 + j\Delta/s) u^{-j\Delta/s}. \end{aligned} \quad (3.6)$$

Expression (3.6) has to be inserted into Eq. (3.1) from which we now evaluate the first additional term to the result of Sec. II. Thus, in first order in the concentration,

$$\begin{aligned} \Phi(u) &= \frac{1}{u} - V_{\Delta} \rho p d^{\Delta} \Gamma(1 - \Delta/s) \Gamma(1 + \Delta/s) \tau^{-\Delta/s} u^{-1-\Delta/s} \\ &= \frac{1}{u} - V_{\Delta} \rho p d^{\Delta} \frac{\Delta\pi}{s \sin(\Delta\pi/s)} \tau^{-\Delta/s} u^{-1-\Delta/s} \end{aligned} \quad (3.7)$$

without backtransfer, and

$$\begin{aligned} \Phi^{\text{BT}}(u) &= \frac{1}{u} - 2^{\Delta/s-1} V_{\Delta} \rho p d^{\Delta} \frac{\Delta\pi}{s \sin(\Delta\pi/s)} \\ &\quad \times \tau^{-\Delta/s} u^{-1-\Delta/s} \end{aligned} \quad (3.8)$$

including backtransfer. In Appendix B we will prove that even a more exact treatment of backtransfer does not change the correction term in Eq. (3.8).

To avoid repeating almost identical formulas, we continue by using the general form Eq. (3.6) for the case with and without backtransfer. In first order in concentration one obtains with Eq. (3.1) the short time result (large u)

$$\begin{aligned} D(u) &\approx V_{\Delta} \rho p d^{\Delta+2} \frac{\pi}{s \sin\left(\frac{\Delta+2}{s}\pi\right)} \tau^{-(\Delta+2)/s} 2^{[(\Delta+2)/s]-2} \\ &\quad \times \left[u^{1-(\Delta+2)/s} + A \frac{s-\Delta-2}{s} \Gamma(1 + \Delta/s) u^{1-(2\Delta+2)/s} \right], \end{aligned} \quad (3.9)$$

which, using Eqs. (2.16), (2.18), and

$$\mathcal{L}(t^{\alpha}) = \int_0^{\infty} e^{-ut} t^{\alpha} dt = u^{-\alpha-1} \Gamma(\alpha+1), \quad (3.10)$$

leads to

$$\langle R^2(t) \rangle = 2\Delta V_{\Delta} \rho p d^{\Delta+2} \frac{\pi}{s \sin\left(\frac{\Delta+2}{s}\pi\right)} \tau^{-(\Delta+2)/s} 2^{(\Delta+2-2s)/s}$$

$$\times \left\{ \frac{t^{(\Delta+2)/s}}{\Gamma[1 + (\Delta+2)/s]} + A \frac{(s-\Delta-2) \Gamma(1 + \Delta/s) t^{(2\Delta+2)/s}}{s \Gamma[1 + (2\Delta+2)/s]} \right\}, \quad (3.11)$$

from which $D(t)$ for short times follows:

$$\begin{aligned} D(t) &= (V_{\Delta} \rho p) (d^s/\tau)^{(\Delta+2)/s} [c_1(\Delta, s) t^{(\Delta+2-2s)/s} \\ &\quad + c_2(\Delta, s) t^{(2\Delta+2-2s)/s}], \end{aligned} \quad (3.12a)$$

where

$$c_1(\Delta, s) = \frac{\pi 2^{(\Delta+2-2s)/s}}{s \sin\left(\frac{\Delta+2}{s}\pi\right) \Gamma[(\Delta+2)/s]}, \quad (3.12b)$$

$$c_2(\Delta, s) = A \frac{\pi 2^{(\Delta+2-2s)/s} (s-\Delta-2) \Gamma(\Delta/s+1)}{s^2 \sin\left(\frac{\Delta+2}{s}\pi\right) \Gamma[(2\Delta+2)/s]}. \quad (3.12c)$$

Here, we note that both $\langle R^2(t) \rangle$ and $D(t)$ have the structure required by the scaling argument of Haan-Zwanzig [see Appendix A, Eqs. (A6) and (A7)]. In the three-dimensional case ($\Delta=3$), the results are, apart from a numerical factor, similar to the Eqs. (6.27)ff. of Ref. 30 derived through a continuous time random walk approach.

In the special case of dipolar interactions ($s=6$) in three dimensions ($\Delta=3$) $D(t)$ has the form

$$D(t) = \left(\frac{4\pi}{3} \rho p\right) d^5 \tau^{-5/6} \left[\alpha_1 t^{-1/6} + \alpha_2 \left(\frac{4\pi}{3} \rho p\right) d^3 \tau^{-1/2} t^{1/3} \right], \quad (3.13)$$

with $\alpha_1=0.4133$ and $\alpha_2=0.1368$ without backtransfer or $\alpha_2=0.0967$ in the backtransfer case. The value for α_1 and the last figure for α_2 are identical with the GAF result in the pair approximation [$D(t)$ obtained from their Eq. (101)]. The result for α_1 is as expected since, as discussed in Sec. II, the first term of Eq. (3.12) is independent of the particular form of the decay law $\Phi(t)$. For the α_2 values we infer that in the multipolar case compatibility with GAF is achieved only if one uses Eq. (2.15) with decay laws $\Phi(t)$ that include backtransfer.

B. Long time limit

We now turn our attention to the long time limit, i.e., to the case of very small u . The Laplace transform of Eq. (3.3) may then be evaluated through the asymptotic expansion

$$\begin{aligned} \Phi(u) &= \int_0^{\infty} \Phi(t) e^{-ut} dt = \sum_{j=0}^{\infty} \frac{(-u)^j}{j!} \int_0^{\infty} \Phi(t) t^j dt \\ &= \sum_{j=0}^{\infty} \frac{(-u)^j}{j!} \int_0^{\infty} dt t^j \exp(-At^{\Delta/s}) \\ &= \frac{s}{\Delta} A^{-s/\Delta} \sum_{j=0}^{\infty} \frac{(-u)^j}{j!} A^{-js/\Delta} \Gamma[(j+1)s/\Delta], \end{aligned} \quad (3.14)$$

where A is given by Eq. (3.4) or (3.5). One should note that in our approximations in the multipolar case all moments of $\Phi(t)$ exist for all Δ and s ($s > \Delta$).³¹

From Eq. (3.14) we obtain, with Eq. (3.1), $D(u)$

TABLE I. Values of the diffusion constant \tilde{D}^{BT} in the multipolar case, when backtransfer is included [Eq. (3.19)].

