Electronic excited state transport among molecules distributed randomly in a finite volume

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A theoretical study of electronic excited state transport among molecules randomly distributed in a finite volume is carried out. Two special cases of the general transport and trapping problem are treated. A truncated series expansion in powers in the chromophore density is used as an approximation for one component systems (i.e., donor–donor transport only). In two component systems of donors and traps, the Förster limit, in which transfer can occur only from donors to traps due to low donor concentrations, is solved exactly for a finite spherical volume. In both cases, the results presented demonstrate that time-dependent observables can be significantly altered in finite volume systems relative to infinite volume systems. These calculations have implications for the interpretation of experiments performed on real finite volume systems, e.g., energy transport among the chromophores of an isolated polymer chain.

I. INTRODUCTION

The problem of electronic excited state transport and trapping in systems composed of molecules randomly distributed in solution has been the subject of extensive theoretical and experimental work. Only relatively recently have the important features of the problem become well understood. Very good approximate theoretical treatments of the transport and trapping problem in infinite random systems have been developed.[1–3] Haan and Zwanzig[1(a)] used an expansion in powers of density to show that transport in one component systems (i.e., no traps present) was nondiffusive for short times. Gochanour, Andersen, and Fayer[2] (hereafter referred to as GAF) used a diagrammatic technique to obtain approximations which are not restricted to short times because they include terms to infinite order in density. They demonstrated that transport in one component systems is diffusive at long times within their approximation and that this is almost certainly a property of the exact solution. Loring, Andersen, and Fayer[3] later extended this technique to include trapping. These theories are able to accurately predict experimental results.[4,5]

There are many physical systems involving energy transport which cannot be reasonably modeled by a uniform chromophore density in an infinite volume. Examples are mixtures of polymers under phase-separated conditions,[6] photosynthetic antenna complexes,[7] and energy transport in micellar systems.[8] In this paper, we address the problem of excited state energy transport when the chromophores are constrained to a volume of microscopic dimensions. Qualitatively, it is not difficult to appreciate the effects of the finite volume on the problem. Molecules near the edge of the volume have a smaller number of nearby chromophores than molecules near the center. Thus, the time required for transport away from the originally excited molecule averaged over all starting positions and chromophore configurations in the finite volume will be slower than in an infinite volume of the same chromophore density. Additionally, transport cannot become diffusive in the long time limit even in the absence of traps. The mean-squared-displacement must approach a constant as excitation probability is equalized throughout the finite volume. Clearly, the effects of the finite volume will be most pronounced when the volume dimensions are comparable to the critical radius for energy transport R_0. The results presented in this paper indicate that finite volumes significantly alter the behavior of time-dependent observables in many cases.

Throughout this paper, we use as our model the simplest possible finite volume in three dimensions, a spherical volume of randomly distributed and oriented chromophores. Here we will not treat the complete problem of arbitrary numbers of donors and traps in a finite spherical volume. Rather, we treat two special cases. In Sec. II, we consider a one-component system. This is analogous to the problem which GAF attacked in an infinite volume. The diagrammatic technique they employed is not directly applicable to the present problem because the finite volume destroys the translational invariance of the Green function. This property is essential in the topological reduction which allows the inclusion of high order terms in powers of the chromophore density. Nevertheless, their theory will provide a valuable comparison to the finite theory in the limit of very large volumes. We have chosen to employ an expansion in powers of density for the finite volume problem. This technique was applied to the infinite volume problem by Haan,[9] and Haan and Zwanzig.[1(a)] It provides results which are most accurate for short times or low concentrations. For certain properties, such as the probability of finding an excitation on the originally excited molecule, the density expansion can provide a reasonable approximation for all experimentally accessible times.

In Sec. III, we consider the case where the number of trap molecules is much greater than the number of donor molecules. Donor–donor interactions can then be ignored. Since back transfer from trap to donor is not allowed the general problem is greatly simplified in this limit (referred to as the Förster limit). Förster solved this problem exactly for an infinite volume.[10] Here we present the exact solution for a finite spherical volume. This solution provides insights into the nature of trapping in finite systems and exact results which can be com-

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pared to those obtained from a density expansion of the same problem. Such a comparison indicates that the approximation used in the finite volume one-component problem (Sec. II) is quite good.

Section IV contains a qualitative discussion of the results. In Sec. V, we discuss the approximations of Sec. II and indicate the conditions under which those results are expected to be reasonably accurate. Although there has been some work previously,[11] to our knowledge this is the first work on the general problem of excitation transport among randomly distributed chromophores in a finite volume. It is hoped that this work will begin to provide a firmer footing for the interpretation of experiments on finite volume systems.

II. ONE COMPONENT SYSTEM–DENSITY EXPANSION APPROXIMATION

In this section, we consider a finite spherical volume Ω of radius R containing N donor molecules and no traps. The quantity we wish to calculate is the probability that an excitation is on the originally excited molecule at time t, in the absence of decay due to the excited state lifetime. This probability, $G^s(N, \Omega, t)$, is the only easily accessible experimental observable for the model under consideration (using time resolved fluorescence depolarization experiments, for example[4]). The mean-squared displacement, which is, in principle, observable in infinite systems,[12] is not an appropriate observable when the excitation is limited to a finite volume with $R \sim R_0$.

