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Diffusion-controlled intrachain reactions of polymers. I Theory^{*,†}

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A theory of diffusion-controlled intramolecularly catalyzed reactions of polymer chains in dilute solution is formulated. A closure approximation yields a soluble integral equation for (essentially) the transient rate of the reaction. The time dependent solution consists of a sum of simple exponential terms whose coefficients and decay constants can be readily calculated. The theory is also applied to luminescence quenching and ring-chain interconversion.

I. INTRODUCTION

A recent article by Morawetz¹ has drawn attention to the substantial amount of information concerning the structure of macromolecules that may be obtained by studying the rates of chemical reactions taking place in polymer solutions. Nishijima² has also discussed the importance of using fluorescence methods to study structural and relaxation properties of polymers.

These techniques can be significantly augmented by the consideration of very fast intramolecular rate processes in polymeric systems. We visualize a dilute solution of linear flexible polymer chains in which each chain is characterized by some distribution of reactive groups along its backbone. If the intrachain reactions are intrinsically very fast, it should be clear that the rates of these processes will be limited by the rates at which conformational changes take place which bring potentially reactive groups into contact. Thus, the experimental investigation of these rate processes is a direct method for studying this relaxation behavior and can provide useful information about the dynamical behavior of polymer chains.

To illustrate the capabilities of this technique consider the case in which only two reactive groups are fixed to the ends of a chain. This is the simplest case to handle theoretically and, probably, experimentally, and it is treated in detail in the following paper. The measured rates will depend directly on the relaxation of the end-to-end distance. In particular, if the probability of the reaction per collision is very near unity (i. e., a very high "intrinsic" rate) the rate measurements give a direct experimental determination of the time dependent probability of first contact between the chain ends. Until now, this probability seems to have been obtainable only from computer studies such as those of Verdier and Stockmayer³ (though they did not bother to obtain it) or from estimates of the diffusion-controlled rate presented by Wang and Davidson.⁴

There is some recent work^{4,5} dealing with intrachain reactions, however, to the best of our knowledge, no detailed study of *diffusion-controlled* intrachain reactions has previously been presented. In addition to fulfilling our objective of applying the formalism of our earlier paper⁶ (hereafter referred to as DCR) to a relatively complex many-particle system, this paper is an attempt to provide a theoretical basis for the experimental study of chain relaxation using chemical reac-

tions and luminescence quenching.

The only work known to us which seems to substantiate the feasibility of such experimental studies is that reviewed by Nishijima⁷ on fluorescence polarization for dilute solutions of macromolecules carrying fluorescent end groups. From this work we infer the possibility of luminescence quenching studies for which the relevant theory is presented herein.

The plan of this paper is the following. After presenting the approximate equations of motion which have previously been developed to treat the dynamics of polymer solutions, the formalism of DCR is employed to treat the kinetics of intramolecularly catalyzed reactions, luminescence quenching, and ring-chain interconversion. Approximate expressions for the quantities of experimental interest are obtained in terms of reduced Green's functions of the polymer diffusion operator. These reduced Green's functions are the kernels of the various integral equations which arise in the analysis, and they are evaluated by using the boson operator formalism.⁸ The solution of the equations is then presented, and the convergence of the approximation scheme is also briefly considered. Extensive numerical results have been obtained for a system featuring a pair of reactive groups attached to the ends of the chain and they are reported in the following paper.

II. SUMMARY OF BASIC MATHEMATICAL FORMALISM

The basic equations and mathematical techniques have been presented in great detail by Fixman.⁸ The pertinent aspects will be summarized here in a manner which reflects their specific use in later sections. Essentially this means that we will be using the hydrodynamic interaction tensor in its pre-averaged form, no external flows or forces will be considered, and the center of mass dependence is neglected. The first specialization is almost routine in the treatment of dynamical problems, and with the potentials we will be using it insures that in the boson representation the diffusion operator will be quadratic in bosons. This is a necessity for the types of operator rearrangements to be employed. The center of mass dependence can be neglected because we are explicitly considering only intramolecular effects in dilute solution.

The chain consists of $N+1$ segments whose position vectors are denoted $\mathbf{r}_1, \dots, \mathbf{r}_{N+1}$. In terms of these coordinates the time dependent distribution function ψ

satisfies the generalized diffusion equation

$$\partial \psi / \partial t + \mathcal{G} \psi = 0, \quad (1)$$

where

$$\mathcal{G} \psi = -kT \sum_{i=1}^{N+1} \sum_{j=1}^{N+1} \nabla_i \cdot (\beta^{-1} \delta_{ij} \mathbf{1} + \mathbf{T}(\mathbf{r}_{ij})) \cdot (\nabla_j \psi + \psi (\nabla_j U) / kT). \quad (2)$$

The hydrodynamic interaction tensor $\mathbf{T}(\mathbf{r}_{ij})$ will later be used in its preaveraged form. In Eq. (2), U is the intersegment potential energy, and β is the friction constant for a chain segment. To facilitate the solution of Eq. (1) we let

$$\psi = \psi^\alpha \rho. \quad (3)$$

A modified Gaussian distribution function, ψ^α , serves as a zeroth approximation to the equilibrium distribution function. With the effective intersegment potential chosen as

$$S^\alpha = (3kT/2(\alpha b_0)^2) \sum_{i=1}^N |\mathbf{r}_{i+1} - \mathbf{r}_i|^2, \quad (4)$$

ψ^α is given by

$$\psi^\alpha = \exp(-S^\alpha/kT) / \int \exp(-S^\alpha/kT) d\mathbf{r}_1 \dots d\mathbf{r}_{N+1}. \quad (5)$$

The parameter α measures the expansion relative to the unperturbed reference length of a segment b_0 . The potential S^α can serve as a crude way of introducing excluded volume forces via the expansion parameter α , but when a more explicit choice for an excluded volume potential is made α is chosen to make ψ^α come as close as possible to the new equilibrium distribution function, and it becomes the expansion factor of only the lowest normal mode.

When Eq. (3) is substituted into Eq. (1) the result is

$$\partial \rho / \partial t + \mathcal{L} \rho = 0, \quad (6)$$

where \mathcal{L} is given in the boson operator representation as

$$\mathcal{L} = \sum_{k=1}^N \sum_{i=1}^N \mathbf{b}_k^\dagger \cdot \Lambda_{ki} \cdot [\mathbf{b}_i + (\mathbf{b}_i, U - S^\alpha) / kT]. \quad (7)$$

Here

$$\Lambda_{ki} = 2kT \alpha_k \alpha_i \sum_{j=1}^{N+1} \sum_{l=1}^{N+1} Q_{kl} Q_{lj} [\beta^{-1} \delta_{ij} \mathbf{1} + \mathbf{T}(\mathbf{r}_{ij})]. \quad (8)$$

and $\mathbf{T}(\mathbf{r})$ is understood to be in its boson representation. The quantities α_i and Q_{jk} are given as

$$\alpha_i = 6^{1/2} (\alpha b_0)^{-1} \sin(i\pi/2N), \quad (9)$$

$$Q_{jk} = N^{-1/2} (2 - \delta_{k0})^{1/2} \cos(jk\pi/N). \quad (10)$$

The center-of-mass dependence has also been neglected in Eq. (7).

The intersegment potential U is taken to be the sum of the potential of interaction between segments close together along the backbone, S , and the excluded volume potential E :

$$U = S + E. \quad (11)$$

We make the conventional choices for S and E :

$$S = \alpha^2 S^\alpha = \frac{3kT}{2b_0^2} \sum_{i=1}^N |\mathbf{r}_i - \mathbf{r}_{i+1}|^2, \quad (12)$$

$$E = kTX \sum_{i>j} \delta(\mathbf{r}_{ij}). \quad (13)$$

The binary cluster integral for a pair of segments, $-X$, represents the effective volume excluded to one segment by another. The boson representations of S^α and S are readily expressible⁸ as

$$S/\alpha^2 = S^\alpha = (kT/2) \sum_{i=1}^N (\mathbf{b}_i + \mathbf{b}_i^\dagger) \cdot (\mathbf{b}_i + \mathbf{b}_i^\dagger). \quad (14)$$

Fixman⁸ has approximated E as

$$E = -kT(X/32\pi^{3/2}) \sum_{i>j} \sum_{l=1}^N \sum_{k=1}^N (c_{ij})^{-5/2} f_k f_l \times (\mathbf{b}_k + \mathbf{b}_k^\dagger) \cdot (\mathbf{b}_i + \mathbf{b}_i^\dagger). \quad (15)$$

Here,

$$f_i = (Q_{ij} - Q_{ii}) / \alpha_i \sqrt{2}, \quad (16)$$

and

$$c_{ij} = \frac{1}{2} \sum_{l=1}^N f_l^2. \quad (17)$$

With Eqs. (9), (10), and (16), Eq. (17) gives

$$c_{ij} = \frac{1}{8} |j - i| \alpha^2 b_0^2 \quad (18)$$

for $N \gg 1$. Next, from Eqs. (11), (14), and (15) we obtain

$$U - S^\alpha = \frac{1}{2} kT \sum_k \sum_l G_{kl} (\mathbf{b}_k^\dagger + \mathbf{b}_k) \cdot (\mathbf{b}_l + \mathbf{b}_l^\dagger), \quad (19)$$

where

$$G_{kl} = (\alpha^2 - 1) \delta_{kl} - (X/16\pi^{3/2}) \sum_{i>j} (c_{ij})^{-5/2} f_k f_l. \quad (20)$$

To obtain the form for \mathcal{L} which will be used in the rest of this analysis further approximations are required.