Δ	\tilde{D}^{BT}		
	$s = 6$	8	10
3	0.4481	0.1309	0.0251
2	0.1126	0.0150	0.0018
1	0.0018	1.3×10^{-5}	6.2×10^{-8}

from which one finds $\langle R^2(u) \rangle$ and its inverse Laplace transform $\langle R^2(t) \rangle$. Only the first two terms in the expansion of $\langle R^2(u) \rangle$ in powers of u correspond to well-behaved functions in the t domain. Keeping thus only the first two terms in Eq. (3.14) leads to

$$D(u) = V_{\Delta} \rho p d^{\Delta+2} (2/\tau)^{(\Delta+2)/s} \pi \left[4s \sin\left(\frac{\Delta+2}{s} \pi\right) \right]^{-1} \\ \times [\Gamma(1+s/\Delta)]^{(\Delta+2-s)/s} A^{(s-\Delta-2)/\Delta} \\ \times \{1 + (s-\Delta-2)A^{-s/\Delta} \Gamma(2s/\Delta) [s\Gamma(s/\Delta)]^{-1} u\} \quad (3.15)$$

and with Eqs. (2.16) and (2.18):

$$\langle R^2(t) \rangle \sim t + (s-\Delta-2)A^{-s/\Delta} \Gamma(2s/\Delta) [s\Gamma(s/\Delta)]^{-1} u. \quad (3.16)$$

We note that only the first term of Eq. (3.16) contributes to $D(t)$:

$$D(t) = \frac{1}{2\Delta} \frac{d}{dt} \langle R^2(t) \rangle \\ = V_{\Delta} \rho p d^{\Delta+2} (2/\tau)^{(\Delta+2)/s} \pi \left[4s \sin\left(\frac{\Delta+2}{s} \pi\right) \right]^{-1} \\ \times [\Gamma(1+s/\Delta)]^{(\Delta+2-s)/s} A^{(s-\Delta-2)/\Delta} \equiv D, \quad (3.17)$$

where D is independent of t . In the backtransfer case we have the following with Eq. (3.5):

$$D^{\text{BT}} = \tilde{D}^{\text{BT}} \frac{d^2}{\tau} (V_{\Delta} \rho p d^{\Delta})^{(s-2)/\Delta}, \quad (3.18)$$

where

$$\tilde{D}^{\text{BT}} = \frac{\pi}{2s \sin\left(\frac{\Delta+2}{s} \pi\right)} \\ \times \{ \Gamma(1-\Delta/s) [\Gamma(1+s/\Delta)]^{-\Delta/s/2} \}^{(s-\Delta-2)/\Delta}. \quad (3.19)$$

The result without backtransfer is larger by a factor of $(2^{(s-\Delta-2)/\Delta} 2^{(\Delta+2-s)/s})$ than the result obtained introducing backtransfer.

Since Eq. (3.18) corresponds to the important case of pure (dispersionless) diffusion, we present in Table I the values for \tilde{D}^{BT} . For the three-dimensional dipolar case the result for \tilde{D}^{BT} is 8% smaller than the two-body GAF expression [Eq. (97) of Ref. 8], which was obtained from a self-consistent method of determining $\Phi(u)$; \tilde{D}^{BT} is larger than the Godzik and Jortner result by 12%. For larger s in three dimensions our results are consistently somewhat larger than those of Ref. 30.

While the two-dimensional results of Table I are still well behaved, the diffusion constant in the one-dimen-

sional case drops sharply by increasing s , which indicates that in the framework of the pair approximation the excitation is practically localized for higher multipolar interactions in one dimension.

We briefly consider the limits of validity of the time independent D value [Eq. (3.17)]. In our derivation for $D(t)$ we made use only of the first two terms of the asymptotic series (3.14); in fact, because of Eq. (3.18) only the first term contributed. We now consider the error made in discarding the rest of the series (3.14); for the case $s/\Delta=2$ it is known [Ref. 32, Eq. (7.1.24)] that the absolute error is less than the absolute value of the first discarded term.

In order to have the error on $D(t)$ small, one thus has to require

$$u A^{-s/\Delta} \Gamma(2s/\Delta) < \Gamma(s/\Delta), \quad (3.20)$$

where we assumed that in general the first discarded term is a good estimate for the error. Thus, in the backtransfer case, with Eq. (3.5),

$$t/\tau > \Gamma(2s/\Delta) [\Gamma(s/\Delta)]^{-1} 2^{(s/\Delta)-1} \\ \times [\Gamma(1-\Delta/s)]^{-s/\Delta} (V_{\Delta} \rho p d^{\Delta})^{-s/\Delta}. \quad (3.21)$$

The condition (3.21) agrees reasonably well with the three-dimensional numerical results of Refs. 8 and 30.

From Eq. (3.21) one sees that the diffusive limit occurs at later times if s gets larger or Δ gets smaller; the limit is also extremely sensitive to concentration: An increase in concentration pushes the diffusive limit to considerably shorter times.

IV. EXCHANGE INTERACTIONS

This section will be concerned with the properties of the mean squared displacement $\langle R^2(t) \rangle$ and the diffusion coefficient $D(t)$ in the case that the interaction between sites occurs via exchange [Eq. (2.25)].

In this case the generalized diffusion coefficient $D(u)$ again follows from Eq. (2.15):

$$D(u) = \frac{V_{\Delta} \rho p}{2} \int_0^{\infty} \frac{dr r^{\Delta+1} w(r)}{1+2\Phi(u)w(r)} \\ = \frac{V_{\Delta} \rho p e^{\gamma_d} \gamma^{-(\Delta+2)}}{2\tau} \int_0^{\infty} \frac{dx x^{\Delta+1}}{e^x + [2\Phi(u) e^{\gamma_d/\tau}]} \\ = V_{\Delta} \rho p e^{\gamma_d} \gamma^{-\Delta-2} (2\tau)^{-1} f_{\Delta+1} [2\Phi(u) e^{\gamma_d/\tau}], \quad (4.1)$$

where we defined the function

$$f_{\Delta}(y) \equiv \int_0^{\infty} dx \frac{x^{\Delta}}{e^x + y}. \quad (4.2)$$

The properties of the function $f_{\Delta}(y)$ are derived in Appendix C.

In order to obtain the function $D(u)$ we use in the following the different forms for the Laplace transform of the decay laws $\Phi(t)$ which were discussed in Sec. II.

A. Short time limit

Let us examine first the forms of $\Phi(t)$ and of $\Phi^{\text{BT}}(t)$ [Eqs. (2.26) and (2.30), respectively] for small times.