In the following, we develop an expression for $\hat{G}^s(N, \Omega, \epsilon)$, the Laplace transform of $G^s(N, \Omega, t)$, and then approximate it through an expansion in powers of density. The inverse Laplace transform of the final result is easily performed to yield $G^s(N, \Omega, t)$. The formalism used here [Eqs. (1)–(10)] follows that of GAF. It is briefly summarized for clarity.

The configuration of the system K is characterized by the locations of the N donor molecules, $(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$. The probability that an excitation is found on the jth molecule for the configuration K at time t, satisfies the master equation

$$\frac{dp_j'(K,t)}{dt} = -\frac{p_j'(K,t)}{\tau} + \sum_{i=1}^{N} w_{ji}\left[p_i'(K,t) - p_j'(K,t)\right] . \quad (1)$$

τ is the measured excited state lifetime and w_{ji} is the transfer rate between molecules j and i ($w_{jj} = 0$). For dipole–dipole interactions, the orientation averaged transfer rate is

$$w_{ji} = \frac{1}{\tau}\left(\frac{R_0^{DD}}{r_{ji}}\right)^6 , \quad (2)$$

where R_0^{DD}, the critical transfer radius for donor–donor transport, contains the strength of the interaction. (The full angular dependence of the transfer rate needs to be considered in calculating some observables.[4] Here we consider the orientation averaged rate because it is the simplest case which allows the effects of the finite volume to be investigated. It is straightforward to consider various angular distributions.[13])

The substitution

$$p_j(K,t) = p_j'(K,t)\exp(t/\tau) \quad (3)$$

eliminates the lifetime decay term in Eq. (1) and allows the transformed Eq. (1) to be written in matrix form as

$$\frac{d\mathbf{p}(K,t)}{dt} = \mathbf{W}\cdot\mathbf{p}(K,t) , \quad (4)$$

where

$$W_{ji} = w_{ji} - \delta_{ji}\sum_{l} w_{il} . \quad (5)$$

Let $P(N, \Omega, \mathbf{r}, t)$ be the ensemble average density of excitations. Then

$$P(N,\Omega,\mathbf{r},t) = \int d\mathbf{r}'\, G(N,\Omega,\mathbf{r},\mathbf{r}',t)P(N,\Omega,\mathbf{r}',0) , \quad (6)$$

where $G(N, \Omega, \mathbf{r}, \mathbf{r}', t)$ is a Green function which can be written as follows:

$$G(N,\Omega,\mathbf{r},\mathbf{r}',t) = G^s(N,\Omega,\mathbf{r},\mathbf{r}',t) + G^m(N,\Omega,\mathbf{r},\mathbf{r}',t) , \quad (7)$$

$$G^s(N,\Omega,\mathbf{r},\mathbf{r}',t) = \Omega\langle\delta(\mathbf{r}_1-\mathbf{r})\delta(\mathbf{r}_1-\mathbf{r}')[\exp(t\mathbf{W})]_{11}\rangle , \quad (8)$$

$$G^m(N,\Omega,\mathbf{r},\mathbf{r}',t) = (N-1)\Omega\langle\delta(\mathbf{r}_2-\mathbf{r})\delta(\mathbf{r}_1-\mathbf{r}') \times[\exp(t\mathbf{W})]_{12}\rangle . \quad (9)$$

The brackets indicate the ensemble average

$$\langle A(K)\rangle = \frac{1}{\Omega^N}\int_\Omega d\mathbf{r}_1\cdots\int_\Omega d\mathbf{r}_N A(K) . \quad (10)$$

In Eqs. (8) and (9), the initially excited molecule has been labeled molecule 1, while the molecule at $\mathbf{r}$ in Eq. (9) is molecule 2. The integral of $G^s(N, \Omega, \mathbf{r}, \mathbf{r}', t)$ over the spatial coordinates

$$G^s(N,\Omega,t) = \frac{1}{\Omega}\int_\Omega d\mathbf{r}\int_\Omega d\mathbf{r}'\, G^s(N,\Omega,\mathbf{r},\mathbf{r}',t) \quad (11)$$

is the probability that the excitation is on the originally excited molecule at time t. Similarly integrating $G^m(N, \Omega, \mathbf{r}, \mathbf{r}', t)$ over the spatial coordinates gives the probability that the excitation is not on the originally excited molecule. Information about the time dependent location of the excitation can be obtained by integrating $G^m(N, \Omega, \mathbf{r}, \mathbf{r}', t)$ over small volumes about $\mathbf{r}$ and $\mathbf{r}'$. This gives the probability of finding the excitation at $\mathbf{r}$ at time t given that it was initially at $\mathbf{r}'$.

