persed in a wide range of host matrices appears to be controlled by the mobility of the medium.

It is observed that the correlation times of the motions involved in the excimer sampling mechanism, and accessible only from transient measurements also follow the temperature dependence of the WLF equation using for the latter a set of parameters related to the nature and morphology of the polymer. Thus, the rotational process of the probe reflects the segmental motions which become available at the glass transition.

The analysis of the emission behavior of intramolecular excimer-forming probes of various sizes, dispersed in polymer host matrices, may afford a unique way to estimate the size of the region over which cooperative motion within the polymer must occur. Indeed, conformational energy calculations performed on the probes in order to determine the most stable conformations may allow us to estimate the volume swept out during the conformational change required for excimer formation. With the use of probe molecules of different size such as diphant, 2,4-diphenylpentane, 2,4-di(*N*-carbazolyl)pentane, etc., it should be possible to determine the lower limit of the volume from which the excimer sampling is controlled by segmental motions of the polymer host matrix.

Further investigations are in progress with other probes and other polymers.

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Electronic Excitation Transport as a Probe of Chain Flexibility

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ABSTRACT: The long-time divergence present in the three-body self-consistent approximation to the Green function for electronic excitation transport on ideal polymer chains (*Macromolecules* **1983**, *16*, 1456) is removed by constructing a Padé approximant for the self-energy. The resulting self-consistent approximation to the Green function is well-behaved at all times and concentrations and is shown to be in good agreement with approximants constructed from a density expansion. The approximation can be used to obtain quantitative measurements of statistical chain flexibility from fluorescence depolarization and trap fluorescence experiments on polymer chains containing a small concentration of randomly placed chromophores.

I. Introduction

In a recent paper[1] (I) we presented a theory to describe the transport of electronic excitations among chromophores attached to an isolated polymer chain. The chromophores were assumed to be randomly distributed along the chain contour and in low concentration. The theory allows fluorescence depolarization experiments on chains in rigid matrices to provide a measurement of statistical chain flexibility (i.e., a measurement of Flory's characteristic ratio, C_∞). In a subsequent paper[2] (II) the theory was extended to include both traps and intermolecular excitation transport. As a result, time-dependent and photostationary trapping experiments can also be used to probe chain flexibility, and experiments can be interpreted for any density of chains. The experimental observables in both trapping and depolarization experiments are related to a portion of the Green function for excitation transport, $G(\mathbf{r},t)$, the probability that an excitation has moved a displacement $\mathbf{r}$ in time t.

In I we investigated several types of approximations for the Green function. One of these was the class of self-consistent (SC) approximations used by Gochanour, Andersen, and Fayer[3] (GAF) for excitation transport among randomly distributed points. We extended the GAF formalism to the problem of Förster transfer on an isolated, ideal polymer chain. The two-body SC approximation was found to be well-behaved, but the next member of the hierarchy, the three-body SC approximation, was found to contain a long-time divergence for the polymeric problem. We also considered a class of Padé approximants that were constructed from a density expansion for the Green function. It was demonstrated that a member of this class, the three-particle Padé approximant, provides an accurate and computationally practical approximation to the Green function for excitation transport on an isolated polymer chain. In II the three-particle Padé was extended to include both intramolecular and intermolecular transport, as well as trapping. Arguments were again presented to support the accuracy of this approximate solution.

In the present paper we investigate the nature of the long-time divergence in the three-body SC approximation for ideal chains and show that it can be removed by constructing a Padé approximant for the three-body self-energy. The result is a well-behaved approximation for the Green function that conserves excitation probability and will allow the calculation of observables in fluorescence depolarization and trapping experiments. The agreement between the present approximation and the three-particle Padé approximant derived in I and II is found to be excellent for the times and concentrations of experimental interest.

Our technique can also be applied to related excitation transport problems. For example, the three-body SC approximation for transport among randomly distributed chromophores in two dimensions exhibits a similar asymptotic divergence.[4] It is likely that the present approach will provide a well-behaved approximate solution to the Green function for this problem.