The function $g_{\Delta}(t)$ defined in Eq. (2.27) has the following expansion series [Eq. (A4) of Ref. 23]:

$$g_{\Delta}(t) = \Delta! t \sum_{j=0}^{\infty} \frac{(-t)^j}{j! (j+1)^{\Delta+1}}. \quad (4.3)$$

The radius of convergence of this series is infinite. Thus, $g_{\Delta}(y)$ is analytical in the whole complex plane. This is also true for the functions $\Phi(t)$ and $\Phi^{\text{BT}}(t)$. The situation is now different from the multipolar case, where an analytical expansion of the decay laws around $t=0$ does not exist. Here, we have simply, for short times, from Eq. (2.26),

$$\begin{aligned} \Phi(t) &= 1 - V_{\Delta} \rho p \gamma^{-\Delta} (e^{\gamma t} / \tau) [\lim_{z \rightarrow 0} g'_{\Delta}(z)] t + \dots \\ &\approx 1 - \Delta! V_{\Delta} \rho p \gamma^{-\Delta} e^{\gamma t} (t / \tau), \end{aligned} \quad (4.4)$$

where we used the relation

$$\lim_{z \rightarrow 0} g'_{\Delta}(z) = \Delta!, \quad (4.5)$$

which is self-evident from Eq. (4.3).

In the backtransfer case we have also from Eq. (2.30)

$$\Phi^{\text{BT}}(t) \approx 1 - \Delta! V_{\Delta} \rho p \gamma^{-\Delta} e^{\gamma t} (t / \tau). \quad (4.6)$$

Thus, $\Phi(t)$ and $\Phi^{\text{BT}}(t)$ are identical to first order in pt , so that, working in first order in p , we do not have to distinguish between the two cases.

The Laplace transform of both Eqs. (4.4) and (4.6) is given by

$$\Phi(u) = \mathcal{L}[\Phi(t)] = u^{-1} - \Delta! V_{\Delta} \rho p \gamma^{-\Delta} e^{\gamma t} / (u^2 \tau). \quad (4.7)$$

Equation (4.1) can be rewritten as

$$D(u) = b f_{\Delta+1} [a \Phi(u)], \quad (4.8)$$

with

$$a = 2e^{\gamma t} / \tau, \quad (4.9)$$

$$b = V_{\Delta} \rho p e^{\gamma t} \gamma^{-\Delta-2} (2\tau)^{-1}. \quad (4.10)$$

Inserting Eq. (4.7) in Eq. (4.8) we obtain to first order in concentration

$$\begin{aligned} D(u) &= b f_{\Delta+1} \left(\frac{a}{u} - 2b \Delta! \gamma^2 \frac{a}{u^2} \right) \\ &= b f_{\Delta+1} (a/u) + 2b^2 \gamma^2 \Delta! \frac{d}{du} f_{\Delta+1} (a/u) \end{aligned} \quad (4.11)$$

and according to Eq. (2.18)

$$\langle R^2(u) \rangle = 2\Delta b u^{-2} \left(1 + 2b \gamma^2 \Delta! \frac{d}{du} \right) f_{\Delta+1} (a/u). \quad (4.12)$$

Using the expressions of Appendix C it is now a simple matter to find the inverse Laplace transform of Eq. (4.12) which gives the mean squared displacement $\langle R^2(t) \rangle$. We find [see for details Eqs. (C17)–(C21)]

$$\begin{aligned} \langle R^2(t) \rangle &= \frac{2\Delta b}{a(\Delta+2)} \left[g_{\Delta+2}(at) - 2b \gamma^2 \Delta! t g_{\Delta+2}(at) \right. \\ &\quad \left. + 4b \gamma^2 \Delta! \int_0^t ds g_{\Delta+2}(as) \right], \end{aligned} \quad (4.13)$$

with a and b given by Eqs. (4.9) and (4.10), respectively. Thus, for small times the diffusion coefficient $D(t)$ has the form

$$\begin{aligned} D(t) &= \frac{1}{2\Delta} \frac{d}{dt} \langle R^2(t) \rangle = \frac{b}{a(\Delta+2)} \{ a g'_{\Delta+2}(at) \\ &\quad + (2b \gamma^2 \Delta!) [g_{\Delta+2}(at) - a t g'_{\Delta+2}(at)] \} \\ &= a^{-1} b \left\{ \frac{g_{\Delta+1}(at)}{t} + 2b \gamma^2 \Delta! \left[\frac{g_{\Delta+2}(at)}{\Delta+2} - g_{\Delta+1}(at) \right] \right\}, \end{aligned} \quad (4.14)$$

where we used the recurrence formula obeyed by the $g_{\Delta}(t)$ functions [Eq. (A5) in Ref. 23]

$$t \frac{d}{dt} g_{\Delta}(t) = \Delta g_{\Delta-1}(t). \quad (4.15)$$

It turns out that the additional term in the short time expression for $D(t)$ is also a simple function of the $g_{\Delta}(t)$ forms. The first term of Eq. (4.14) is, as expected, identical to Eq. (2.38) of Sec. II.

We remark that for $t \rightarrow 0$, $D(t)$ behaves as t^{-1} , whereas in the multipolar case $D(t) \sim t^{(\Delta+2-s)/s}$ [Eq. (3.12) or (A7)]. In this limit the exchange case is very similar to multipolar interactions with large s .

B. Long time limit

We now turn our attention to the long time limit of $\langle R^2(t) \rangle$ and of $D(t)$. As we will see, in the pair approximation in the long time limit case, different dimensions lead to *qualitatively* different results.

We start by evaluating $\Phi(0)$, which when inserted into Eq. (4.1) yields the diffusion constant. Using the back-transfer expression [Eq. (2.30)] results in

$$\begin{aligned} \Phi(0) &= \int_0^{\infty} \Phi^{\text{BT}}(t) dt = (\tau/2 e^{\gamma t}) \\ &\quad \times \int_0^{\infty} \exp[-\frac{1}{2} V_{\Delta} \rho p \gamma^{-\Delta} g_{\Delta}(z)] dz. \end{aligned} \quad (4.16)$$

We observe that the functions $g_{\Delta}(z)$ have asymptotic expansions in powers of $\ln z$ [Eq. (A12) of Ref. 23]:

$$g_1(z) \approx \ln z + 0.58, \quad (4.17a)$$

$$g_2(z) \approx \ln^2 z + 1.15 \ln z + 1.98, \quad (4.17b)$$

$$g_3(z) \approx \ln^3 z + 1.73 \ln^2 z + 5.93 \ln z + 5.44, \quad (4.17c)$$

and generally

$$g_{\Delta}(z) \approx \sum_{j=0}^{\Delta} c_{j\Delta} (\ln z)^j. \quad (4.18)$$

If the concentration is not too high ($\frac{1}{2} V_{\Delta} \rho p \gamma^{-\Delta} \ll 1$), we may split the integration in Eq. (4.16) and use Eq. (4.18), obtaining

$$\begin{aligned} \Phi(0) &\approx (\tau/2 e^{\gamma t}) \left\{ 1 + \int_1^{\infty} \exp\left[-\frac{1}{2} V_{\Delta} \rho p \gamma^{-\Delta} \sum_{j=0}^{\Delta} c_{j\Delta} (\ln z)^j\right] dz \right\} \\ &= (\tau/2 e^{\gamma t}) \left\{ 1 + \int_0^{\infty} \exp\left[t - \frac{1}{2} V_{\Delta} \rho p \gamma^{-\Delta} \sum_{j=0}^{\Delta} c_{j\Delta} t^j\right] dt \right\}. \end{aligned} \quad (4.19)$$

The structure of the integral in Eq. (4.19) is considerably different for one, two, and three dimensions, warranting special treatment in every case.