It is convenient to deal with the Laplace transform of G^m:

$$\hat{G}^m(N,\Omega,\mathbf{r},\mathbf{r}',\epsilon) = (N-1)\Omega\langle\delta(\mathbf{r}_2-\mathbf{r})\delta(\mathbf{r}_1-\mathbf{r}')[(\epsilon\mathbf{I}-\mathbf{W})^{-1}]_{12}\rangle . \quad (12)$$

Following Haan and Zwanzig, we write this as an expansion in density $[(N-1)/\Omega \sim \rho = \text{number density}]$.

$$\hat{G}^m(N,\Omega,\mathbf{r},\mathbf{r}',\epsilon) = \frac{N-1}{\Omega}B_2^m(\Omega,\mathbf{r},\mathbf{r}',\epsilon) + \frac{(N-1)(N-2)}{\Omega^2}B_3^m(\Omega,\mathbf{r},\mathbf{r}',\epsilon) + \cdots . \quad (13)$$

The functions B_2^m and B_3^m are readily obtained using $N = 2$, 3 in the above equation.

$$B_2^m(\Omega, \mathbf{r}, \mathbf{r}', \epsilon) = \Omega \hat{G}^m(2, \Omega, \mathbf{r}, \mathbf{r}', \epsilon) \ , \tag{14}$$

$$B_3^m(\Omega, \mathbf{r}, \mathbf{r}', \epsilon) = \frac{\Omega^2}{2} [\hat{G}^m(3, \Omega, \mathbf{r}, \mathbf{r}', \epsilon) - 2\hat{G}^m(2, \Omega, \mathbf{r}, \mathbf{r}', \epsilon)] \ . \tag{15}$$

The $\hat{G}^m$ terms in these two equations are just the exact solutions of the two and three particle problems. The quantity we desire to calculate is $\hat{G}^s(N, \Omega, \epsilon)$, the Laplace transform of the probability of finding the excitation on the originally excited molecule averaged over all possible paths for the excitation, i.e.,

$$\hat{G}^s(N, \Omega, \epsilon) = \frac{1}{\epsilon} - \frac{1}{\Omega} \int_\Omega d\mathbf{r} \int_\Omega d\mathbf{r}' \, \hat{G}^m(N, \Omega, \mathbf{r}, \mathbf{r}', \epsilon) \ . \tag{16}$$

Using the Laplace transforms of the two and three particle solutions we obtain the following truncated expansion

$$\hat{G}^s(N, \Omega, \epsilon) = \frac{1}{\epsilon} - \frac{(N-1)}{\Omega^2} \int_\Omega d\mathbf{r}_1 \int_\Omega d\mathbf{r}_2 \frac{w_{12}}{\epsilon(\epsilon + 2w_{12})} - \frac{(N-1)(N-2)}{2\Omega^3} \int_\Omega d\mathbf{r}_1 \int_\Omega d\mathbf{r}_2 \int_\Omega d\mathbf{r}_3$$
$$\times \left\{ \frac{\epsilon w_{12} + w_{12}w_{13} + w_{12}w_{23} + w_{13}w_{23}}{\epsilon[\epsilon^2 + 2\epsilon(w_{12} + w_{13} + w_{23}) + 3(w_{12}w_{13} + w_{12}w_{23} + w_{13}w_{23})]} - \frac{w_{12}}{\epsilon(\epsilon + 2w_{12})} \right\} \ , \tag{17}$$

where the particles are now numbered 1, 2, 3. Neither of these integrals can be performed analytically when Ω is a sphere of radius R. The first integral reduces to a two-dimensional numerical integral while the second integral is six dimensional. These integrals can be written as functions of one dimensionless parameter

$$\beta = \left(\frac{R}{R_0^{DD}}\right)^3 \sqrt{\frac{\epsilon\tau}{2}} \ . \tag{18}$$

Hence, the previous equation can be written as

$$\hat{G}^s(N, \beta, \epsilon) = \frac{1}{\epsilon} \left[1 - \frac{(N-1)}{2^{1/2}\beta} f_2(\beta) + \frac{(N-1)(N-2)}{2\beta^2} f_3(\beta) \right] \ . \tag{19}$$

All the information about the effects of the finite volume are contained in $f_2(\beta)$ and $f_3(\beta)$. They are monotonically increasing functions which asymptotically approach 1.110 72 and 0.805 55, respectively, as β, $\Omega \to \infty$. In this limit, Eq. (19) agrees with the result obtained by Haan for the infinite volume problem.[9] Equation (19) is the exact solution to the finite spherical volume problem for three or less particles. It is a reasonable but not very good approximation for larger numbers of particles. Following Haan, we can rewrite this expansion as

$$\hat{G}^s(N, \beta, \epsilon) = \epsilon^{-1} \left\{ 1 + \frac{C_D}{(\epsilon\tau)^{1/2}} \left(1 - \frac{1}{N}\right) f_2(\beta) + \frac{C_D^2}{\epsilon\tau} \left(1 - \frac{1}{N}\right) \left[\left(1 - \frac{1}{N}\right) (f_2(\beta))^2 - \left(1 - \frac{2}{N}\right) f_3(\beta) \right] \right\}^{-1} , \tag{20}$$

where

$$C_D = \tfrac{4}{3}\pi (R_0^{DD})^3 N/\Omega = N(R_0^{DD}/R)^3 \ . \tag{21}$$

Equation (20) is equal to Eq. (19) to order ϵ^{-2} when the β dependence of f_2 and f_3 is weak, and is a Padé approximant of Eq. (19) in this limit.