Following Fixman,⁸ the G_{kl} for $k \neq l$ are neglected, and we set $G_{ii} = G_i$. Further, all off-diagonal Λ_{kl} are neglected, $\mathbf{T}(\mathbf{r})$ is replaced by its equilibrium average $\langle \mathbf{T} \rangle_{\text{eq}}$, and we can then set $\Lambda_{ii} = \Lambda_i \mathbf{1}$. In view of the relative success of this latter approximation for the theory of intrinsic viscosity near the Theta point at vanishing shear rates it is believed that this will not be a serious source of error particularly because our numerical calculations were performed mainly for molecules at the Theta point. Excluded volume forces are explicitly included in the general formalism principally to illustrate that it is possible to do so and to be able to investigate their qualitative effects on chain relaxation.

The average of any function f of coordinates,

$$\langle f \rangle = \int \psi^\alpha f \rho d\mathbf{r}_1 \dots d\mathbf{r}_{N+1}, \quad (21)$$

is expressed in the boson representation as

$$\langle f \rangle = \langle 0 | f | \rho \rangle, \quad (22)$$

where $|\rho\rangle$ may be either the equilibrium or nonequilibrium solution of Eq. (6). With Eq. (22) we have

$$\langle \mathbf{T} \rangle_{\text{eq}} = \langle 0 | \mathbf{T} | \rho_{\text{eq}} \rangle. \quad (23)$$

With the above restrictions Eqs. (7), (19), and (23) give

$$\mathcal{L} = \sum_{i=1}^N \Lambda_i \mathbf{b}_i^\dagger \cdot [\mathbf{b}_i + G_i [\mathbf{b}_i + \mathbf{b}_i^\dagger]], \quad (24)$$

where

$$\Lambda_i \mathbf{1} = 2kT\alpha_i^2 \sum_{j=1}^{N+1} \sum_{l=1}^{N+1} Q_{ij} Q_{lj} (\beta^{-1} \delta_{ij} \mathbf{1} + \langle 0 | \mathbf{T}(\mathbf{r}_{ij}) | \rho_{\text{eq}} \rangle). \quad (25)$$

In Eqs. (23) and (25) $|\rho_{\text{eq}}\rangle$ is the solution to

$$\mathcal{L} |\rho_{\text{eq}}\rangle = 0, \quad (26)$$

and is approximately given by Fixman⁸ as

$$|\rho_{\text{eq}}\rangle = \exp \left[-\frac{1}{2} \sum_{i=1}^N G_i (1 + G_i)^{-1} \mathbf{b}_i^\dagger \cdot \mathbf{b}_i^\dagger \right] |0\rangle. \quad (27)$$

The parameter α is chosen to make $G_1 = 0$, and the remaining G_i are functions of the strength of the excluded volume interaction which also vanish at the Theta point. In the $U = S^\alpha$ approximation Eq. (24) reduces to

$$\mathcal{L} = \sum_{i=1}^N \Lambda_i \mathbf{b}_i^\dagger \cdot \mathbf{b}_i, \quad (28)$$

and we also have

$$|\rho_{\text{eq}}\rangle = |0\rangle. \quad (29)$$

In the absence of excluded volume forces $\alpha = 1$, and Eq. (24) again reduces to Eq. (28); Λ_i , of course, is now evaluated for $\alpha = 1$. More explicit expressions for $\langle \mathbf{T} \rangle_{\text{eq}}$ and Λ_i can be found in the following paper where they are used in the calculations.

III. FORMAL DEVELOPMENT FOR SPECIFIC REACTION PROCESSES

Beginning with this section the mathematical developments of DCR and the polymer formalism summarized in the preceding section will be combined in a detailed explication of several types of intramolecular rate processes. The development will be mainly formal at first with detailed mathematical calculations being deferred to later sections.

A. Intramolecular catalysis

The polymer chain of $N+1$ segments is now additionally characterized by the presence of m special segments which can catalyze the reaction of the single reactive segment. As noted in DCR, more than one reactive segment could be present in the chain, but since the reactivities of these segments are independent it is sufficient to consider only one. The basic equation for this type process was discussed in DCR, and it reads

$$\partial \psi / \partial t + \mathcal{G} \psi = -k \mathcal{S} \psi, \quad (30)$$

where \mathcal{G} is the same operator that appears in Eq. (1) and

$$\mathcal{S} = \sum_{i=1}^m \mathcal{S}_i(\mathbf{r}^{(i)}). \quad (31)$$

The vector $\mathbf{r}^{(i)}$ connects the active segment at, say, \mathbf{r}_i to the i th catalytic segment located at, say, \mathbf{r}_j , and in the coordinate system originally presented is given as $\mathbf{r}^{(i)} = \mathbf{r}_j - \mathbf{r}_i$. The probability $\phi(t)$ that the segment is active is given by

$$\phi(t) = \int \psi d\mathbf{r}_1 \dots d\mathbf{r}_{N+1} = \langle 0 | \rho \rangle, \quad (32)$$

where Eqs. (3) and (22) have been used.

Integrating Eq. (30) over all coordinates gives

$$d\phi/dt = -k v(t), \quad (33)$$

where

$$v(t) = \langle 0 | \mathcal{S} | \rho \rangle = \sum_i \langle 0 | \mathcal{S}_i(\mathcal{L}^{(i)}) | \rho \rangle. \quad (34)$$

The function $v(t)$ is the joint probability density that the reactive site is active and is in the vicinity of any catalytic segment.

Using Eq. (3), Eq. (30) becomes

$$\partial \rho / \partial t + \mathcal{L} \rho = -k \mathcal{S} \rho. \quad (35)$$

With the identity

$$\frac{\partial \rho}{\partial t} + \mathcal{L} \rho = e^{-\mathcal{L}t} \frac{\partial}{\partial t} (e^{\mathcal{L}t} \rho) \quad (36)$$

a formal solution of Eq. (35) can be written as

$$|\rho\rangle = e^{-\mathcal{L}t} |\rho(0)\rangle - k \int_0^t d\tau e^{-\mathcal{L}(t-\tau)} \mathcal{S} |\rho(\tau)\rangle. \quad (37)$$

For the initial condition, $|\rho(0)\rangle$, the equilibrium distribution is chosen

$$|\rho(0)\rangle = |\rho_{\text{eq}}\rangle. \quad (38)$$

Employing Eqs. (34) and (38) and acting with $\langle 0 | \mathcal{S}$ on Eq. (37) gives

$$v(t) = v_{\text{eq}} - k \int_0^t d\tau \langle 0 | \mathcal{S} e^{-\mathcal{L}(t-\tau)} \mathcal{S} |\rho(\tau)\rangle, \quad (39)$$

where, with Eq. (31),

$$v_{\text{eq}} = \langle 0 | \mathcal{S} | \rho_{\text{eq}} \rangle = \sum_{i=1}^m \langle 0 | \mathcal{S}_i(\mathbf{r}^{(i)}) | \rho_{\text{eq}} \rangle. \quad (40)$$

To make further progress it is necessary to introduce an approximation for $|\rho\rangle$ in Eq. (39). If the intrinsic rate constant k is not too large, the internal distribution would remain very close to the equilibrium distribution and $|\rho\rangle$ would be proportional to $\phi(t)$. Then \mathcal{L} in Eq. (39) would act only on \mathcal{S} . Therefore, as a zeroth approximation to $|\rho\rangle$ we set

$$\mathcal{S} |\rho\rangle = v(t) \mathcal{S} |\rho_{\text{eq}}\rangle, \quad (41)$$

and $v(t)$ is to be determined by requiring the ground state average of Eq. (41) to be correct in this order of approximation:

$$\langle 0 | \mathcal{S} | \rho \rangle = v(t) \langle 0 | \mathcal{S} | \rho_{\text{eq}} \rangle. \quad (42)$$

From Eqs. (34) and (40) $v(t)$ can be identified as

$$v(t) = v(t)/v_{\text{eq}}. \quad (43)$$

We now see that $|\rho\rangle$ is proportional to $v(t)$. For small k or high diffusivity this is rigorous, since in either of those limits $v(t) = \phi(t)v_{\text{eq}}$. For large k or small diffusivity the approximation may also be reasonably suitable. We know from the discussion of DCR that regions

of configuration space in which active and catalytic sites are found in proximity are rapidly depleted by the reaction. Since \mathcal{S} acting on $|\rho\rangle$ singles out those particular regions of configuration space and since $\nu(t)$ initially decreases very rapidly and changes slowly thereafter, the approximation preserves the correct qualitative behavior in the distribution function for the reaction region.