Consider the one-dimensional case for which the leading term of the exponent in the integral Eq. (4.19)

is linear in t . The integral diverges for $1 > 2^{-1} V_1 \rho b \gamma^{-1} = p/(\gamma d)$. A more careful analysis is performed in Appendix D, where we evaluate Eq. (4.16) for the exact one-dimensional decay law without backtransfer. The result is similar in that the integral does not exist for $p < 1 - e^{-(\gamma d)/2}$. For these concentrations, therefore, our approach indicates the absence of diffusion $D(u=0) = 0$ in one dimension.

In two dimensions the leading term in the exponent of Eq. (4.19) is always negative and the integral exists:

$$\begin{aligned} \int_0^\infty \exp(-t^2 + a_1 t + a_2) dt \\ = \exp(a_2 + a_1^2/4) \int_{-a_1/2}^\infty e^{-x^2} dx \\ = \sqrt{\pi}/2 \exp(a_2 + a_1^2/4) \operatorname{erfc}(-a_1/2), \end{aligned} \quad (4.20)$$

with $\operatorname{erfc}(z)$ being the complementary error function [Eq. (7.1.2) in Ref. 32]. Therefore, in two dimensions we always find diffusive behavior in the pair approximation approach. However, assuming $V_\Delta \rho b \gamma^{-\Delta}$ to be small leads to

$$\Phi(0) \approx (\tau/2) e^{\gamma d} \sqrt{2\pi} e^{-c_E} \gamma (\pi \rho b)^{-1/2} \exp[\gamma^2 (2\pi \rho b)^{-1}], \quad c_E = 0.58, \quad (4.21)$$

which is thus a large number, and then $D(0)$ turns out to be quite small. We note that we could have obtained

$$\Phi(0) \approx (\tau/2) e^{\gamma d} \sqrt{2\pi} \gamma (\pi \rho b)^{-1/2} \exp[\gamma^2 (2\pi \rho b)^{-1}] \quad (4.22)$$

directly from Eq. (4.19) by keeping in the expansion of $g_2(t)$ the leading term $\ln^2 t$ only. The difference between the expressions is only $e^{-c_E} = 0.56$.

In three dimensions we have to consider the integral

$$\int_0^\infty \exp(-t^3 + a_1 t^2 + a_2 t + a_3) dt, \quad (4.23)$$

which is connected to the function $Hi(z)$ [Eq. (10.4.44) of Ref. 32, and Ref. 13]:

$$Hi(z) = \pi^{-1} \int_0^\infty \exp(-\frac{1}{3}t^3 + zt) dt. \quad (4.24)$$

Since we do not have a simple way to handle (4.23), we will again consider only the case of very low concentrations, and approximate $g_3(t)$ [Eq. (4.17c)] by its leading term $\ln^3 t$, obtaining

$$\begin{aligned} \Phi(0) &\approx (\tau/2) e^{\gamma d} \int_0^\infty \exp\left[t - \frac{2\pi}{3} \rho b \gamma^{-3} t^3\right] dt \\ &= (\tau/2) e^{\gamma d} \gamma (2\pi \rho b)^{-1/3} \pi Hi[\gamma (2\pi \rho b)^{-1/3}] \\ &= (\tau/2) e^{\gamma d} \pi^{1/2} \gamma^{3/4} (2\pi \rho b)^{-1/4} \exp\left[\frac{2}{3} \gamma^{3/2} (2\pi \rho b)^{-1/2}\right]. \end{aligned} \quad (4.25)$$

In Eq. (4.25) we used the asymptotic form of $Hi(x)$ for large x [Eq. (10.4.90) of Ref. 32]:

$$Hi(x) \sim \pi^{-1/2} x^{-1/4} \exp\left(\frac{2}{3} x^{3/2}\right). \quad (4.26)$$

The diffusion constant $D(0)$ follows simply by inserting into Eq. (4.1) either Eq. (4.22) for the two-dimensional case or Eq. (4.25) for three dimensions. We

present exemplarily only the three-dimensional result for $D(0)$; the two-dimensional expression follows analogously. Inserting Eq. (4.25) into Eq. (4.1) we obtain

$$\begin{aligned} D(0) &\approx \frac{4\pi}{3} \rho b e^{\gamma d} \gamma^{-5} (2\tau)^{-1} \\ &\times f_4\left[\pi^{1/2} \gamma^{3/4} (2\pi \rho b)^{-1/4} \exp\left[\frac{2}{3} \gamma^{3/2} (2\pi \rho b)^{-1/2}\right]\right] \\ &\approx 10^{-3} \frac{e^{\gamma d}}{\tau} \gamma^{7/4} (\rho b)^{-5/4} \exp\left[-\frac{2}{3} \gamma^{3/2} (2\pi \rho b)^{-1/2}\right], \end{aligned} \quad (4.27)$$

which is identical to the long time limit of $D(t)$. In Eq. (4.27) we have used the asymptotic value of $f_\Delta(y)$ [Eq. (C8)]. Due to the many approximations involved, the value of Eq. (4.27) is only of a qualitative nature.

V. CONCLUSIONS

In this work we have studied the dynamical properties of the migration of the excitation among impurity molecules in the framework of the pair approximation. We demonstrated that, from a simple equation (2.15), we obtain, using known forms for $\Phi(t)$, in a completely straightforward fashion, the multipolar and the exchange behavior, for all dimensions, for both short and relatively long times. Our results agree with results obtained in special cases (mainly three-dimensional) by independent, more elaborate methods. In particular, they agree well with the self-consistent results of GAF.

Our procedure was motivated by the observation that Eq. (2.15) connects, in the framework of the pair approximation [see the discussion before Eq. (2.12)], the dynamical properties of the migration of the excitation with the decay law $\Phi(t)$. We use decay laws varying in their degree of sophistication but always in a pair approximation and obtain the short and long time behavior of the generalized diffusion coefficient and of the mean squared displacement.