Padé approximants are frequently used in statistical mechanics to approximate truncated power series expansions such as Eq. (19).[14] No matter how many terms were calculated in the expansion for $G^s(N, \beta, \epsilon)$, the result would be ill behaved for large N or small ϵ. Equation (20), in contrast, shows the proper asymptotic behavior in these limits, and is a much better approximation to $\hat{G}^s(N, \beta, \epsilon)$. It will be demonstrated in Sec. V that Eq. (20) is a very good approximation over a wide range of parameters and in even a wider range of cases illustrates correctly the differences between infinite and finite volume systems.

$f_2(\beta)$ and $f_3(\beta)$ have been fit to analytical functions which are presented in the Appendix. These analytical functions aid in performing the numerical inverse Laplace transform of $\hat{G}^s$. Note that Eq. (20) does not include the excited state lifetime decay process. This is included in the time domain by multiplying $G^s(N, \Omega, t)$ by $\exp(-t/\tau)$.

III. EXACT SOLUTION IN FÖRSTER LIMIT

In this section we consider a finite spherical volume of radius R containing M traps and few enough donors that donor–donor interactions can be neglected (for small R, only one donor can be present). In this case the master equation contains only loss terms. Labeling the donor "1," and the traps "2" through $M+1$ we obtain

$$\frac{dp_1'(K, t)}{dt} = \frac{-p_1'(K, t)}{\tau} - \sum_{i=2}^{M+1} v_{1i} p_1'(K, t) \ , \tag{22}$$

$$v_{1i} = \frac{1}{\tau} \left(\frac{R_0^{DT}}{r_{1i}} \right)^6 , \tag{23}$$

where R_0^{DT} is the transfer radius for donor to trap transfer. As in Sec. II, we use a variable transformation to remove the lifetime from the problem. This result can be immediately integrated to yield

$$p_1(K, t) = \exp\left(- \sum_{i=2}^{M+1} v_{1i} t \right) \ . \tag{24}$$

The configuration average over the position of the donor in the sphere and the positions of all the acceptors yields $G^s(N, \Omega, t)$:

$$G^s(N,\Omega,t) = \frac{1}{\Omega^{N+1}} \int_\Omega d\mathbf{r}_1 \int_\Omega d\mathbf{r}_2 \exp(-v_{12}t) \times \int_\Omega d\mathbf{r}_3 \exp(-v_{13}t)\cdots = \frac{1}{\Omega}\int_\Omega d\mathbf{r}_1 \left[\frac{1}{\Omega}\int_\Omega d\mathbf{r}_2 \exp(-v_{12}t)\right]^N . \tag{25}$$

The interior integral is more conveniently handled in Laplace space (the inverse Laplace transform is indicated by $\mathcal{L}^{-1}$):

$$G^s(N,\Omega,t) = \frac{1}{\Omega}\int_\Omega d\mathbf{r}_1 \left[\mathcal{L}^{-1}\left(\frac{1}{\Omega}\int_\Omega d\mathbf{r}_2 \frac{1}{v_{12}+\epsilon}\right)\right]^N . \tag{26}$$

Four of the remaining integrals can be evaluated analytically, yielding the final result

$$G^s(N,\Omega,t) = \int_0^1 dy \left\{1 - \mathcal{L}^{-1}\left[\frac{1}{2\epsilon\alpha}\int_{-1}^1 \operatorname{atan}(\alpha f(q,y))\,dq\right]\right\}^N , \tag{27}$$

where

$$\alpha = \left(\frac{R}{R_0^D\tau}\right)^3 \sqrt{\epsilon\tau} , \tag{28}$$

and

$$f(q,y) = [qy^{1/3} - \sqrt{1-y^{2/3}(1-q^2)}]^3 . \tag{29}$$

Equation (27) can be readily evaluated numerically. It is the exact solution in a finite spherical volume in the absence of donor–donor interactions. It yields the result obtained by Förster in an infinite volume analytically as α, $\Omega \to \infty$.

Note that the loss of excitation probability on the donor due to the excited state lifetime is not included in this result. It is included by multiplying $G^s(N,\Omega,t)$ by $\exp(-t/\tau)$. In contrast to Sec. II, $G^s(N,\Omega,t)$ obtained here is directly observable in the unpolarized decay of the donor fluorescence.

IV. RESULTS

In this section, we present calculations of $G^s(t)$ based on the previous two sections to illustrate the nature of the results. The accuracy of the approximations used in the density expansion will be discussed in Sec. V where we will show that the approximation is expected to be quite good for most values of the parameters including those used in the following discussion. Whenever a comparison to the infinite volume one component theory is desired, we will use the three-body calculation of GAF, which we regard as essentially exact in the time range of interest. The numerical inverse Laplace transforms were performed with the Stehfest algorithm.[15]

Figure 1 shows the effect of the finite volume for two different reduced concentrations as a function of R/R_0. The curves were obtained by taking the inverse Laplace transform of Eq. (20). The results are approximate, based on the density expansion for a one component system. Curve 2B, e.g., corresponds to 128 molecules in a sphere with $R = 4\ R_0$ (for a molecule like Rhodamine 6G, $R_0 \approx 50$ Å). Although these curves are not exponential, the $1/e$ points give some measure of the time dependence of the decays. Curve 2B has a $1/e$ point 1.6 times the $1/e$ point for the infinite volume solution with the same reduced concentration (2D). Curve 2A which has 16 molecules and $R = 2\ R_0$, falls to its $1/e$ point at a time 3.3 times that predicted by the infinite volume theory. Clearly, the accurate investigation of energy transport in finite volumes requires explicit consideration of the conditions imposed by the volume's surface. Infinite volume theoretical treatments can be in serious error if they are applied to the interpretation of experimental data on finite systems.