Utilizing Eqs. (41) and (43), Eq. (39) becomes

$$\nu(t) = 1 - (k/v_{\text{eq}}) \int_0^t d\tau D(t-\tau) \nu(\tau), \quad (44)$$

where

$$D(t) = \langle 0 | \mathcal{S} e^{-\mathcal{L}t} \mathcal{S} | \rho_{\text{eq}} \rangle. \quad (45)$$

The explicit evaluation of $D(t)$ is deferred to Sec. IV. Equation (44), an inhomogeneous Volterra equation of the second kind, has the convolution form, and its solution is conveniently obtained in terms of the Laplace transform defined by

$$\hat{g}(s) = \int_0^\infty e^{-st} g(t) dt.$$

Taking the transform of Eq. (44) we obtain

$$\hat{\nu}(s) = [s(1 + (k/v_{\text{eq}})\hat{D}(s))]^{-1}. \quad (46)$$

Taking the transform of Eq. (33) gives exactly

$$\hat{\phi}(s) = s^{-1}(1 - kv_{\text{eq}}\hat{\nu}(s)). \quad (47)$$

It will be seen in Sec. IV that

$$\lim_{t \rightarrow \infty} D(t) = (v_{\text{eq}})^2. \quad (48)$$

Hence, defining $H(t)$ to be

$$H(t) = D(t) - (v_{\text{eq}})^2 \quad (49)$$

the transform of $D(t)$ becomes

$$\hat{D}(s) = \hat{H}(s) + s^{-1}(v_{\text{eq}})^2, \quad (50)$$

and Eqs. (46) and (47) may be rewritten as

$$\hat{\nu}(s) = [s + s(k/v_{\text{eq}})\hat{H} + kv_{\text{eq}}]^{-1}, \quad (51)$$

$$\hat{\phi}(s) = [1 + (k/v_{\text{eq}})\hat{H}]\hat{\nu}. \quad (52)$$

Thus, $\nu(t)$ and $\phi(t)$ may be obtained if the inversion of Eqs. (51) and (52) is performed. In Sec. V this analysis will be carried out.

Equations (37) and (39) can be used in an iterative scheme to generate higher order approximations to $\nu(t)$ and $\phi(t)$ starting with Eq. (41). This is readily pursued in the Laplace transform representation. Formally, the Laplace transform of Eq. (37) is

$$|\hat{\rho}\rangle = s^{-1}|\rho_{\text{eq}}\rangle - k(\mathcal{L} + s)^{-1}\mathcal{S}|\hat{\rho}\rangle. \quad (53)$$

Using Eq. (41), a first order approximation for $|\hat{\rho}\rangle$ is generated.

$$|\hat{\rho}_1\rangle = s^{-1}|\rho_{\text{eq}}\rangle - k(\mathcal{L} + s)^{-1}\mathcal{S}|\rho_{\text{eq}}\rangle\hat{\nu}, \quad (54)$$

where $\hat{\nu}$ is given by Eq. (51). After dividing Eq. (39) by v_{eq} , taking its transform, and using Eq. (54) for $|\hat{\rho}\rangle$, the first order expression for $\hat{\nu}$ is given by

$$\hat{\nu}^1 = \frac{1 - (k/v_{\text{eq}})^2[(\hat{D})^2 - v_{\text{eq}}\hat{Y}]}{s + s(k/v_{\text{eq}})\hat{H}(s) + kv_{\text{eq}}}, \quad (55)$$

where

$$\hat{Y}(s) = \langle 0 | \mathcal{S}(\mathcal{L} + s)^{-1}\mathcal{S}(\mathcal{L} + s)^{-1}\mathcal{S} | \rho_{\text{eq}} \rangle. \quad (56)$$

Equations (47) and (55) may be used to give a first order expression for $\hat{\phi}$. The result is

$$\hat{\phi}^1 = \frac{s + s(k/v_{\text{eq}})H + (k/v_{\text{eq}})^3[(\hat{D})^2 - v_{\text{eq}}Y]}{s[s + s(k/v_{\text{eq}})\hat{H} + kv_{\text{eq}}]}. \quad (57)$$

The implications of these expressions will be discussed after the solutions of Eqs. (51) and (52) are presented.

B. Luminescence quenching

As in DCR, the quenching process is treated as a type (i) reaction. Equation (30) is modified by the addition of source decay terms, and the basic equation reads

$$\partial\psi/\partial t + \mathcal{G}\psi = -k\mathcal{S}\psi - \gamma\psi + F(t)(\psi_{\text{eq}} - \psi). \quad (58)$$

Employing Eqs. (3) and (36), Eq. (58) can be transformed to read

$$\begin{aligned} |\rho\rangle = & |\rho_{\text{eq}}\rangle \int_0^t d\tau e^{-\gamma(t-\tau)} F(\tau) \exp[-\int_\tau^t F(t')dt'] \\ & - k \int_0^t d\tau \exp[-(\mathcal{L} + \gamma)(t-\tau)] \exp[-\int_\tau^t F(t')dt'] \\ & \times \mathcal{S}|\rho(\tau)\rangle. \end{aligned} \quad (59)$$

The initial condition is $|\rho(0)\rangle = 0$ since the source term will account for the excitation of the active sites. Acting with $\langle 0|\mathcal{S}$ on Eq. (59), making the same closure approximation used in the preceding section and defining

$$\mathcal{O}(t) = \langle 0 | \mathcal{S} | \rho \rangle / v_{\text{eq}}, \quad (60)$$

$$\mathcal{O}(t) = \xi(t) e^{-\gamma t} \exp[-\int_0^t F(t')dt'], \quad (61)$$

$$\sigma(t) = F(t) e^{\gamma t} \exp[\int_0^t F(t')dt'], \quad (62)$$

we obtain an equation for $\xi(t)$ whose transform readily gives

$$\hat{\xi}(s) = \hat{\nu}(s)\hat{\sigma}(s). \quad (63)$$

The probability density ν is identical to that of the preceding section, and its transform $\hat{\nu}$ is defined by Eq. (46). Equation (40) defines v_{eq} .

In analogy with Eq. (32) let

$$\Phi(t) = \langle 0 | \rho \rangle \quad (64)$$

so when Eq. (58) is integrated over all coordinates, the resulting exact equation reads

$$d\Phi/dt = -kv_{\text{eq}}\mathcal{O}(t) - [\gamma + F(t)]\Phi(t) + F(t). \quad (65)$$

Equations (61), (62), and (65) with

$$\Phi(t) = \zeta(t) e^{-\gamma t} \exp[-\int_0^t F(t')dt'] \quad (66)$$

give an equation for $\zeta(t)$ whose transform, using Eqs. (47) and (63), can be written as

$$\hat{\zeta}(s) = \hat{\phi}(s)\hat{\sigma}(s). \quad (67)$$

Upon inverting Eq. (67), Eq. (66) gives

$$\Phi(t) = \int_0^t d\tau F(\tau)\phi(t-\tau) e^{-\gamma(t-\tau)} \exp[-\int_\tau^t F(t')dt']. \quad (68)$$

Thus, knowledge of $\phi(t)$ enables the calculation of transient effects in luminescence quenching to be made straightforwardly.

If the specialization to a constant light source, $F(t) = F$,

is made, the steady state probability, Φ_{ss} , that the special site is in the excited state may be obtained via Eq. (39) of DCR by evaluating $s\hat{\Phi}(s)$ as $s \rightarrow 0$. Calculation of the transform from Eq. (68) with Eqs. (51) and (52) yields for the limit:

$$\Phi_{ss} = \frac{F[1 + (k/v_{eq})\hat{H}(\gamma + F)]}{(\gamma + F)[1 + (k/v_{eq})\hat{H}(\gamma + F) + (\gamma + F)^{-1}kv_{eq}]} \quad (69)$$

C. Reversible ring opening and closing

Though most ring closing reactions of macromolecules may be too slow to show the effects of slow relaxation rates, this example is still worth pursuing because it illustrates nicely the complications which ensue if the reaction greatly modifies the potential of interaction between reactive particles. We exclude the possibility of multiple ring formation.