II. Three-Body Rational Approximation

The polymeric system considered in this paper is identical with the one discussed in II. The Fourier–Laplace transform of the ensemble-averaged Green function for excitation transport in such a system can be written[2,5]

$$\hat{G}(\mathbf{k},\epsilon) = \hat{G}^{\mathrm{S}}(\epsilon) + \hat{G}^{\mathrm{M}}(\mathbf{k},\epsilon) + \hat{G}^{\mathrm{T}}(\mathbf{k},\epsilon) \qquad (1)$$

where ϵ is the Laplace variable conjugate to the time, t, and $\mathbf{k}$ is the spatial wave vector. The three functions defined in this equation describe the probability that an excitation initially on a donor chromophore has remained on the same donor, migrated to a different donor, or migrated to a trap, respectively. Following the approach in I, the three portions of the Green function are given a diagrammatic representation. Conservation of probability, which is expressed by

$$\lim_{\mathbf{k}\to 0} \hat{G}(\mathbf{k},\epsilon) = \epsilon^{-1} \qquad (2)$$

can be used to obtain an exact relation between $\hat{G}^{\mathrm{S}}(\epsilon)$, $\hat{G}^{\mathrm{M}}(0,\epsilon)$, and $\hat{G}^{\mathrm{T}}(0,\epsilon)$. In the limit of infinite chains, this relation can be written

$$\epsilon\hat{G}^{\mathrm{S}}(\epsilon) = 1 - \tilde{\Delta}(0,\hat{G}^{\mathrm{S}}(\epsilon))/\hat{G}^{\mathrm{S}}(\epsilon) - \epsilon\tilde{\Gamma}(0,\epsilon,\hat{G}^{\mathrm{S}}(\epsilon)) \qquad (3)$$

Equation 3 is identical in form with the result of Loring, Andersen, and Fayer[5] (LAF) for a homogeneous system, except that a very different ensemble is used to calculate the configuration-averaged quantities appearing in the equation. $\tilde{\Gamma}(0,\epsilon,\hat{G}^{\mathrm{S}}(\epsilon))$ is a renormalized propagator that consists of the subset of $\hat{G}^{\mathrm{T}}(0,\epsilon)$ diagrams without the topological features, loops or nodes. Loops and nodes were defined in I. Similarly, $\tilde{\Delta}(0,\hat{G}^{\mathrm{S}}(\epsilon))$ is a renormalized propagator that contains the subset of $\hat{G}^{\mathrm{M}}(0,\epsilon)$ diagrams without loops or nodes.

Since $\tilde{\Delta}$ and $\tilde{\Gamma}$ are functionals of $\hat{G}^{\mathrm{S}}(\epsilon)$, approximations for these quantities can be substituted into eq 3 to provide closed-form self-consistent equations for $\hat{G}^{\mathrm{S}}(\epsilon)$. The two- and three-body SC approximations[1,3,5] are obtained by retaining all diagrams in $\tilde{\Delta}$ and $\tilde{\Gamma}$ that have two sites and all diagrams that contain two or three sites, respectively. For ideal chain statistics and the isotropic Förster transfer rate, the two-body approximation is calculated in the manner described in I

$$\tilde{\Delta}_2(0,\hat{G}^{\mathrm{S}}(\epsilon))/\hat{G}^{\mathrm{S}}(\epsilon) = \frac{2^{4/3}}{3^{1/2}}\hat{C}_{\mathrm{DB}} + \frac{\pi}{2^{3/2}}\hat{C}_{\mathrm{D}} \qquad (4)$$

$$\epsilon\tilde{\Gamma}_2(0,\epsilon,\hat{G}^{\mathrm{S}}(\epsilon)) = \frac{4}{3^{1/2}}\hat{C}_{\mathrm{TB}} + \frac{\pi}{2}\hat{C}_{\mathrm{T}} \qquad (5)$$

where

$$\hat{C}_{\mathrm{DB}} = \bar{C}_{\mathrm{D}}(\hat{G}^{\mathrm{S}}(\epsilon)/\tau)^{1/3} \qquad (6a)$$