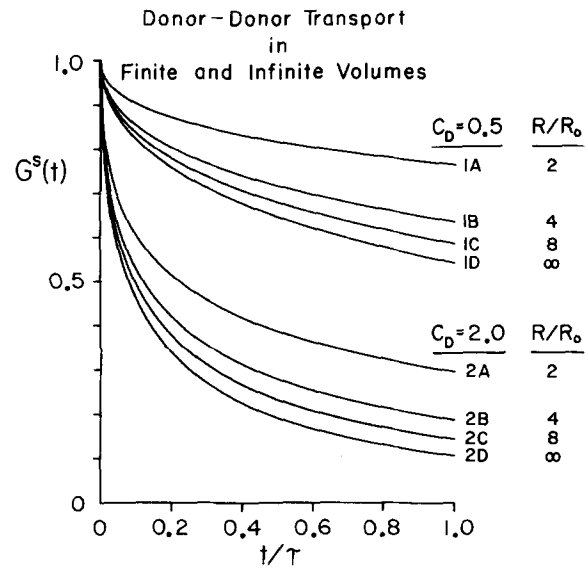

FIG. 1. The probability that the excitation is on the originally excited molecule $G^s(t)$ for one component finite volume systems calculated with the density expansion Eq. (20). Each set of four curves shows that for a given chromophore density, the volume size can significantly affect $G^s(t)$. All curves labeled 1 have $C_D = 0.5$, while all curves labeled 2 have $C_D = 2.0$. The A, B, C, and D curves have $R/R_0 = 2$, 4, 8, and ∞, respectively. Curves 1A, 1B, and 1C correspond to 4, 32, and 256 molecules in the sphere, respectively, while curves 2A, 2B, and 2C correspond to spheres of 16, 128, and 1024 molecules. Time is in units of τ, the excited state lifetime. To better illustrate the effects of transport on $G^s(t)$, decay due to the excited state lifetime has been eliminated from the calculations for this and all subsequent figures.

Figure 2 shows curves obtained from Eq. (27). These are exact results for the Förster limit in a finite spherical volume. The effect of the finite volume is qualitatively the same as that shown for the one component system in Fig. 1. Curve 2C in Fig. 2, e.g., corresponding to 1024 molecules with $R = 8\ R_0$, shows ~20% difference in its $1/e$ point compared to the infinite case. In a careful experiment, this difference is readily observable. Thus finite volume effects are important even for a very large number of molecules in a relatively large volume.

Curves A, B, and C in Fig. 3 illustrate the effect of finite volume on donor–donor transport for a very small number of molecules in the volume. They were calculated from Eq. (19) for various values of R/R_0 with

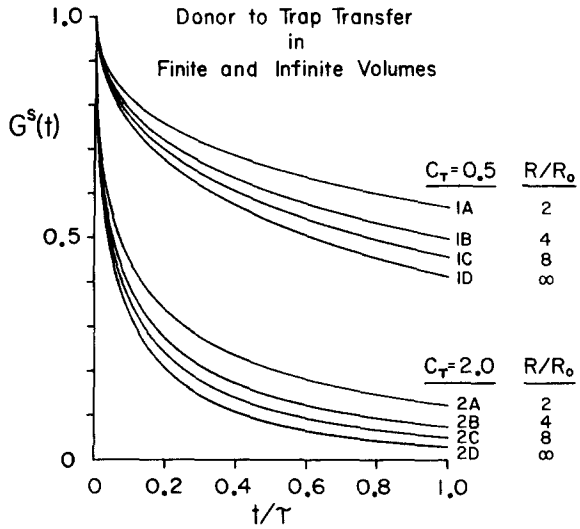

FIG. 2. $G^s(t)$ for two component finite volume systems with donor to trap transfer only (Förster limit). For a given chromophore density, $G^s(t)$ is strongly affected by the volume size. All curves labeled 1 have $C_T = 0.5$, while all curves labeled 2 have $C_T = 2.0$. [C_T is defined in Eq. (32).] Curves A–D have $R/R_0 = 2$, 4, 8, and ∞, respectively. Curves are exact calculations using Eq. (27).