If the reaction is irreversible, then the formalism of Sec. IIIA is applicable. Of course, the sink function \mathcal{S} must now depend only on the coordinates of the two particles which are capable of forming the new bond. If the reaction is reversible, a source term must be added to Eq. (30) which accounts for the reconversion of rings into chains. The discussion of DCR regarding source terms is now inadequate. The reason is that the generalized diffusion operator which governs the time development of the ring distribution function differs from Eq. (1) for chains because the bonding of the formerly free chain ends causes a substantial alteration of the intersegment potential.

The diffusion-reaction equation now has the form

$$\partial\psi/\partial t + \mathcal{G}\psi = -k\mathcal{S}\psi + k_r\psi_r, \quad (70)$$

where k_r is the intrinsic first order rate constant for ring opening, and ψ_r is the time dependent distribution function for ring molecules. The distribution function ψ_r satisfies its own diffusion-reaction equation:

$$\partial\psi_r/\partial t + \mathcal{G}_r\psi_r = k\mathcal{S}\psi - k_r\psi_r. \quad (71)$$

The operator \mathcal{G}_r differs from \mathcal{G} because of the altered intersegment potential. There is no necessity for an \mathcal{S} function to multiply $k_r\psi_r$ in either Eq. (70) or (71) because the ring can presumably reconvert to a chain from any of its internal configurations. Though some of these configurations are undoubtedly more favorable for reaction than others, a weighting factor would most surely prove to be a useless complication.

Thus, a complete specification of the problem requires the simultaneous solution of Eqs. (70) and (71). However, a useful approximation which would greatly simplify this procedure consists of putting ψ_r in Eq. (70) equal to its equilibrium value multiplied by the fraction, $1 - p(t)$, of rings present at time t and ignoring Eq. (71). The approximate equation reads

$$\partial\psi/\partial t + \mathcal{G}\psi = -k\mathcal{S}\psi + k_r\psi_r^{eq} [1 - p(t)], \quad (72)$$

and integrating over all coordinates gives

$$dp/dt = -kv_{eq}c(t) + k_r[1 - p(t)] \quad (73)$$

which is exact and could have been obtained from Eq. (70).

It is possible to write ψ_r^{eq} as the product of ψ^α and a correction function:

$$\psi_r^{eq} = \psi^\alpha \rho_r. \quad (74)$$

Then, using Eq. (3) and following the same steps which led to the integral equations presented earlier, we obtain from Eq. (72)

$$c(t) = 1 - (k/v_{eq}) \int_0^t d\tau D(t - \tau) c(\tau) + (k_r/v_{eq}) \int_0^t d\tau R(t - \tau) [1 - p(\tau)], \quad (75)$$

where

$$R(t) = \langle 0 | s e^{-\mathcal{L}t} | \rho_r \rangle, \quad (76)$$

and the initial condition $|\rho(0)\rangle = |\rho_{eq}\rangle$ was chosen. Upon taking the Laplace transform of Eqs. (73) and (75) we obtain

$$\hat{p} = s^{-1} - kv_{eq}(s + k_r)^{-1}\hat{c} \quad (77)$$

and

$$\hat{c} = s^{-1} - (k/v_{eq})\hat{D}\hat{c} + (k_r/v_{eq})\hat{R}[s^{-1} - \hat{p}]. \quad (78)$$

It will be shown in Sec. IV that

$$\lim_{t \rightarrow \infty} R(t) = v_{eq}. \quad (79)$$

Hence, we may define $Q(t)$ through

$$R(t) = Q(t) + v_{eq},$$

and we also have

$$\hat{R} = \hat{Q} + v_{eq}s^{-1}. \quad (80)$$

With Eqs. (50) and (80), Eqs. (77) and (78) give

$$\hat{c}(s) = (s + k_r)s^{-1} [(s + k_r)(1 + (k/v_{eq})\hat{H}) + kv_{eq} - k k_r \hat{Q}]^{-1} \quad (81)$$

and

$$\hat{p}(s) = [1 + (k/v_{eq})\hat{H} - k k_r (s + k_r)^{-1} \hat{Q}] \hat{c}. \quad (82)$$

The steady state value of $p(t)$ is given by

$$p_{ss} = k_r / (k_r + kv_{eq} [1 + (k/v_{eq})\hat{H}(0) - k\hat{Q}(0)]^{-1})$$

which can be contrasted with the prediction of the simple equilibrium theory

$$p_{ss}^{eq} = k_r / (k_r + kv_{eq}).$$

IV. EVALUATION OF GREEN'S FUNCTIONS

A. General considerations

The Green's function for the polymer diffusion equation describes the propagation in time of the $N+1$ segment chain, initially in an arbitrary discrete state, subject to the various forces which may be present. The final state is independent of time and of the initial state and is determined only by these forces, so the long time limit of the Green's function must be the equilibrium distribution.

Now, the operator $\exp(-\mathcal{L}t)$ is a formal representation of the full Green's function. Its representation in the occupation number basis set, \mathcal{W} , can be obtained by using the identity operator, \mathcal{g} ;

$$\mathcal{g} = \sum |\mathbf{n}\rangle \langle \mathbf{n}|. \quad (83)$$

Then,

$$\mathcal{W} = \mathcal{g} e^{-\mathcal{L}t} \mathcal{g} \quad (84)$$

$$= \sum_{\mathbf{n}} |\mathbf{n}\rangle e^{-\mathcal{L}\mathbf{n}t} \langle \mathbf{n}| + \sum_{\mathbf{n} \neq \mathbf{m}} \sum |\mathbf{n}\rangle \langle \mathbf{n}| e^{-\mathcal{L}t} |\mathbf{m}\rangle \langle \mathbf{m}|, \quad (85)$$

where we have defined

$$L_{\mathbf{n}} = \langle \mathbf{n} | \mathcal{L} | \mathbf{n} \rangle. \quad (86)$$

If \mathcal{L} were diagonal on this basis, the double sum in Eq. (85) would be absent and \mathcal{W} would be given by the familiar eigenfunction expansion of the Green's function. However, even \mathcal{L} defined in Eq. (24) is not diagonal on this basis unless excluded volume forces are neglected or the $U = S^\alpha$ approximation is used. So neglect of the double sum in Eq. (85) to get an approximate diagonal expansion for \mathcal{W} results in the incorrect long time limit for \mathcal{W} when excluded volume forces are explicitly retained. A better approximation is probably

$$\mathcal{W} = |\rho_{\text{eq}}\rangle \langle 0| + \sum_{\mathbf{n} \neq 0} |\mathbf{n}\rangle e^{-L_{\mathbf{n}}t} \langle \mathbf{n}| \quad (87)$$

which effectively sums a large class of terms in the double sum of Eq. (85) to give the correct time independent term in Eq. (87). In the $U = S^\alpha$ approximation Eq. (87) correctly reduces to

$$\mathcal{W} = |0\rangle \langle 0| + \sum_{\mathbf{n} \neq 0} |\mathbf{n}\rangle e^{-L_{\mathbf{n}}t} \langle \mathbf{n}|, \quad (88)$$

the diagonal approximation of Eq. (85).

Equations (87) or (88) could be used in an attempt to evaluate the various reduced Green's functions such as D and R which have arisen in this analysis, but such an effort seems to be prohibitively difficult. However, knowledge of the first few terms of the expansion for D in terms of Eq. (88) will prove very useful in the later analysis, and these terms are calculated in the Appendix of the following paper. Fortunately, there exists a very powerful technique for obtaining closed form expressions for the reduced Green's functions which involves appropriate rearrangements of the various groupings of boson operators that appear in these expressions. In the following sections we will carry out the evaluation of these reduced Green's functions or structure functions as they could alternatively be called since they depend explicitly on the structure of the polymer model through the operator \mathcal{L} .

The complete evaluation of these reduced Green's functions requires a specific choice for \mathcal{S} , the sink function. However, in general, the s_i are functions of $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$, and they may be given a boson representation through the relation

$$s_i(\mathbf{r}_{ij}) = \int d\mathbf{r} \delta(\mathbf{r}_{ij} - \mathbf{r}) s_i(\mathbf{r}) \quad (89)$$

when the boson representation of the delta function is

employed. So a specific choice for $s_i(\mathbf{r})$ may still be postponed.