$$\hat{C}_{\mathrm{D}} = C_{\mathrm{D}}(\hat{G}^{\mathrm{S}}(\epsilon)/\tau)^{1/2} \qquad (6b)$$

$$\hat{C}_{\mathrm{TB}} = \bar{C}_{\mathrm{T}}(\hat{G}^{\mathrm{S}}(\epsilon)/\tau)^{1/3} \qquad (6c)$$

$$\hat{C}_{\mathrm{T}} = C_{\mathrm{T}}(\hat{G}^{\mathrm{S}}(\epsilon)/\tau)^{1/2} \qquad (6d)$$

In these equations, τ is the measured lifetime of an excitation on a donor, $\bar{C}_{\mathrm{D}}$ and $\bar{C}_{\mathrm{T}}$ are dimensionless *intramolecular* donor and trap concentrations, and C_{D} and C_{T} are dimensionless *intermolecular* donor and trap concentrations. The dimensionless chromophore concentrations were defined in II. When eq 4 and 5 are substituted into eq 3 for $\tilde{\Delta}$ and $\tilde{\Gamma}$, we obtain the two-body SC equation for $\hat{G}^{\mathrm{S}}(\epsilon)$.

The three-body approximation for ideal chains and the Förster rate can be calculated by using the approach of LAF with modifications analogous to those described in I[6]

$$\begin{aligned}\tilde{\Delta}_3/\hat{G}^{\mathrm{S}} = {} & 1.455\hat{C}_{\mathrm{DB}} + 1.111\hat{C}_{\mathrm{D}} - 0.9933\hat{C}_{\mathrm{DB}}^{2} - 0.1887\hat{C}_{\mathrm{D}}^{2} + (4.480 - \alpha_1)\hat{C}_{\mathrm{DB}}\hat{C}_{\mathrm{TB}} + {} \\ & (3.848 - \alpha_3)\hat{C}_{\mathrm{D}}\hat{C}_{\mathrm{TB}} + 3.047\hat{C}_{\mathrm{DB}}\hat{C}_{\mathrm{T}} - 1.405\hat{C}_{\mathrm{DB}}\hat{C}_{\mathrm{D}} + (2.617 - \alpha_2)\hat{C}_{\mathrm{D}}\hat{C}_{\mathrm{T}}\end{aligned} \qquad (7)$$

$$\begin{aligned}\epsilon\tilde{\Gamma}_3 = {} & 2.309\hat{C}_{\mathrm{TB}} + 1.571\hat{C}_{\mathrm{T}} - 2.159\hat{C}_{\mathrm{TB}}^{2} - 0.3371\hat{C}_{\mathrm{T}}^{2} + (\alpha_4 - 2.240)\hat{C}_{\mathrm{DB}}\hat{C}_{\mathrm{TB}} + (\alpha_6 - 1.710)\hat{C}_{\mathrm{D}}\hat{C}_{\mathrm{TB}} - {} \\ & 1.143\hat{C}_{\mathrm{DB}}\hat{C}_{\mathrm{T}} - 2.857\hat{C}_{\mathrm{T}}\hat{C}_{\mathrm{TB}} + (\alpha_5 - 0.8723)\hat{C}_{\mathrm{D}}\hat{C}_{\mathrm{T}}\end{aligned} \qquad (8)$$

The quantities $\alpha_1, ..., \alpha_6$ are numerical integrals that depend on the ratio of the Förster radii, $R_0^{\mathrm{DT}}/R_0^{\mathrm{DD}}$, and are given in Table I of paper II. When eq 7 and 8 are substituted into eq 3, we obtain the three-body SC equation for $\hat{G}^{\mathrm{S}}(\epsilon)$. As discovered in I, the inverse Laplace transform of the solution to this equation exhibits a long-time divergence for nonzero intramolecular concentrations.