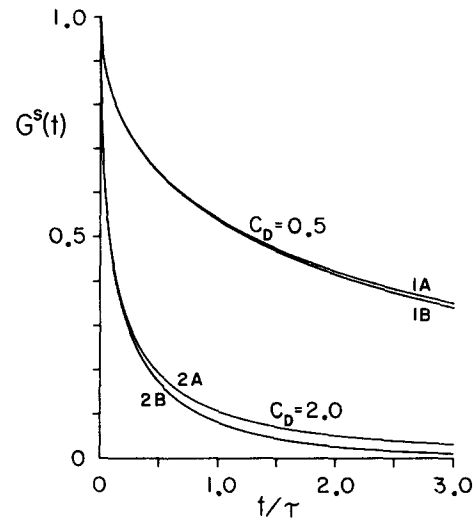

FIG. 4. $G^s(t)$ for a one component system in an infinite volume. Curves 1 and 2 have $C_D = 0.5$ and 2.0, respectively. The limit of Eq. (20) for infinite volume is designated as A, while B is the essentially exact result of GAF. The close agreement between the curves demonstrates that the density expansion employed in this paper is an excellent approximation in this limit.

three particles in the sphere ($N = 3$). These results are exact. In an infinite volume, $G^s(t)$ always goes to zero for sufficiently long time. In a finite volume, $G^s(t)$ goes to $1/N$, indicating an equalization of excitation probability among all donors in the sphere. All of the top three curves asymptotically approach 1/3. Curve C′ is the GAF result for an infinite volume with the same reduced concentration as curve C ($C_D = 7.1$). The infinite volume curve falls much faster than the finite volume curve and goes to zero. This is due to transport to the infinite number of molecules in the infinite system which are not present in the finite system (curve C).

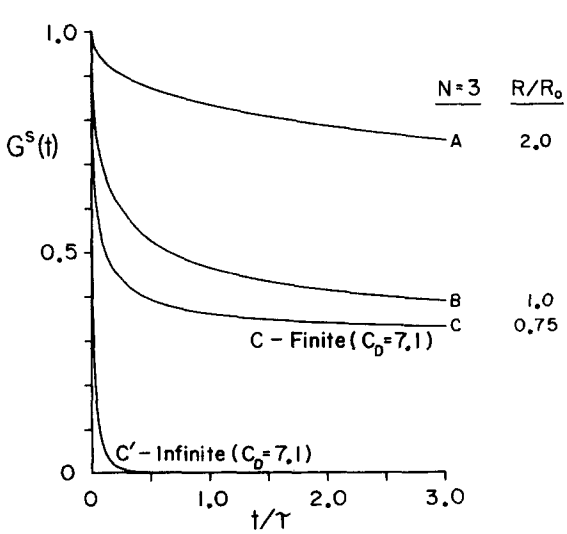

FIG. 3. $G^s(t)$ for a one component system. Curves A, B, and C are the exact solution for the finite spherical volume with three particles. The ratio of the sphere radius to the critical radius for excited state transport R/R_0 is 2.0, 1.0, and 0.75, respectively. All three curves asymptotically approach 1/3, the long time limit for a three particle system. Curve C' is the infinite volume result for $C_D = 7.1$ and should be compared to the finite volume curve C which has the same reduced concentration.

V. VALIDITY OF THE DENSITY EXPANSION APPROXIMATION

In this section, we discuss the validity of the density expansion approximation given by Eq. (20). We first examine the limit of this equation as β, $\Omega \to \infty$. (In this limit, the equation is identical to that obtained by Haan.) Figure 4 shows the comparison of this result with the self-consistent three-body calculation of GAF for two different reduced concentrations. The agreement is quite good and the differences are probably not experimentally distinguishable. Since both Eq. (20) (in the $\beta \to \infty$ limit) and the GAF result scale as $C_D^2 t/\tau$, similar agreement will occur for all values of C_D.

If the transformation of Eq. (19) to Eq. (20) had been rigorously justified for all values of β, the accuracy of Eq. (20) as demonstrated in Fig. 4 would have been expected for all values of N and β. In order to ascertain the accuracy of our approximation for small R/R_0, we will make two comparisons.

First, the exact results of Eq. (19) for three particles are compared with the approximation of Eq. (20) in Fig. 5. The agreement is good for $R/R_0 \geq 1.5$. When $R/R_0 = 1$, Eq. (20) is somewhat in error. Even so, the approximation is much better than the infinite volume solution (curve 3′) for the same reduced concentration ($C_D = 3$). Thus even when R/R_0 is quite small the density expansion yields reasonable results.

The second approach to evaluating the accuracy of

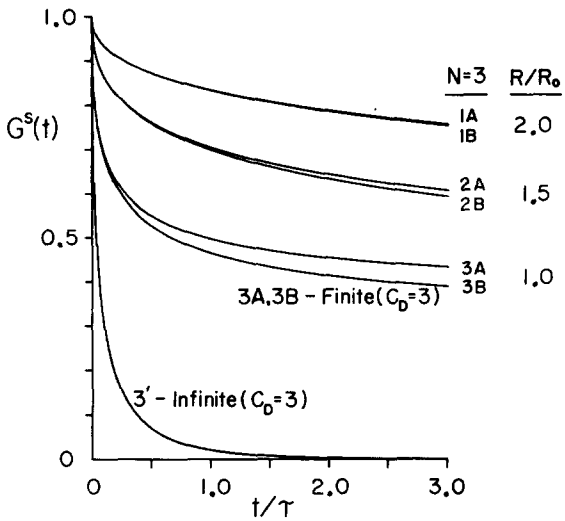

FIG. 5. $G^s(t)$ for a one component system. This is a comparison of the exact result for three particles with the approximate form given by Eq. (20). The approximate curves are labeled A while B designates the exact solution. $R/R_0 = 2.0$, 1.5, and 1.0 for curves 1, 2, and 3, respectively. Curve 3′ is the infinite volume result ($R/R_0 = \infty$) for the same reduced concentration as curves 3A and 3B. The approximate (3A) and exact result (3B) for the finite volume are in close agreement and both differ significantly from the infinite curve (3′). (Note that 1A and 1B are almost indistinguishable.)