We found that in the short time limit the dynamical properties are not sensitive to the detailed way in which backtransfer is included. For example, the first term in the series expansion of the diffusion coefficient is completely independent of the form of $\Phi(t)$. In the exchange case the second term also does not depend on whether backtransfer is included or not. The multipolar case differs in that inclusion of backtransfer leads to an additional factor to the second term; however, two different ways of including backtransfer into $\Phi(t)$ lead to precisely the same result for the second term of the diffusion coefficient.

For the long time behavior, because of the assumption of the pair approximation, our results may only be viewed as qualitative; we expect that one has to go well beyond the pair approximation in order to test the reliability of the long time expressions. However, the results for the diffusion coefficient at long times agree closely with the results derived by other methods.^{9,30}

Our results are qualitatively different for multipolar and for exchange interactions. In the multipolar case, we find for long times diffusive behavior in all dimen-

sions; however, the numerical values for one-dimensional high multipolar interactions strongly suggest that the excitation is more and more localized as the interaction becomes shorter ranged. The long time limit in the exchange case depends *qualitatively* on dimension. In the one-dimensional case we find localization (i.e., $D=0$) for moderate and low concentrations of impurity molecules. It is interesting to note that already the pair approximation leads to the localized behavior in one dimension, behavior which has been tested by independent calculations.³¹ In two dimensions, for exchange interactions we find diffusive behavior; however, the value of the diffusion constant is rather small for low concentrations of impurities. The three-dimensional case shows, as with multipolar interactions, typical diffusive behavior at long times.

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APPENDIX A: THE HAAN-ZWANZIG SCALING ARGUMENT

In Sec. II we derived the short time limits of both $\langle R^2(t) \rangle$ and $D(t)$, corresponding to $\Phi(u)=1/u$. These derivations hold for exchange and multipolar interactions and for all dimensionalities Δ .

Here we verify the short time multipolar results using the Haan-Zwanzig scaling argument extended to include arbitrary Δ and s (s being the power of the multipolar interaction).⁷

Let λ be an arbitrary positive number and replace r by λr ; then the density $\tilde{\rho} = \rho \lambda^{\Delta}$, the wave vector k , and the time t scale as

$$\begin{aligned}\tilde{\rho} &\rightarrow \lambda^{-\Delta} \tilde{\rho}, \\ k &\rightarrow \lambda^{-1} k, \\ t &\rightarrow \lambda^s t.\end{aligned}\quad (\text{A1})$$

The generalized $D(\tilde{\rho}, k, u)$, having the dimensions of $[\text{length}]^2/\text{time}$, scales as λ^{2-s} . Since in the continuum approximation the transformed diffusion coefficient describes the same physical problem, the D value is invariant if (Haan-Zwanzig argument)

$$D(\tilde{\rho}, k, u) = \lambda^{2-s} D(\lambda^{-\Delta} \tilde{\rho}, \lambda^{-1} k, \lambda^{-s} u). \quad (\text{A2})$$

We consider the $k=0$ limit of D which determines the migration of an excitation at large displacements and choose $\lambda = u^{1/s}$. Then

$$D(\tilde{\rho}, 0, u) = u^{(s-2)/s} D(u^{-\Delta/s} \tilde{\rho}, 0, 1). \quad (\text{A3})$$

Assuming $D(u^{-\Delta/s} \tilde{\rho}, 0, 1)$ to be an analytical function of $\tilde{\rho}$ one has:

$$D(\tilde{\rho}, 0, u) = u^{(s-2)/s} \sum_{j=1}^{\infty} c_j (u^{-\Delta/s} \tilde{\rho})^j. \quad (\text{A4})$$

In Eq. (A4) the summation starts at $j=1$, since we suppose that for small densities (or short times) D is proportional to $\tilde{\rho}$. From Eq. (A4) we now have readily, with Eqs. (2.16), (2.18), and (2.19)

$$\begin{aligned}\langle R^2(u) \rangle &= 2\Delta u^{-2} \sum_{j=1}^{\infty} c_j \tilde{\rho}^j u^{(s-2-j\Delta)/s} \\ &= 2\Delta \sum_{j=1}^{\infty} c_j \tilde{\rho}^j u^{-1-(2+j\Delta)/s},\end{aligned}\quad (\text{A5})$$

$$\begin{aligned}\langle R^2(t) \rangle &= \mathcal{L}^{-1} \langle R^2(u) \rangle \\ &= 2\Delta \sum_{j=1}^{\infty} c_j \tilde{\rho}^j t^{(2+j\Delta)/s} / \Gamma[1 + (2+j\Delta)/s],\end{aligned}\quad (\text{A6})$$

$$\begin{aligned}D(t) &= \frac{1}{2\Delta} \frac{d}{dt} \langle R^2(t) \rangle \\ &= \sum_{j=1}^{\infty} c_j \tilde{\rho}^j t^{(2+j\Delta)/s} / \Gamma[(2+j\Delta)/s].\end{aligned}\quad (\text{A7})$$

The time behavior of Eqs. (A6) and (A7) is identical to the results for the multipolar interactions, which we derived in Secs. II and III.

APPENDIX B: BACKTRANSFER IN THE SHORT TIME LIMIT

In the course of this work we have utilized forms for backtransfer which were obtained from the known equations in the absence of backtransfer by the transformation $t \rightarrow 2t$, $p \rightarrow p/2$. This procedure was motivated by the Huber *et al.* approximation¹⁹ for the short time behavior of $\Phi(t)$ in the presence of backtransfer:

$$\begin{aligned}\Phi(t) &= \prod_{i=1}^N \{1 - p \{1 - e^{-w(r_i)t} \cosh[w(r_i)t]\}\} \\ &= \prod_{i=1}^N \left[1 - \frac{p}{2} (1 - e^{-2w(r_i)t})\right],\end{aligned}\quad (\text{B1})$$

while

$$\Phi(t) = \prod_{i=1}^N [1 - p(1 - e^{-w(r_i)t})] \quad (\text{B2})$$

is the *exact* solution of the transfer problem in the absence of back transfer.^{22,28} The products in Eqs. (B1) and (B2) extend over all sites. One obtains Eq. (B1) by a configurational averaging of decay laws of the form

$$P_{i=0}(t) = \prod \{1 - e^{-w(r_i)t} \cosh[w(r_i)t]\}, \quad (\text{B3})$$

where the product extends only over the positions occupied by impurity molecules. (For details see Ref. 23.)