To investigate this divergence we consider excitation transport on an isolated chain in the absence of traps ($C_{\mathrm{D}} \ll \bar{C}_{\mathrm{D}}$, $\bar{C}_{\mathrm{T}} = C_{\mathrm{T}} = 0$). For this problem, which was investigated in I, the two- and three-body SC equations are respectively

$$\epsilon\hat{G}^{\mathrm{S}}(\epsilon) = 1 - 1.455[\bar{C}_{\mathrm{D}}^{3}\hat{G}^{\mathrm{S}}(\epsilon)/\tau]^{1/3} \qquad (9)$$

$$\epsilon\hat{G}^{\mathrm{S}}(\epsilon) = 1 - 1.455[\bar{C}_{\mathrm{D}}^{3}\hat{G}^{\mathrm{S}}(\epsilon)/\tau]^{1/3} + 0.9933[\bar{C}_{\mathrm{D}}^{3}\hat{G}^{\mathrm{S}}(\epsilon)/\tau]^{2/3} \qquad (10)$$

In Figure 1 the right and left sides of each equation are plotted as a function of $\bar{C}_{\mathrm{D}}^{3}\hat{G}^{\mathrm{S}}/\tau$. For a specified value of ϵ, the intersection between a line through the origin of slope $\epsilon\tau/\bar{C}_{\mathrm{D}}^{3}$ and the function $1 - \tilde{\Delta}(0,\hat{G}^{\mathrm{S}})/\hat{G}^{\mathrm{S}}$ provides a graphical solution of eq 9 and 10. $\hat{G}^{\mathrm{S}}(0)$ is seen to be finite in the two-body approximation, but not in the three-body result. The long-time divergence in the three-body approximation is related to the behavior of $1 - \tilde{\Delta}_3/\hat{G}^{\mathrm{S}}$ for large $\hat{G}^{\mathrm{S}}$. In particular, $\tilde{\Delta}_3$ becomes negative for sufficiently large physical values of $\hat{G}^{\mathrm{S}}$.

It is easy to show that this property of $\tilde{\Delta}_3$ is not a property of the *exact* $\tilde{\Delta}$ when treated as a function of $\hat{G}^{\mathrm{S}}$.

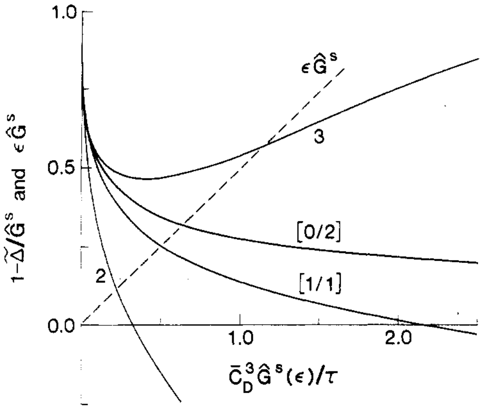

Figure 1. Graphical solution of the self-consistent equation for the isolated chain (low density) limit of the pure transport problem, $\bar{C}_T = C_T = 0$, $C_D \ll \bar{C}_D$. The curves labeled 2, 3, [1/1], and [0/2] are respectively the two-body, three-body, [1/1] Padé, and [0/2] Padé approximations for $1 - \tilde{\Delta}/\hat{G}^S$.

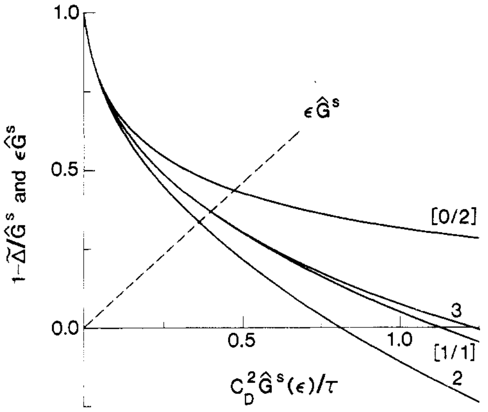

Figure 2. Graphical solution of the self-consistent equation for the high chain density limit of the pure transport problem, $\bar{C}_T = C_T = 0$, $\bar{C}_D \ll C_D$. The curves labeled 2, 3, [1/1], and [0/2] are respectively the two-body, three-body, [1/1] Padé, and [0/2] Padé approximations for $1 - \tilde{\Delta}/\hat{G}^S$.