Eq. (20) is less direct. We have taken the Förster limit problem solved exactly in Sec. III, and performed an expansion in density analogous to that performed in Sec. II. The resulting truncated series is

$$\hat{G}^s(M,\beta,\epsilon) = \frac{1}{\epsilon}\left[1 - \frac{Mg_2(\beta)}{2^{1/2}\beta} + \frac{M(M-1)}{2\beta^2}\, g_3(\beta)\right] . \tag{30}$$

Equation (30) can be rewritten as

$$\hat{G}^s(M,\beta,\epsilon) = \epsilon^{-1}\left\{1 + \frac{C_T}{(\epsilon\tau)^{1/2}}\, g_2(\beta) + \frac{C_T^2}{\epsilon\tau}\left[(g_2(\beta))^2 - \left(1 - \frac{1}{M}\right)g_3(\beta)\right]\right\}^{-1} , \tag{31}$$

where

$$C_T = \tfrac{4}{3}\pi(R_0^{DT})^3 M/\Omega = M(R_0^{DT}/R)^3 . \tag{32}$$

$g_2(\beta)$ and $g_3(\beta)$ are monotonically increasing functions quite similar in shape to f_2 and f_3.

Although the approximate solution here is for a different problem than that treated in Sec. II, the form of the equations is very similar [Eq. (30) corresponds to Eq. (19) and Eq. (31) to Eq. (20)]. In particular, the transformation of Eq. (30) to Eq. (31) rests on exactly the same assumption as was required in Sec. II. Therefore, a comparison of Eq. (31) to the exact solution in the finite Förster limit should be a strong indicator of the accuracy of the density expansion approximation for the one component problem for moderately small R/R_0.

A representative comparison of the inverse Laplace transform of Eq. (31) and the exact solution [Eq. (27)] is shown in Fig. 6. In each pair of curves the approximate result is the upper of the two curves. The agreement is quite reasonable. The following generalizations can be made about our comparisons of Eq. (31) and the exact solution: For $R/R_0 \geq 2$, no value of C_T of the many we investigated gave worse agreement than that shown in Fig. 6. For $0.5 < R/R_0 < 2$, the agreement was typically the same as the worst case shown in Fig. 5 ($R/R_0 = 1$). And finally, except when the finite and infinite results are essentially the same because R/R_0 is large ($R/R_0 > 10$), the exact finite result was always significantly closer to the approximate finite result than to the exact infinite result when $R/R_0 > 0.5$. Since the approximation discussed here is of the same nature as that made in Sec. II, the errors indicated in Fig. 6 and the generalizations made above should apply to the approximate results for the one component system.

VI. SUMMARY

The problem of electronic excited state transport among randomly distributed chromophores in a finite spherical volume has been addressed. The exact solution in the limit of low donor concentration (no donor–donor interactions) has been given. An expansion in powers of chromophore density was used to treat the one component problem of donor–donor transport. Comparison with infinite volume results and exact finite volume results indicates that this approximation is good for a wide range of conditions. Both the transport and the trapping calculations predict significant deviations in the behavior of finite volume systems compared to that of infinite volume systems as the dimensions of the finite volume become comparable to the distances as-

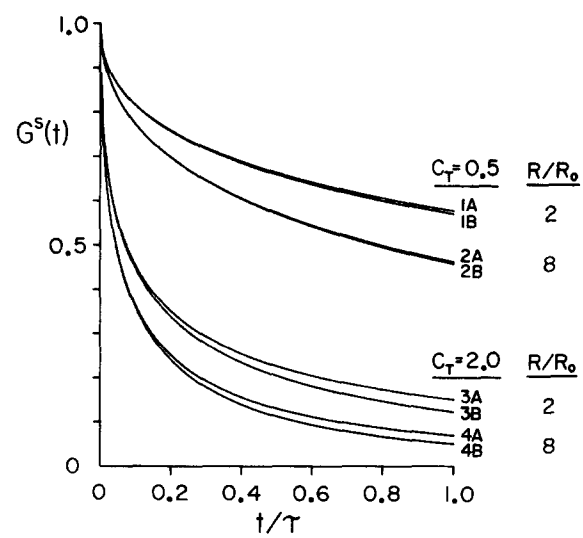

FIG. 6. Comparison of the three particle finite volume density expansion in the Förster limit to the exact solution. For curves labeled 1 or 2, $C_T = 0.5$, while $C_T = 2.0$ for curves labeled 3 or 4. The density expansion approximation is designated A and the exact solution B. $R/R_0 = 2$ for curves 1 and 3. $R/R_0 = 8$ for curves 2 and 4. For every pair of curves, the agreement is quite good. Similar accuracy is expected for the density expansion approximation in the one component problem. (Note that 2A and 2B are almost indistinguishable.)

sociated with excitation transfer. Thus, interpreting experimental data on a finite volume system requires explicit consideration of the surface boundary if an accurate physical description of the system is to emerge.