One should remark that, apart from the case of a single pair of molecules present, Eq. (B3) is *no* solution of any master equation of the form (2.1). For long times, for any $P_i(t)$ which are solution of a master equation (2.1), that includes backtransfer

$$\lim_{t \rightarrow \infty} P_i(t) = \frac{1}{m} \quad (\text{all } i), \quad (\text{B4})$$

where m is the total number of impurity molecules present, whereas from Eq. (B3)

$$\lim_{t \rightarrow \infty} \prod \{1 - e^{-w(r_i)t} \cosh[w(r_i)t]\} = \frac{1}{2^{m-1}}. \quad (\text{B5})$$

An equation which is the solution to a reduced master equation of the general problem and which includes back-transfer was given by Lyo.²¹ In the low concentration limit he finds, using the continuum approximation for multipolar interactions in three dimensions, the following form for $\Phi(u)$ [Eq. (2.6) of Ref. 21]:

$$\Phi(u) = \frac{1}{u} \int_0^\infty e^{-x} \exp\left[-p\rho d^3 \left(\frac{1}{\pi u}\right)^{3/s} G_s(x)\right] dx, \quad (\text{B6})$$

where [Eq. (2.7) of Ref. 21]

$$G_s(x) = \frac{8\pi x}{3} \int_0^{\pi/2} \cos\theta \sin\theta \tan^{\delta/s}\theta \exp(-x \cos^2\theta) d\theta, \quad (\text{B7})$$

which, by setting $t = \cos^2\theta$, transforms to

$$G_s(x) = \frac{4\pi}{3} x \int_0^1 \left(\frac{1-t}{t}\right)^{3/s} e^{-xt} dt. \quad (\text{B8})$$

One may observe that the integral in Eq. (B8) may be expressed in terms of the beta and the hypergeometric functions [Eq. (3.383) of Ref. 29]:

$$\int_0^1 t^{-3/s}(1-t)^{3/s} e^{-xt} dt = B(1+3/s, 1-3/s) {}_1F_1(1-3/s; 2; -x). \quad (\text{B9})$$

However, to calculate the first two terms in the asymptotic expansion of $\Phi(u)$ one has simply to expand the exponent to the second term in Eq. (B6):

$$\Phi(u) = \frac{1}{u} \int_0^\infty e^{-x} dx - \frac{1}{u^{1+3/s}} \frac{p\rho d^3}{\tau^{3/s}} \frac{4\pi}{3} \cdot I, \quad (\text{B10})$$

with

$$\begin{aligned} I &= \int_0^\infty dx x e^{-x} \int_0^1 \left(\frac{1-t}{t}\right)^{3/s} e^{-xt} dt \\ &= \int_0^1 dt \left(\frac{1-t}{t}\right)^{3/s} \int_0^\infty dx x e^{-x(1+t)} \\ &= \int_0^1 dt \frac{1}{(1+t)^2} \left(\frac{1-t}{t}\right)^{3/s} = \int_0^\infty \frac{dz}{(z+1)^2} \frac{(z+1)^2}{(z+2)^2} z^{3/s} \\ &= 2^{(3/s)-1} \int_0^\infty \frac{dt t^{3/s}}{(t+1)^2} = 2^{3/s-1} \frac{3}{s} \frac{\pi}{\sin\left(\frac{3\pi}{s}\right)}. \end{aligned} \quad (\text{B11})$$

In the last line we made use of Eq. (3.194.6) of Ref. 29. Thus, in the multipolar three-dimensional case we obtain from Lyo

$$\Phi(u) = \frac{1}{u} - \frac{1}{u^{1+3/s}} \frac{p\rho d^3}{\tau^{3/s}} \frac{4\pi}{3} 2^{(3/s)-1} \frac{3\pi}{s \sin\left(\frac{3\pi}{s}\right)}, \quad (\text{B12})$$

which is identical to Eq. (3.8) in three dimensions:

$$\Phi(u) = \frac{1}{u} - \frac{1}{u^{1+\Delta/s}} \frac{p\rho d^\Delta V_\Delta}{\tau^{\Delta/s}} 2^{\Delta/s-1} \frac{\Delta}{s} \frac{\pi}{\sin\left(\frac{\Delta\pi}{s}\right)}. \quad (\text{B13})$$

As discussed in Sec. II, the first term in the expansion of $\Phi(u)$ is always $1/u$. Here we find that also

the second term in the expansion of $\Phi(u)$ is insensitive to the way in which back transfer was included in the approximate forms for $\Phi(t)$.

APPENDIX C: THE FUNCTION $f_\Delta(y)$

In Sec. IV we introduced the function $f_\Delta(y)$ [Eq. (4.2)]:

$$f_\Delta(y) \equiv \int_0^\infty dx \frac{x^\Delta}{e^x + y} \quad (y \geq 0). \quad (\text{C1})$$

One verifies readily the following properties of the function $f_\Delta(y)$:

$$f_\Delta(0) = \int_0^\infty dx x^\Delta e^{-x} = \Delta!, \quad \text{for all } \Delta, \quad (\text{C2})$$

$$f_\Delta(1) = \int_0^\infty dx x^\Delta (e^x + 1)^{-1} = (1 - 2^{-\Delta}) \Delta! \zeta(\Delta + 1), \quad (\text{C3})$$

where ζ is the Riemann zeta function and we made use of Eq. (23.2.8) of Ref. 32. Also, $f_\Delta(y)$ is a monotonically strictly decreasing function of y , with $\lim_{y \rightarrow \infty} f_\Delta(y) = 0$.

If $y < 1$, then one may expand the integrand in Eq. (C1) and integrate each term of the resulting series separately:

$$\begin{aligned} f_\Delta(y) &= \int_0^\infty dx x^\Delta e^{-x} \sum_{j=0}^\infty (-1)^j y^j e^{-jx} \\ &= \sum_{j=0}^\infty (-y)^j \int_0^\infty dx x^\Delta e^{-(j+1)x} = \Delta! \sum_{j=0}^\infty \frac{(-y)^j}{(j+1)^{\Delta+1}}. \end{aligned} \quad (\text{C4})$$

For $y > 1$ we obtain upper and lower bounds on $f_\Delta(y)$ by splitting the integration in Eq. (C1) at $x_0 = \ln y$:

$$\begin{aligned} f_\Delta(y) &= \int_0^{x_0} dx \frac{x^\Delta}{e^x + y} + \int_{x_0}^\infty dx \frac{x^\Delta}{e^x + y} \\ &\leq \int_0^{x_0} dx x^\Delta y^{-1} + \int_{x_0}^\infty dx x^\Delta e^{-x} \\ &= \frac{x_0^{\Delta+1}}{y(\Delta+1)} + \Delta! \cdot e^{-x_0} \cdot \sum_{j=0}^\infty \frac{x_0^j}{j!}. \end{aligned} \quad (\text{C5})$$

In the last line of Eq. (C5) we have integrated repeatedly by parts. Thus,

$$f_\Delta(y) \leq \frac{\Delta!}{y} \sum_{j=0}^{\Delta+1} \frac{(\ln y)^j}{j!} \quad (y > 1) \quad (\text{C6})$$

and similarly

$$f_\Delta(y) \geq \frac{1}{2} \int_0^{x_0} dx x^\Delta y^{-1} + \frac{1}{2} \int_{x_0}^\infty dx x^\Delta e^{-x} = \frac{\Delta!}{2y} \sum_{j=0}^{\Delta+1} \frac{(\ln y)^j}{j!} \quad (y > 1). \quad (\text{C7})$$