Combining the formally exact equations 1–3 allows the identification of $\hat{G}^M(0,\epsilon)$ with the quantity $\tilde{\Delta}(0,\hat{G}^S(\epsilon))/(\epsilon\hat{G}^S(\epsilon))$. $\hat{G}^M(0,\epsilon)$ is the Laplace transform of the probability that an excitation has moved to a different donor site and must be real and nonnegative for real, positive ϵ. Similarly, $\hat{G}^S(\epsilon)$ is the transform of a probability and must be real and nonnegative for real, positive ϵ. This implies that $\tilde{\Delta}$ is real and nonnegative when treated as a function of ϵ. Since $\hat{G}^S(\epsilon)$ assumes real values between zero and $\hat{G}^S(0)$, the exact $\tilde{\Delta}$ must also be real and nonnegative when treated as a function of $\hat{G}^S(\epsilon)$ ($\leq \hat{G}^S(0)$). We conclude that since $\tilde{\Delta}_3 < 0$ for physical values of $\hat{G}^S(\epsilon)$, the three-body approximation to $\tilde{\Delta}$ is unacceptable for transport on an isolated chain.

An acceptable approximation for $\tilde{\Delta}$, however, can be obtained by constructing a Padé approximant for $\tilde{\Delta}_3$ that is nonnegative for $\hat{G}^S(\epsilon) \leq \hat{G}^S(0)$. Both the [1/1] and the [0/2] Padé approximants for $1 - \tilde{\Delta}_3/\hat{G}^S$ have this property and are shown in Figure 1.

As an aid in deciding which approximant should be selected, we consider another special case of the pure transport problem: the high chain density limit ($C_D \gg \bar{C}_D$, $\bar{C}_T = C_T = 0$). In this limit the importance of the intramolecular correlations vanishes and the transport problem reduces to the one considered by GAF. The two-body, three-body, [0/2] Padé, and [1/1] Padé approximations to $1 - \tilde{\Delta}/\hat{G}^S$ for the GAF problem are shown in Figure 2. We believe the three-body result to be accurate because it is similar to the two-body curve for physical values of $\hat{G}^S(\epsilon)$ and because the three-body SC expression for $\hat{G}^S(\epsilon)$ has given excellent agreement with experiment.[7] Figure 2 shows that the diagonal Padé approximant is very similar to the three-body curve for $C_D^2\hat{G}^S/\tau \lesssim 1.23$, which indicates that it should be an accurate approximation for $1 - \tilde{\Delta}/\hat{G}^S$ in the high chain density regime. Furthermore, the [1/1] Padé is an acceptable nonnegative approximation to $\tilde{\Delta}$ for all real, positive $\hat{G}^S$.

Since the [1/1] Padé is accurate and appears to be the best approximant at high chain density, we expect that it will also be good in the isolated chain problem and for the various limits of the trapping problem. We have constructed four-variable approximants for $1 - \tilde{\Delta}_3/\hat{G}^S$ and $1 - \tilde{\Delta}_3/\hat{G}^S - \epsilon\tilde{\Gamma}_3$ that reduce to the usual single-variable [1/1] Padé's if any three dimensionless concentrations vanish and that agree with eq 7 and 8 to second order in the four concentrations. The approximants are given by

$$\begin{aligned}1 - \tilde{\Delta}_{3R}/\hat{G}^S = \{&1 - 0.7721\hat{C}_{DB} - 0.9409\hat{C}_D\}/\{1 + 0.6827\hat{C}_{DB} + 0.1698\hat{C}_D - 0.3995\hat{C}_D\hat{C}_{DB} + \\ &(4.480 - \alpha_1)\hat{C}_{DB}\hat{C}_{TB} + 3.047\hat{C}_{DB}\hat{C}_T + (3.848 - \alpha_3)\hat{C}_D\hat{C}_{TB} + (2.617 - \alpha_2)\hat{C}_D\hat{C}_T\}\end{aligned} \tag{11}$$