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APPENDIX

The functions listed below were fit to $f_2(\beta)$ and $f_3(\beta)$ over the ranges indicated and have a relative error of 0.5% or better. When used with Eqs. (18) and (19) they resulted in an absolute error in $G^s(t)$ of less than 0.01 for all values of the parameters which we checked, and were usually much better than this. The ranges indicated overlap significantly because the algorithm used for the inverse Laplace transform is extremely sensitive to discontinuities. The overlapping ranges allow each time point to be calculated from ϵ values obtained from only one of the following equations:

$$f_2(\beta) = 0.708\,12\beta - 0.043\,73\beta^2 - 2.9191\beta^3 + 6.6524\beta^4 - 4.793\beta^5 (10^{-4} < \beta < 0.4)\ , \tag{A1}$$

$$f_2(\beta) = 0.083\,779 - 0.732\,08\beta^{1/3} + 2.0837\beta^{2/3} - 1.3943\beta + 0.311\,04\beta^{4/3} (0.1 < \beta < 4)\ , \tag{A2}$$

$$f_2(\beta) = 1.1107[0.012\,335 + 0.987\,67(1 - 0.3344\beta^{-0.344})^{2.907}] \quad (\beta > 1)\ , \tag{A3}$$

$$f_3(\beta) = 2.752\times10^{-8}\beta + 0.332\,94\beta^2 + 0.043\,868\beta^3 - 4.3816\beta^4 + 15.685\beta^5 - 24.328\beta^6 + 14.449\beta^7 (10^{-4} < \beta < 0.4)\ , \tag{A4}$$

$$f_3(\beta) = 0.013\,03 - 0.105\,78\beta^{1/2} + 0.26\,187\beta - 0.079\,933\beta^{3/2} - 0.020\,128\beta^2 + 0.010\,583\beta^{5/2} (0.1 < \beta < 3.2)\ , \tag{A5}$$

$$f_3(\beta) = 10^{-4}(-864.02 + 1754.2\beta^{1/2} - 49.632\beta - 47.12\beta^{3/2} + 5.6253\beta^2)(0.8 < \beta < 22.4)\ , \tag{A6}$$

$$f_3(\beta) = 0.805\,55[0.012\,335 + 0.987\,67(1 - 0.602\beta^{-0.344})^{2.907}] \quad (\beta > 5.6)\ . \tag{A7}$$

[1](a) Steven W. Haan and Robert Zwanzig, J. Chem. Phys. **68**, 1879 (1978); (b) J. Klafter and R. Silbey, *ibid.* **72**, 843 (1980); (c) K. Godzik and J. Jortner, *ibid.* **72**, 4471 (1980); (d) D. L. Huber, Phys. Rev. B **20**, 2307, 5333 (1979).
[2]C. R. Gochanour, H. C. Andersen, and M. D. Fayer, J. Chem. Phys. **70**, 4254 (1979).
[3]R. F. Loring, H. C. Andersen, and M. D. Fayer, J. Chem. Phys. **76**, 2015 (1982).
[4]C. R. Gochanour and M. D. Fayer, J. Phys. Chem. **85**, 1989 (1981).
[5]R. J. Dwayne Miller, M. Pierre, and M. D. Fayer, J. Chem. Phys. (to be published).
[6]J. A. Manson and L. H. Sperling, *Polymer Blends and Composites* (Plenum, New York, 1976), p. 77ff; C. W. Frank, M.-A. Gashgari, P. Chutikamontham, and V. J. Haverly, in *Studies in Physical and Theoretical Chemistry*, edited by A. G. Walton (Elsevier, Amsterdam, 1980), Vol. X, pp. 187–209.
[7]G. S. Beddard and G. Porter, Nature **260**, 366 (1976); K. Sauer, Annu. Rev. Phys. Chem. **30**, 155 (1979).
[8]G. A. Kenney-Wallace, J. H. Flint, and S. C. Wallace, Chem. Phys. Lett. **32**, 71 (1975); Y. Kusumoto and H. Sato, *ibid.* **68**, 13 (1979).
[9]S. W. Haan, Ph.D. thesis, University of Maryland, 1977.
[10]Th. Förster, Z. Naturforsch Teil A **4**, 321 (1949); for a review on this problem see U. Gösele, M. Hauser, and U. K. A. Klein, Z. Phys. Chem. **99**, 81 (1976).
[11]M. Hauser, U. K. A. Klein, and U. Gösele, Z. Phys. Chem. **101**, 255 (1976); T. N. Estep and J. E. Thompson, Biophys. J. **26**, 195 (1979).
[12]See Sec. VIII, Ref. 2.
[13]A. Blumen, J. Chem. Phys. **74**, 6926 (1981).
[14]D. A. McQuarrie, *Statistical Mechanics* (Harper and Row, New York, 1976), p. 256.
[15]H. Stehfest, Commun. Assoc. Comput. Mach. **13**, 47, 624 (1970).