The boson representation of the delta function has been given by Fixman⁸ as

$$\delta(\mathbf{r}_{ij} - \mathbf{r}) = (2\pi)^{-3} \int d\mathbf{u} \exp(-c^{(i)}u^2 + i\mathbf{u} \cdot \mathbf{r}) \times \exp(-i\mathbf{u} \cdot \mathbf{r}_+^{(i)}) \exp(-i\mathbf{u} \cdot \mathbf{r}_-^{(i)}). \quad (90)$$

The superscript notation will be used to designate implicitly a particular pair of segments. In Eq. (90), (i) designates the (i, j) pair. Thus $\mathbf{r}_{ij} = \mathbf{r}^{(i)}$ as in Eq. (31); in addition $c^{(i)} = c_{ij}$, which is evaluated in Eqs. (17) and (18), and

$$\mathbf{r}_+^{(i)} = \sum_{s=1}^N f_s^{(i)} \mathbf{b}_s^+, \quad (91)$$

$$\mathbf{r}_-^{(i)} = \sum_{s=1}^N f_s^{(i)} \mathbf{b}_s^-, \quad (92)$$

where $f_s^{(i)}$ was defined previously in Eq. (16) for the (i, j) pair.

B. Evaluation of $D(t)$

Equations (31) and (45) give for $D(t)$:

$$D(t) = \sum_{k=1}^m \sum_{l=1}^m \langle 0 | s_k(\mathbf{r}^{(k)}) e^{-\mathcal{L}t} s_l(\mathbf{r}^{(l)}) | \rho_{\text{eq}} \rangle. \quad (93)$$

Employing Eq. (89), Eq. (93) may be written as

$$D(t) = \int d\rho_1 d\rho_2 \sum_k \sum_l s_k(\rho_1) s_l(\rho_2) D_{kl}(\rho_1, \rho_2, t), \quad (94)$$

where

$$D_{kl}(\rho_1, \rho_2, t) = \langle 0 | \delta(\mathbf{r}^{(k)} - \rho_1) e^{-\mathcal{L}t} \delta(\mathbf{r}^{(l)} - \rho_2) | \rho_{\text{eq}} \rangle. \quad (95)$$

Using Eq. (90), Eq. (95) becomes

$$D_{kl} = (2\pi)^{-6} \int d\mathbf{u}_1 d\mathbf{u}_2 d_{kl}(\mathbf{u}_1, \mathbf{u}_2, t) \times \exp(-c^{(k)}u_1^2 - c^{(l)}u_2^2 + i\mathbf{u}_1 \cdot \rho_1 + i\mathbf{u}_2 \cdot \rho_2), \quad (96)$$

where

$$d_{kl} = \langle 0 | \exp(-i\mathbf{u}_1 \cdot \mathbf{r}_-^{(k)}) \exp(-\mathcal{L}t) \times \exp(-i\mathbf{u}_2 \cdot \mathbf{r}_+^{(l)}) \exp(-i\mathbf{u}_2 \cdot \mathbf{r}_-^{(l)}) | \rho_{\text{eq}} \rangle, \quad (97)$$

and use has been made of the annihilation property of b^+ when acting on $\langle 0|$,

$$\langle 0 | \exp(-i\mathbf{u}_1 \cdot \mathbf{r}_+^{(k)}) = \langle 0 |. \quad (98)$$

Equation (97) has been evaluated¹⁰ for the general case in which excluded volume forces are approximately retained explicitly in \mathcal{L} and in $|\rho_{\text{eq}}\rangle$ as given by Eqs. (24) and (27). However, for convenience the calculation will be performed only in the $U = S^\alpha$ approximation. The more general result can be obtained in an obvious manner once the results for the special case are available for inspection.

Taking into account Eqs. (28) and (29) and noting that

$$\exp(-i\mathbf{u}_2 \cdot \mathbf{r}_-^{(l)}) | 0 \rangle = | 0 \rangle, \quad (99)$$

and that in this special case

$$\mathcal{L} | 0 \rangle = 0,$$

Eq. (97) may be recast as

$$d_{kl} = \langle 0 | \exp(-i \mathbf{u}_1 \cdot \mathbf{r}_-^{(k)}) \exp(-ie^{-\Lambda t} \mathbf{u}_2 \cdot \mathbf{r}_+^{(l)} e^{\Lambda t}) | 0 \rangle. \quad (100)$$

Since bosons of different modes commute

$$e^{-\Lambda t} \mathbf{r}_+^{(l)} e^{\Lambda t} = \sum_{s=1}^N f_s^{(l)} \exp(-\Lambda_s \mathbf{b}_s^* \cdot \mathbf{b}_s t) \mathbf{b}_s^* \times \exp(\Lambda_s \mathbf{b}_s^* \cdot \mathbf{b}_s t). \quad (101)$$

Since different components of the same mode also commute, we may restrict our attention to one of the components of \mathbf{b}_s^* , for which the required transform is

$$q(t) = e^{-\Lambda b^* b t} b^* e^{\Lambda b^* b t}. \quad (102)$$

Differentiating $q(t)$ gives

$$dq/dt = \Lambda e^{-\Lambda b^* b t} (b^*, b^* b) e^{\Lambda b^* b t}. \quad (103)$$

The commutator in Eq. (103) is given as

$$(b^*, b^* b) = -b^*. \quad (104)$$

Therefore,

$$q(t) = e^{-\Lambda t} b^*. \quad (105)$$

With Eq. (105) for the required transform, Eq. (101) gives

$$e^{-\Lambda t} \mathbf{r}_+^{(l)} e^{\Lambda t} = \sum_{s=1}^N f_s^{(l)} e^{-\Lambda_s t} \mathbf{b}_s^*, \quad (106)$$

and with this result Eq. (100) becomes

$$d_{kl} = \langle 0 | \exp(-i \mathbf{u}_1 \cdot \mathbf{r}_-^{(k)}) \times \exp\left(-i \sum_{s=1}^N f_s^{(l)} e^{-\Lambda_s t} \mathbf{u}_2 \cdot \mathbf{b}_s^*\right) | 0 \rangle. \quad (107)$$

The evaluation of Eq. (107) may be completed by using the properties evinced in Eqs. (98) and (99) and the relation¹¹

$$e^a e^a = e^a e^a e^{-\langle a, a \rangle}$$

for any two operators which commute with their commutator. The result is

$$d_{kl}(\mathbf{u}_1, \mathbf{u}_2, t) = \exp[-\mathbf{u}_1 \cdot \mathbf{u}_2 n^{(lk)}(t)], \quad (108)$$

where

$$n^{(lk)}(t) = \sum_s f_s^{(l)} f_s^{(k)} e^{-\Lambda_s t}. \quad (109)$$

Substitution of Eq. (108) into Eq. (96) gives

$$D_{kl}(\rho_1, \rho_2, t) = (2\pi)^{-6} \int d\mathbf{u}_1 d\mathbf{u}_2 \times \exp\left[-\sum_{i=1}^2 \sum_{j=1}^2 A_{ij} \mathbf{u}_1 \cdot \mathbf{u}_2 + i \sum_{i=1}^2 \rho_i \cdot \mathbf{u}_i\right], \quad (110)$$

where the elements of the matrix \mathbf{A} are given as

$$A_{11} = c^{(k)}, \quad (111a)$$

$$A_{22} = c^{(l)}, \quad (111b)$$

$$A_{12} = A_{21} = \frac{1}{2} n^{(lk)}(t). \quad (111c)$$

The integrand of Eq. (110) is recognizable as the Fourier transform of a bivariate Gaussian probability distribution for ρ_1 and ρ_2 . The integration may be readily performed¹² with the result

$$D_{kl}(\rho_1, \rho_2, t) = (4\pi |\mathbf{A}|^{1/2})^{-3} \times \exp\left[-(4|\mathbf{A}|)^{-1} \sum_{i=1}^2 \sum_{j=1}^2 A^{ij} \rho_i \cdot \rho_j\right], \quad (112)$$

where A^{ij} is the cofactor of the element A_{ij} and $|\mathbf{A}|$ is the determinant of \mathbf{A} . Using Eq. (111) these quantities may be expressed as

$$A^{11} = c^{(l)}, \quad (113a)$$

$$A^{22} = c^{(k)}, \quad (113b)$$

$$A^{12} = A^{21} = -\frac{1}{2} n^{(lk)}(t), \quad (113c)$$

$$|\mathbf{A}| = c^{(l)} c^{(k)} - \frac{1}{4} [n^{(lk)}(t)]^2. \quad (114)$$

To complete the evaluation of D a specific choice for the sink function must be made. This choice will be deferred until the numerical calculations are discussed in the following paper.

The sole effect of the inclusion of the excluded volume potential via Eq. (24) and (27) is the modification of the elements of the matrix \mathbf{A} . Instead of the relations given by Eq. (17) and (109) we now have

$$c^{(l)} = \frac{1}{2} \sum_s (1 + G_s)^{-1} (f_s^{(l)})^2 \quad (115)$$

and

$$n^{(lk)}(t) = \sum_s f_s^{(l)} f_s^{(k)} (1 + G_s)^{-1} e^{-\Lambda_s(1+G_s)t}. \quad (116)$$

The form of these modifications will be intelligible once the results of Sec. IVE are presented.