Asymptotically, $f_\Delta(y) \approx (\ln y)^{\Delta+1}/[(\Delta+1)y]$ or, equivalently,

$$\lim_{y \rightarrow \infty} (\Delta+1)y f_\Delta(y) (\ln y)^{-\Delta-1} = 1 \quad (\text{C8})$$

as may be verified readily by setting $y = e^t$, observing that

$$h(t) \equiv e^t f_\Delta(e^t) = \int_0^\infty \frac{dx x^\Delta}{e^{x+t} + 1} = \int_{-t}^\infty \frac{dx (x+t)^\Delta}{e^x + 1} \quad (\text{C9})$$

and applying L'Hôpital's rule $(\Delta+1)$ times to the quotient $\lim_{t \rightarrow \infty} [(\Delta+1)h(t)/t^{\Delta+1}]$.

The functions $f_{\Delta}(y)$ are closely related to the $g_{\Delta}(t)$ functions [Eq. (2.27)]:

$$g_{\Delta}(t) \equiv \Delta \int_0^{\infty} [1 - \exp(-te^{-x})] x^{\Delta-1} dx \quad (\Delta \neq 0) \quad (C10)$$

that appear in the expressions for the excitation decay of a donor molecule, when the direct energy transfer to randomly distributed acceptors is due to exchange [Ref. 4, Eq. (21), Ref. 18, Eq. (3.13), Ref. 23, Eqs. (A1)ff.]. The Laplace transform of $g_{\Delta}(t)$ is $\Delta u^{-2} f_{\Delta-1}(u^{-1})$:

$$\mathcal{L}[g_{\Delta}(t)] = \frac{\Delta}{u^2} f_{\Delta-1}\left(\frac{1}{u}\right), \quad (C11)$$

since

$$\begin{aligned} \mathcal{L}[g_{\Delta}(t)] &= \Delta \int_0^{\infty} dt e^{-ut} \int_0^{\infty} dx x^{\Delta-1} [1 - \exp(-te^{-x})] \\ &= \Delta \int_0^{\infty} dx x^{\Delta-1} \left(\frac{1}{u} - \frac{1}{u+e^{-x}} \right) \\ &= \frac{\Delta}{u^2} \int_0^{\infty} \frac{dx x^{\Delta-1}}{e^x + u^{-1}}. \end{aligned} \quad (C12)$$

Also, integrating Eq. (C10) by parts one obtains

$$g_{\Delta}(t) = t \int_0^1 \exp(-tx) (-\ln x)^{\Delta} dx \quad (C13)$$

and thus

$$\begin{aligned} \mathcal{L}[g_{\Delta}(t)/t] &= \int_0^{\infty} dt e^{-ut} \int_0^1 dx e^{-tx} (-\ln x)^{\Delta} \\ &= \int_0^1 dx (-\ln x)^{\Delta} (x+u)^{-1} \\ &= \int_0^{\infty} dy \frac{e^{-y} y^{\Delta}}{e^{-y} + u} = \frac{1}{u} \int_0^{\infty} dx \frac{x^{\Delta}}{e^x + u^{-1}}. \end{aligned} \quad (C14)$$

Therefore,

$$\mathcal{L}[g_{\Delta}(t)/t] = u^{-1} f_{\Delta}(u^{-1}). \quad (C15)$$

Remembering that $g_{\Delta}(t) \approx (\ln t)^{\Delta}$ as $t \rightarrow \infty$, Eqs. (4.17), (4.18) [Ref. 4, Eq. (28); Ref. 23, Eq. (A12)], and that

$$f_{\Delta}\left(\frac{1}{u}\right) \approx \frac{1}{\Delta+1} u [\ln(1/u)]^{\Delta+1}, \quad \text{as } u \rightarrow 0.$$

Equation (C11) turns out to be a special case of the Tauberian theorem of Hardy-Littlewood and Karamata,³³ stating that if $\mathcal{L}[f_1(t)] = f_2(u)$, and $f_2(u) \approx u^{-k} A(1/u)$ as $u \rightarrow 0$, and A is a slowly varying function, i.e., for $\lambda > 0$, $A(\lambda u)/A(u) \approx 1 \approx A(\lambda/u)/A(1/u)$ as $u \rightarrow 0$, and $k > 0$, then

$$f_1(t) \approx t^{k-1} A(t)/\Gamma(k). \quad (C16)$$

In Eq. (C11), $A(1/u) = [\ln(1/u)]^{\Delta}$ and $k=1$; from the theorem follows that $g_{\Delta}(t) \approx (\ln t)^{\Delta}$, as is indeed the case.

On the other hand, Eq. (C15) shows that the condition that k be strictly larger than zero is essential. In Eq. (C15) one has

$$u^{-1} f_{\Delta}(u^{-1}) \approx \frac{1}{\Delta+1} [\ln(1/u)]^{\Delta+1} \text{ and } g_{\Delta}(t)/t \approx \frac{1}{t} (\ln t)^{\Delta};$$

thus, the exponent of the logarithmic function entering the Laplace transform differs from that of the original function.

As an example for the utility of the relations between

$g_{\Delta}(t)$ and $f_{\Delta}(u)$ derived in this Appendix, we now present the steps that lead from Eq. (4.12) to Eq. (4.13) of the main text.

Observing that for $a > 0$ from $\mathcal{L}[f_1(t)] = f_2(u)$, it follows that $\mathcal{L}[af_1(at)] = f_2(u/a)$; one has with Eq. (C11) immediately for the first term of Eq. (4.12):

$$\mathcal{L}^{-1} \left[\frac{(\Delta+2)a^2}{u^2} f_{\Delta+1}(a/u) \right] = ag_{\Delta+2}(at). \quad (C17)$$

For the second term of Eq. (4.12) we note that

$$\begin{aligned} \mathcal{L}^{-1} \left[u^{-2} \frac{d}{du} f_{\Delta+1}(a/u) \right] &= \mathcal{L}^{-1} \left\{ \frac{d}{du} [u^{-2} f_{\Delta+1}(a/u)] \right\} \\ &\quad + 2\mathcal{L}^{-1} \left\{ \frac{1}{u} [u^{-2} f_{\Delta+1}(a/u)] \right\}. \end{aligned} \quad (C18)$$

Since $\mathcal{L}[f_1(t)] = f_2(u)$ implies

$$\mathcal{L} \left[\int_0^t ds f_1(s) \right] = \frac{1}{u} f_2(u) \quad (C19)$$

and

$$\mathcal{L}[tf_1(t)] = -\frac{d}{du} f_2(u), \quad (C20)$$

one obtains from Eq. (C17)

$$\begin{aligned} \mathcal{L}^{-1} \left[u^{-2} \frac{d}{du} f_{\Delta+1}(a/u) \right] &= (\Delta+2)^{-1} a^{-1} \left[-tg_{\Delta+2}(at) + 2 \int_0^t ds g_{\Delta+2}(as) \right], \end{aligned} \quad (C21)$$

from which Eq. (4.13) follows.