$$\begin{aligned}1 - \tilde{\Delta}_{3R}/\hat{G}^S - \epsilon\tilde{\Gamma}_{3R} = \{&1 - 0.7721\hat{C}_{DB} - 0.9409\hat{C}_D - 1.374\hat{C}_{TB} - 1.356\hat{C}_T\}/\{1 + 0.6827\hat{C}_{DB} + 0.1698\hat{C}_D + \\ &0.9350\hat{C}_{TB} + 0.2146\hat{C}_T - 0.3995\hat{C}_D\hat{C}_{DB} + (5.177 + \alpha_4 - \alpha_1)\hat{C}_{DB}\hat{C}_{TB} + 3.289\hat{C}_{DB}\hat{C}_T + (3.569 + \\ &\alpha_6 - \alpha_3)\hat{C}_D\hat{C}_{TB} + (2.250 + \alpha_5 - \alpha_2)\hat{C}_D\hat{C}_T - 0.8926\hat{C}_{TB}\hat{C}_T\}\end{aligned} \tag{12}$$

Equations 11 and 12 will be referred to as the *three-body rational approximation* to $\tilde{\Delta}$ and $\tilde{\Gamma}$ in order to distinguish them from the three-particle Padé approximants investigated in I and II. When eq 12 is substituted into eq 3, we obtain the three-body *rational* SC equation for $\hat{G}^S(\epsilon)$. For Förster radii of experimental interest ($0.1 \leq R_0^{DT}/R_0^{DD} \leq 10$), $1 - \tilde{\Delta}_{3R}/\hat{G}^S - \epsilon\tilde{\Gamma}_{3R}$ is less than unity and the SC equation has a well-behaved physical root. It is possible, however, that the approximation can fail for extreme values of R_0^{DT}/R_0^{DD} outside this range.

The physical root of the three-body rational SC equation provides $\hat{G}^S(\epsilon)$, which is directly proportional to the Laplace transform of the time-dependent anisotropy in a fluorescence depolarization experiment.[1,7] The observables in trap fluorescence experiments are related to the Laplace transform of the donor excitation probability, $\hat{G}^D(\epsilon)$[2,5]

$$\hat{G}^D(\epsilon) = \hat{G}^S(\epsilon) + \hat{G}^M(0,\epsilon) = \hat{G}^S(\epsilon)/(1 - \tilde{\Delta}/\hat{G}^S(\epsilon)) \tag{13}$$

In the three-body rational SC approximation, $\hat{G}^D(\epsilon)$ is evaluated by using eq 11 with $\hat{G}^S(\epsilon)$ obtained from the solution of eq 3 and 12. For physical values of $\hat{G}^S(\epsilon)$ and $0.1 \leq R_0^{DT}/R_0^{DD} \leq 10$, $1 - \tilde{\Delta}_{3R}/\hat{G}^S(\epsilon)$ is less than unity and eq 13 provides a well-behaved approximation to $\hat{G}^D(\epsilon)$.

III. Numerical Results and Discussion

We now have a hierarchy of well-behaved approximations that conserve probability for the total Green function—the two-body SC approximation and the three-body rational SC approximation. To verify the accuracy of the three-body rational solution, numerical results are presented for time-dependent transport in the absence of traps, $\bar{C}_T = C_T = 0$.