Finally, the verification of Eq. (48) will be made. This is most easily done by substituting Eq. (84) into Eqs. (45); then employment of Eq. (87) for \mathcal{W} gives

$$D(t) = \langle 0 | s | \rho_{\text{eq}} \rangle^2 + \sum_{\mathbf{n} \neq 0} \langle 0 | s | \mathbf{n} \rangle \langle \mathbf{n} | s | \rho_{\text{eq}} \rangle e^{-L \mathbf{n} t}. \quad (117)$$

When the limit $t \rightarrow \infty$ is taken, Eq. (117) gives

$$D(\infty) = \langle 0 | s | \rho_{\text{eq}} \rangle^2 \quad (118)$$

which, using Eq. (40) we see is identical to Eq. (48). This result could also be established by directly considering the long time limit of Eq. (112) when substituted in Eq. (94).

The calculation of \hat{D} from Eqs. (117) and (40) is simple:

$$\hat{D}(s) = \frac{v_{\text{eq}}^2}{s} + \sum_{\mathbf{n} \neq 0} \frac{\langle 0 | s | \mathbf{n} \rangle \langle \mathbf{n} | s | \rho_{\text{eq}} \rangle}{L_{\mathbf{n}} + s}. \quad (119)$$

C. Evaluation of \hat{Y}

Equation (56) for \hat{Y} may be rewritten as

$$\hat{Y}(s) = \int_0^\infty dt e^{-st} \int_0^t d\tau X(t, \tau), \quad (120)$$

where

$$X(t, \tau) = \langle 0 | s e^{-\Lambda(t-\tau)} s e^{-\Lambda\tau} s | \rho_{\text{eq}} \rangle. \quad (121)$$

Equation (121) can be evaluated¹⁰ using boson operator rearrangements. The result, which is not reproduced here, is a trivariate Gaussian distribution function. Instead we evaluate $\hat{Y}(s)$ in the occupation number basis since this representation of \hat{Y} will be useful in discussing the convergence of the approximation scheme.

From Eq. (84) we find

$$(\mathcal{L} + s)^{-1} = \mathcal{G}(\mathcal{L} + s)^{-1} \mathcal{G} = \hat{\mathcal{W}} \quad (122)$$

Calculating $\hat{\mathcal{W}}$ from Eq. (87) gives

$$\hat{\mathcal{W}} = |\rho_{\text{eq}}\rangle \langle 0 | s^{-1} + \sum_{n \neq 0} |n\rangle \langle n| (L_n + s)^{-1}, \quad (123)$$

and Eqs. (56), (122), and (123) give

$$\hat{Y}(s) = \frac{v_{\text{eq}}^3}{s^2} + \frac{2v_{\text{eq}}}{s} \sum_{n \neq 0} \frac{\langle 0 | s | n \rangle \langle n | s | \rho_{\text{eq}} \rangle}{L_n + s} + \sum_{n \neq 0} \sum_{m \neq 0} \frac{\langle 0 | s | n \rangle \langle n | s | m \rangle \langle m | s | \rho_{\text{eq}} \rangle}{(L_m + s)(L_n + s)}. \quad (124)$$

D. Consideration of $R(t)$

Equations (76), (89), and (90) give

$$R(t) = (2\pi)^{-3} \int d\mathbf{r} d\mathbf{u} R_1(\mathbf{u}, t) S(\mathbf{r}) \times \exp(-c_{N+1,1} u^2 + i\mathbf{u} \cdot \mathbf{r}), \quad (125)$$

where

$$R_1(\mathbf{u}, t) = \langle 0 | e^{-i\mathbf{u} \cdot \mathbf{r}_N} e^{-\mathcal{L}t} | \rho_r \rangle. \quad (126)$$

The superscript notation has been dropped since we are dealing with only a pair of reactive segments figuratively connected by the end-to-end vector $\mathbf{r}_{N+1} - \mathbf{r}_1$. Neglecting consideration of excluded volume forces, a zeroth approximation for the ring distribution function could be

$$\psi_r^{\text{eq}} = \psi^\alpha \exp[-(3kT/2b^2) |\mathbf{r}_{N+1} - \mathbf{r}_1|^2]. \quad (127)$$

Equations (74) and (127) imply

$$|\rho_r\rangle = \exp[-(3kT/2b^2) |\mathbf{r}_{N+1} - \mathbf{r}_1|^2] |0\rangle, \quad (128)$$

where $|\mathbf{r}_{N+1} - \mathbf{r}_1|^2$ would be given in the boson representation. No explicit evaluation of Eq. (126) will be given, though this could easily be done.

Equation (79) can be verified in the same fashion as Eq. (48) by employing Eqs. (76), (84), and (87). Then

$$R(t) = \langle 0 | S | \rho_{\text{eq}} \rangle + \sum_{n \neq 0} \langle 0 | S | n \rangle \langle n | \rho_r \rangle e^{-L_n t},$$

and, as $t \rightarrow \infty$

$$R(\infty) = v_{\text{eq}}$$

by Eq. (40).

E. Reduced Green's functions and time correlation functions

Following Verdier,^{3b} we may write for the time correlation function $\rho(f, g, t)$ of two scalar functions, f and g ,

$$\rho(f, g, t) = \frac{\langle f(0)g(t) \rangle_{\text{eq}} - \langle f \rangle_{\text{eq}} \langle g \rangle_{\text{eq}}}{(\langle f^2 \rangle_{\text{eq}} - \langle f \rangle_{\text{eq}}^2)^{1/2} (\langle g^2 \rangle_{\text{eq}} - \langle g \rangle_{\text{eq}}^2)^{1/2}} \quad (129)$$

and for the time correlation function $\rho_v(\mathbf{u}, \mathbf{v}, t)$ of two vector quantities, \mathbf{u} and \mathbf{v} ,

$$\rho_v(\mathbf{u}, \mathbf{v}, t) = \frac{\langle \mathbf{u}(0) \cdot \mathbf{v}(t) \rangle_{\text{eq}} - \langle \mathbf{u} \rangle_{\text{eq}} \cdot \langle \mathbf{v} \rangle_{\text{eq}}}{(\langle \mathbf{u} \cdot \mathbf{u} \rangle_{\text{eq}} - \langle \mathbf{u} \rangle_{\text{eq}} \cdot \langle \mathbf{u} \rangle_{\text{eq}})^{1/2} (\langle \mathbf{v} \cdot \mathbf{v} \rangle_{\text{eq}} - \langle \mathbf{v} \rangle_{\text{eq}} \cdot \langle \mathbf{v} \rangle_{\text{eq}})^{1/2}} \quad (130)$$

All of the quantities f , g , \mathbf{u} , and \mathbf{v} are assumed to be functions of the chain coordinates $\mathbf{r}_1, \dots, \mathbf{r}_{N+1}$ and the bracketed expressions in Eqs. (129) and (130) are given by

$$\langle f(0)g(t) \rangle_{\text{eq}} = \int d\{\mathbf{r}\} d\{\mathbf{r}^0\} f(\{\mathbf{r}^0\}) \psi_{\text{eq}}(\{\mathbf{r}^0\}) \times \mathcal{W}(\{\mathbf{r}\}, \{\mathbf{r}^0\}, t) g(\{\mathbf{r}\}) \quad (131)$$

and

$$\langle f \rangle_{\text{eq}} = \int d\{\mathbf{r}\} f(\{\mathbf{r}\}) \psi_{\text{eq}}(\{\mathbf{r}\}), \quad (132)$$

where \mathcal{W} is, of course, the Green's function for the polymer diffusion equation expressed in chain coordinates.

With Eqs. (22) and (84), Eqs. (131) and (132) may be written as

$$\langle f(0)g(t) \rangle_{\text{eq}} = \langle 0 | g e^{-\mathcal{L}t} f | \rho_{\text{eq}} \rangle \quad (133)$$

and

$$\langle f \rangle_{\text{eq}} = \langle 0 | f | \rho_{\text{eq}} \rangle. \quad (134)$$

Besides enabling ρ and ρ_v to be evaluated in terms of the boson representation, Eqs. (133) and (134) are rather suggestive of the nature of the various time dependent functions which have been obtained in this investigation.