APPENDIX D: THE ONE-DIMENSIONAL EXCHANGE CASE

In the course of this paper we made use of different approximations to $\Phi(0)$, expressing them as integrals over different decay functions $\Phi(t)$:

$$\Phi(0) = \int_0^{\infty} \Phi(t) dt. \quad (D1)$$

It is worth observing that for fixed t , $\Phi(t)$ in the absence of backtransfer is smaller or at most equal to any $\Phi(t)$ obtained by including some backtransfer. Therefore, it is of interest that in the one-dimensional exchange case, the integral (D1) is already divergent for a certain range of concentrations, for $\Phi(t)$ that does not include backtransfer. It is this fact that we now proceed to show.

The exact $\Phi(t)$ in the absence of backtransfer for the one-dimensional exchange problem is^{22,28}

$$\begin{aligned} \Phi(t) &= \prod_{i=1}^{\infty} \left\{ 1 - p \left[1 - \exp \left(-\frac{t}{\tau} e^{\gamma_d} e^{-|t|\gamma_d} \right) \right] \right\} \\ &= \prod_{i=1}^{\infty} \left\{ 1 - p \left[1 - \exp \left(-\frac{t}{\tau} e^{(1-i)\gamma_d} \right) \right] \right\}^2, \end{aligned} \quad (D2)$$

which may be transformed in standard fashion to^{5,22}

$$\ln \Phi(t) = - \sum_{k=1}^{\infty} \frac{p^k}{k} S_k(t) \quad (p < 1), \quad (D3)$$

with

$$S_k(t) = 2 \sum_{i=1}^{\infty} \left[1 - \exp \left(-\frac{t}{\tau} e^{(1-i)\gamma d} \right) \right]^k$$

$$= 2 \sum_{i=1}^{\infty} [M_i(t)]^k, \quad (\text{D4})$$

where we introduced

$$M_i(t) = 1 - \exp \left(-\frac{t}{\tau} e^{(1-i)\gamma d} \right). \quad (\text{D5})$$

We now establish a lower bound for the *exact* $\Phi(t)$, and show that this lower bound, inserted into Eq. (D1), leads to divergent expressions for a range of p values.

From Eq. (D5) we have

$$0 \leq M_i(t) < 1, \quad \text{for } t \text{ finite}, \quad (\text{D6})$$

$$M_i(t) < M_j(t), \quad \text{for } 0 \leq j < i, \quad (\text{D7})$$

$$M_i(t) < M_i(t'), \quad \text{for } t < t'. \quad (\text{D8})$$

From Eq. (D6) it follows that

$$S_k(t) = 2 \sum_{i=1}^{\infty} [M_i(t)]^k \leq 2 \sum_{i=1}^{\infty} M_i(t) = S_1(t) \quad (\text{D9})$$

and therefore, with Eq. (D3),

$$\ln \Phi(t) = - \sum_{k=1}^{\infty} \frac{p^k}{k} S_k(t)$$

$$\geq - \sum_{k=1}^{\infty} \frac{p^k}{k} S_1(t) = S_1(t) \ln(1-p). \quad (\text{D10})$$

Furthermore, since $M_i(t)$ is a monotonically decreasing function of i [Eq. (D7)], one has

$$S_1(t) = 2 \sum_{i=1}^{\infty} M_i(t)$$

$$\leq 2 \int_0^{\infty} M_x(t) dx = 2 \int_0^{\infty} \left[1 - \exp \left(-\frac{t}{\tau} e^{\gamma d} e^{-x\gamma d} \right) \right] dx$$

$$= \frac{2}{\gamma d} g_1 \left(\frac{t}{\tau} e^{\gamma d} \right), \quad (\text{D11})$$

where we used definition (C10). Since $\ln(1-p)$ is negative for $p < 1$, one has by combining Eq. (D10) and (D11)

$$\ln \Phi(t) \geq S_1(t) \ln(1-p) \geq \frac{2 \ln(1-p)}{\gamma d} g_1 \left(\frac{t}{\tau} e^{\gamma d} \right). \quad (\text{D12})$$

We observe now that

$$g_1(t) = \int_0^{\infty} [1 - \exp(-te^{-x})] dx = \int_0^t \frac{dy}{y} (1 - e^{-y}) \quad (\text{D13})$$

and thus, for $t > 1$,

$$g_1(t) = g_1(1) + \int_1^t \frac{dy}{y} (1 - e^{-y}) \leq g_1(1) + \ln(t), \quad (\text{D14})$$

since $\int_1^t dy y^{-1} (1 - e^{-y})$ exists and is positive for $t > 1$.

Defining now an auxiliary function $h(t)$ as

$$h(t) = \begin{cases} g_1(1), & \text{if } t \leq 1, \\ g_1(1) + \ln(t), & \text{if } t > 1, \end{cases} \quad (\text{D15})$$

we have, again because $\ln(1-p)$ is negative,

$$\ln \Phi(t) \geq 2 \ln(1-p) \cdot h \left(\frac{t}{\tau} e^{\gamma d} \right) / (\gamma d). \quad (\text{D16})$$

Finally

$$\int_0^{\infty} \Phi(t) dt \geq \int_0^{\infty} \exp [2 \ln(1-p) h(e^{\gamma d} t / \tau) / (\gamma d)] dt$$

$$= \tau e^{-\gamma d} \exp [2 g_1(1) \ln(1-p) / (\gamma d)]$$

$$\times \left\{ 1 + \int_1^{\infty} dt \cdot t^{2 \ln(1-p) / (\gamma d)} \right\}. \quad (\text{D17})$$

The integral on the rhs of Eq. (D17) is divergent for $2 \ln(1-p) / (\gamma d) > -1$, i.e., for $p < 1 - e^{-\gamma d/2}$. Thus, for concentrations smaller than $p = 1 - e^{-\gamma d/2}$, $\Phi(0)$ given by Eq. (D1) does not exist.

One may observe that for $p = 1$ Eq. (D2) leads to an exponential decay

$$\Phi(t) = \exp \left(-\frac{2t e^{\gamma d}}{\tau} \sum_{j=1}^{\infty} e^{-j\gamma d} \right) = \exp(-\text{const.} \cdot t), \quad (\text{D18})$$

which, inserted into Eq. (D1), gives a finite result.

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