In the $C_D \ll \bar{C}_D$ limit of low chain density, $G^S(t)$ is a universal function of $\bar{C}_D^3 t/\tau$. The inverse Laplace transform[8] of $\hat{G}^S(\epsilon)$ for this concentration regime in the two-body SC and three-body rational SC approximations is shown in Figure 3. The curve labeled P is the inverse transform of the three-particle Padé for isolated chains, given in I. The close agreement between the Padé and the

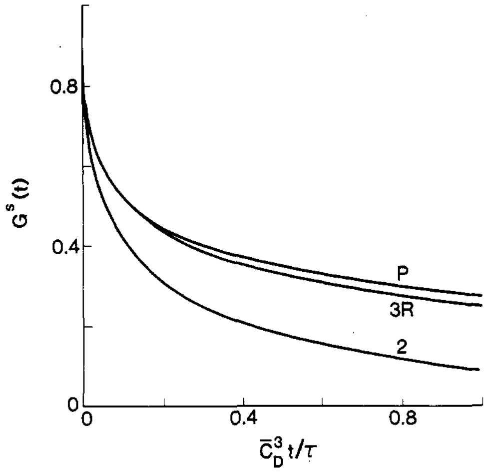

Figure 3. Inverse Laplace transform of $\hat{G}^S(\epsilon)$ in the two-body (2), three-body rational (3R), and three-particle Padé (P) approximations for the isolated chain (low density) limit of the pure transport problem $\bar{C}_T = C_T = 0$, $C_D \ll \bar{C}_D$.

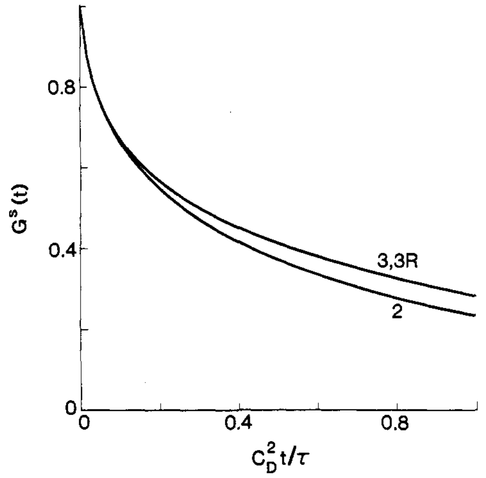

Figure 4. Inverse Laplace transform of $\hat{G}^S(\epsilon)$ in the two-body (2), three-body (3), and three-body rational (3R) approximations for the high density limit of the pure transport problem $\bar{C}_T = C_T = 0$, $\bar{C}_D \ll C_D$. The three-body result is identical with the GAF three-body approximation and numerically indistinguishable from the three-body rational approximation.

three-body rational SC approximation over the times of experimental interest ($t \leq \tau/\bar{C}_D{}^3$) supports the accuracy of the SC result for isolated chains.

For excitation transport among donors in the limit of high chain density, $\bar{C}_D \ll C_D$, the [1/1] Padé for $1 - \tilde{\Delta}_3/\hat{G}^S$ was found to be very similar to the three-body approximation of GAF. As Figure 4 shows, the three-body GAF result for $G^S(t)$ is numerically indistinguishable from the three-body rational SC approximation at high chain density. The GAF solution is believed to be an excellent approximation to the exact $G^S(t)$ in this regime.[7]

Since the three-body rational SC approximation for $G^S(t)$ is accurate at both low and high chain density, we expect it to be accurate at all intermediate concentrations for the pure transport problem. In the various limits of the more general trapping problem discussed in II, the three-body rational result for $G^D(t)$ is also found to be accurate. At high chain density the three-body rational approximation is numerically equivalent to the LAF three-body SC result, an excellent approximation to $G^D(t)$ in this concentration range.[5] For isolated chains the three-body rational approximation gives very good agreement with the three-particle Padé throughout the decay of $G^D(t)$, $t \lesssim \tau/(\bar{C}_D + \bar{C}_T)^3$.

The three-particle Padé approximant and the three-body rational SC approximation provide results for the Green function that are very similar and are believed to be accurate for the times and concentrations of experimental interest. The SC solution, however, satisfies the additional condition of conservation of probability (eq 2) and is therefore expected to be more accurate at long times and large concentrations. Both approximations are related to the observables in fluorescence experiments (see LAF, I, and II) and will allow such experiments to provide measurements of $\bar{C}_D$ and $\bar{C}_T$, which contain information on statistical chain flexibility.

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