In particular, if $f = g = s$, we see from Eq. (45) that the reduced Green's function, $D(t)$, or structure function as it has also been called, is directly related to the autocorrelation function for the reaction sink function, s . Furthermore, from Eq. (49) we see that the function $H(t)$, whose transform stands so prominently in Eqs. (51), (52), (69), and (82), is directly proportional to this autocorrelation function:

$$\rho(s, s, t) \propto H(t) = D(t) - v_{\text{eq}}^2. \quad (135)$$

Regarding the time dependence of $D(t)$ and $H(t)$, using Eqs. (17), (109), (114)–(116), and (130)–(134) and the boson representation⁸ of $\mathbf{r}^{(i)}$ it may be seen that

$$c^{(i)} = \frac{1}{6} \langle \mathbf{r}^{(i)} \cdot \mathbf{r}^{(i)} \rangle_{\text{eq}}, \quad (136)$$

$$n^{(ik)}(t) = \frac{1}{3} \langle \mathbf{r}^{(i)}(0) \cdot \mathbf{r}^{(k)}(t) \rangle_{\text{eq}}, \quad (137)$$

and

$$|\mathbf{A}| = c^{(i)} c^{(k)} [1 - \rho_v^2(\mathbf{r}^{(i)}, \mathbf{r}^{(k)}, t)]. \quad (138)$$

These relations enabled us to account for the effects of excluded volume forces so easily in Sec. IVB.

For the specific case considered in the numerical calculations, the time dependence is related to the square of the autocorrelation function for the end-to-end vector \mathbf{L} , $\rho_v(\mathbf{L}, \mathbf{L}, t)$. Finally, it is notable and rather curious that the autocorrelation function for L^2 should turn out to be the square of the autocorrelation function for \mathbf{L} ,

$$\rho(L^2, L^2, t) = [\rho_v(\mathbf{L}, \mathbf{L}, t)]^2, \quad (139)$$

as can be verified by direct calculation with the operator \mathcal{L} of Eq. (24). This perhaps correlates with Verdier's^{3c} remark that L^2 relaxes twice as fast as the end-to-end length.

V. SOLUTION OF APPROXIMATE EQUATIONS

In this section the (numerical) inversion of Eqs. (51) and (52) for $\hat{\nu}$ and $\hat{\phi}$ will be discussed. The significant features of the inversion technique are well illustrated by consideration of a simple model for a pair of reactive groups on the ends of a polymer chain. In this model the two molecular groups are undergoing Brownian motion and are connected by a long weak harmonic spring. Since only the relative motion is of interest, the relevant equation of motion is the Smoluchowski equation for a harmonically bound particle. The mathematical particularities of this model are presented in the Appendix. The expressions for $\hat{\nu}$ and $\hat{\phi}$ resulting from the use of this model are formally identical to Eqs. (51) and (52), but the reduced Green's function appearing in these expressions has a simpler time dependence than its counterpart associated with the complex chain model. Despite the simplicity of the model, all of the correct qualitative features of the solution are preserved. Also, note that no special choice for the sink function \mathcal{S} is made in this discussion unless explicitly stated. The significance of higher order terms in the approximation scheme will also be considered.

A. Inversion procedure

Evidence will now be presented that $\nu(t)$ and $\phi(t)$ are given exactly as a sum of exponentially decaying terms whose coefficients and time constants can be calculated, in principle, exactly. In order to carry out this calculation it is necessary to be able to calculate $\hat{D}(s)$ for $s \leq 0$, and we deal with this problem first.

The integral representation of $\hat{D}(s)$,

$$\hat{D}(s) = \int_0^\infty e^{-st} D(t) dt, \quad (140)$$

with Eqs. (A11) and (A14) for $D(t)$ is moderately well suited for numerical calculation, but unfortunately Eq. (140) is not defined for $s \leq 0$. The integral diverges unless $s > 0$. On the other hand, the eigenfunction expansion of $\hat{D}(s)$, obtainable from Eqs. (A10), (A14), and (140) as

$$\hat{D}(s) = \sum_{\mathbf{n}} D_{\mathbf{n}}^2 (s + \lambda_{\mathbf{n}})^{-1}, \quad (141)$$

where

$$D_{\mathbf{n}} = \int d\mathbf{r} \psi_0(\mathbf{r}) \mathcal{S}(\mathbf{r}) h_{\mathbf{n}}(\mathbf{r}), \quad (142)$$

is defined for all $s \neq -\lambda_{\mathbf{n}}$, but is not well suited for calculation in this infinite series form. To remedy this situation consider the functions $H(t)$ and $\hat{H}(s)$ defined in Eqs. (49) and (50). Since $D_0 = v_{\text{eq}}$,

$$\hat{H}(s) = \sum_{\mathbf{n} \neq 0} D_{\mathbf{n}}^2 (s + \lambda_{\mathbf{n}})^{-1}. \quad (143)$$

This function is defined for $s = 0$ since the $\mathbf{n} = 0$ term (with $\lambda_0 = 0$) is missing. In fact, the first singularity of $\hat{H}(s)$ is now seen to be located at $s = -\lambda_{(1)}$ where $\lambda_{(1)}$ is

the smallest eigenvalue associated with a nonvanishing coefficient $D_{(1)}$. It may be seen intuitively that $\hat{H}(s)$ defined through its integral representation,

$$\hat{H}(s) = \int_0^\infty e^{-st} H(t) dt, \quad (144)$$

will also be defined for all $s > -\lambda_{(1)}$. This means that the integral representation of $\hat{D}(s)$ can be analytically continued partly into the negative half plane by successively subtracting out the singularities of $\hat{D}(s)$. The result can be established with more rigor by employing a theorem¹³ which, loosely stated, guarantees the convergence of $\hat{H}(s)$ defined through Eq. (144) for $s > a_c$ with

$$a_c = \lim_{t \rightarrow \infty} \ln(\alpha(t) - \alpha(\infty))/t \quad (145)$$

and

$$d\alpha(t) = H(t) dt. \quad (146)$$

With

$$H(t) = D_{(1)} e^{-\lambda_{(1)} t} + \sum_{\substack{\mathbf{n} \neq 0, \\ (1)}} D_{\mathbf{n}}^2 e^{-\lambda_{\mathbf{n}} t}, \quad (147)$$

we find for $(\alpha(t) - \alpha(\infty))$:

$$\alpha(t) - \alpha(\infty) = D_{(1)} \lambda_{(1)}^{-1} e^{-\lambda_{(1)} t} + \sum_{\substack{\mathbf{n} \neq 0, \\ (1)}} D_{\mathbf{n}} \lambda_{\mathbf{n}}^{-1} e^{-\lambda_{\mathbf{n}} t}. \quad (148)$$

Taking the limit, we obtain $a_c = -\lambda_{(1)}$. When the region of convergence is extended further, the successive limits are determined by which of the $D_{\mathbf{n}}$ are nonzero. A little consideration of the properties of Hermite polynomials will show that for symmetric \mathcal{S} functions the only nonvanishing $D_{\mathbf{n}}$ are those arising from eigenfunctions which contain only even orders of Hermite polynomials. The generalization to the more complicated chain models is that the basis functions contain only even numbers of excitations of the components of normal modes.

As evidence for the exponential decay, note first that the derivatives of $\hat{\nu}$ and $\hat{\phi}$ with respect to s , evaluated at $s = 0$, are finite for all orders. This is most easily seen by considering Eqs. (A12) and (A13) for $\hat{\nu}$ and $\hat{\phi}$ in terms of \hat{H} . The essential effect of repeated differentiation is to produce powers of t multiplying $H(t)$. The Laplace transform of $t^n H(t)$ is convergent for $s = 0$ as may be seen by using the theorem expressed in Eq. (145). This property of the derivatives is one (though not unique) characteristic of exponential behavior.

We next note that $\hat{\nu}$ and $\hat{\phi}$ possess a series of simple poles, and that there are no complex roots in the denominator. Set the denominator of Eq. (A12) or (A13) equal to zero and rewrite it as

$$s = -kv_{\text{eq}}/[1 + (k/v_{\text{eq}})\hat{H}(s)]. \quad (149)$$

With $\hat{H}(s)$ defined through its integral representation (for purposes of calculation), Eq. (149) is defined for $s > -\lambda_{(1)}$, and, in fact, it possesses a solution for $-\lambda_{(1)} < s < 0$ which is easily found iteratively. Though we have no mathematical proof that the solution is unique, evidence for this exists on physical grounds. This will be discussed shortly. First we prove the absence of any complex roots.

The existence of a complex root requires that the real and imaginary parts of Eq. (149) each separately equal zero. So, assume $s = -\epsilon + i\mu$, $\lambda_{(1)} > \epsilon$ and use Eq. (144) for $\hat{H}(s)$. Then, setting the imaginary part of Eq. (149) equal to zero and solving for μ results in

$$\mu = \frac{-\epsilon(k/v_{\text{eq}}) \int_0^\infty e^{\epsilon t} \sin(\mu t) H(t) dt}{1 + (k/v_{\text{eq}}) \int_0^\infty e^{\epsilon t} \cos(\mu t) H(t) dt} \quad (150)$$

for which one solution is $\mu = 0$. Now assume $\mu > 0$. Since $e^{\epsilon t} H(t)$ is a monotonically decreasing function of t , both integrals in Eq. (150) are positive and the minus sign in the numerator implies that the right hand side is negative which contradicts our assumption. If $\mu < 0$ is assumed, a similar contradiction is reached. Thus $\mu = 0$ is the only solution, and no complex roots exist for $s > -\lambda_{(1)}$. The proof may be extended to cover a larger region of the negative s plane by concomitantly extending the region of convergence of the integral representation of $\hat{D}(s)$ in the suggested manner and repeating the above argument. The proof in these extended cases depends on D_n^2 being positive, which is trivial since D_n is real. For example, if

$$J(t) = D(t) - v_{\text{eq}}^2 - D_{(1)}^2 e^{-\lambda_{(1)} t}, \quad (151)$$

and

$$\hat{J}(s) = \int_0^\infty e^{-st} J(t) dt, \quad (152)$$

then $\hat{J}(s)$ is defined for $s > -\lambda_{(2)}$, where $\lambda_{(2)}$ is the smallest eigenvalue greater than $\lambda_{(1)}$ associated with a non-vanishing coefficient. The equation

$$0 = s + s(k/v_{\text{eq}}) \hat{J}(s) + (k/v_{\text{eq}}) D_{(1)}^2 s(s + \lambda_{(1)})^{-1} + kv_{\text{eq}} \quad (153)$$

is just the denominator of $\hat{\nu}$ or $\hat{\phi}$ set equal to zero. Besides the solution of Eq. (149), an additional solution exists for $-\lambda_{(1)} > s > -\lambda_{(2)}$ which is easily found iteratively. Equation (153) can also be used in the fashion of Eqs. (149) and (150) to establish the absence of complex roots in the strip $-\lambda_{(1)} > s > -\lambda_{(2)}$.

The physical grounds for the existence of unique roots is this: Each time a root is found it has the form $s = -\lambda - \epsilon$ where $-\lambda$ is the previous limit of convergence for the integral representation of \hat{D} . For Eq. (149), $\lambda = 0$; for Eq. (153), $\lambda = \lambda_{(1)}$. The λ are, of course, frequencies for the various relaxation modes of the chain, so that the poles of $\hat{\nu}$ and $\hat{\phi}$ are the poles of the reduced Green's function, \hat{D} , perturbed by the ongoing reaction. Each active relaxation frequency λ is shifted by an amount $\epsilon(\lambda)$ which, in general, differs for each pole. It seems reasonable that these should be the only poles of $\hat{\nu}$ and $\hat{\phi}$ since they appear so intimately related to the natural relaxation frequencies of the nonreacting chain. From Eqs. (A12) and (A13) or (51) and (52), it can also be seen that the poles of \hat{H} are the zeros of $\hat{\nu}$ and have no effect on $\hat{\phi}$.

Once the existence and location of each pole is ascertained, the calculation of the coefficient for the exponential term is no problem. If the i th pole is found at $-\delta_i$ and ϕ and ν are given by

$$\phi(t) = \sum_i \phi_i e^{-\delta_i t}, \quad (154)$$

$$\nu(t) = \sum_i \nu_i e^{-\delta_i t}, \quad (155)$$

then, by the calculus of residues

$$\phi_i = \lim_{s \rightarrow -\delta_i} (s + \delta_i) \hat{\phi}(s), \quad (156)$$

$$\nu_i = \lim_{s \rightarrow -\delta_i} (s + \delta_i) \hat{\nu}(s). \quad (157)$$

Equations (156) and (157) may be evaluated for $i=1$ as

$$\nu_1 = [1 + (k/v_{\text{eq}}) [\hat{H}(-\delta_1) - \delta_1 \hat{H}'(-\delta_1)]]^{-1}, \quad (158)$$

$$\phi_1 = [1 + (k/v_{\text{eq}}) \hat{H}(-\delta_1)] \nu_1, \quad (159)$$

where

$$\hat{H}'(s) = -\int_0^\infty t e^{-st} H(t) dt. \quad (160)$$

The procedure may be extended indefinitely, calculating as many terms as is deemed necessary to represent the full solution. In most cases, one term is sufficient to obtain in excess of 99% of the complete solution for ϕ . The integrals of $\nu(t)$ and $\phi(t)$ may be used as criteria for completeness. From the definition of the Laplace transform we have

$$\int_0^\infty \phi(t) dt = \hat{\phi}(0), \quad (161)$$

$$\int_0^\infty \nu(t) dt = \hat{\nu}(0). \quad (162)$$

The values of Eqs. (161) and (162) can be compared with those obtained by integrating Eqs. (154) and (155).

The above discussion was made primarily for the simple model for which the Green's function is rigorously diagonal and with a symmetric S function used in the formal evaluation of $D(t)$ or $\hat{D}(s)$. As mentioned, the exclusion of complex roots depends on the positive definiteness of the expansion coefficients of $D(t)$. In considering the application of these results to the complex chain models we note first that with the retention of excluded volume forces the expansion coefficients are no longer manifestly positive as may be seen by inspection of Eqs. (117) and (119). The asymmetry in these coefficients is probably attributable to the neglect of off diagonal terms as discussed at the beginning of Sec. IV. Even when excluded volume forces are neglected or retained only through the $U = S^\infty$ approximation it may happen that the particular choice of sink function leaves doubt concerning the positive definiteness of the coefficients. Such a case arises for the choice made in our numerical calculations. There is no general proof that the coefficients remain positive, but direct calculation, presented in the Appendix of the following paper, shows that the coefficients of terms in $\lambda_{(1)}$ and $\lambda_{(2)}$ for the harmonic spring model and in $\lambda_{(1)}$ for the more complex model are positive.

Judging by these results, it may be generally true that the expansion coefficients are always positive. However, even if this assertion were violated, the results for the strip $0 > s > -\lambda_{(1)}$ would still be valid. Thus, the long time relaxation behavior of the reacting system would still be purely exponential.

B. Convergence of approximation scheme

A complete investigation of the convergence of the approximation scheme has not been attempted. Instead, we present a brief discussion about the qualitative changes introduced by the first order approximation.

Equations (119) and (124) give

$$(\hat{D})^2 - v_{eq} \hat{Y} = \sum_{\mathbf{n} \neq 0} \sum_{\mathbf{m} \neq 0} \frac{\langle 0 | \mathbf{s} | \mathbf{n} \rangle \langle \mathbf{m} | \mathbf{s} | \rho_{eq} \rangle}{(s + L_{\mathbf{m}})(s + L_{\mathbf{n}})} \times \{ \langle 0 | \mathbf{s} | \mathbf{m} \rangle \langle \mathbf{n} | \mathbf{s} | \rho_{eq} \rangle - v_{eq} \langle \mathbf{n} | \mathbf{s} | \mathbf{m} \rangle \}. \quad (163)$$

The expressions for $\hat{\nu}^1$ and $\hat{\phi}^1$ were given in Eqs. (55) and (57):

$$\hat{\nu}^1 = \frac{1 - (k/v_{eq})^2 [(\hat{D})^2 - v_{eq} \hat{Y}]}{s + s(k/v_{eq})\hat{H} + kv_{eq}}, \quad (164)$$

$$\hat{\phi}^1 = \frac{s + s(k/v_{eq})\hat{H} + (k/v_{eq})^3 [(\hat{D})^2 - v_{eq} \hat{Y}]}{s[s + s(k/v_{eq})\hat{H} + kv_{eq}]}. \quad (165)$$

The first notable consequence is the existence of a new set of poles in $\hat{\nu}^1$ and $\hat{\phi}^1$ located at $s = -L_{\mathbf{n}}$ which arise from terms in the double sum with $\mathbf{n} = \mathbf{m}$. The time dependence that is governed by the denominator has not been affected, however (assuming exponential behavior that is determined by the poles of $\hat{\nu}^1$ and $\hat{\phi}^1$). In particular, the long time dependence for the rate that would be obtained from these expressions is identical to that obtained in zeroth order. Other consequences are disturbing.

First, the expressions are undefined for $k = \infty$. Second, since it seems reasonable to believe that Eq. (163) is well defined and nonzero for $s = 0$, $\hat{\phi}^1$ is seen to possess a singularity at $s = 0$. This corresponds to $\phi(t)$ approaching a constant, nonzero, limit as $t \rightarrow \infty$, clearly an unphysical result.

Since Eqs. (33) and (47) are exact, and since we must have $\phi(t) \rightarrow 0$ as $t \rightarrow \infty$ we can determine exactly the integral of $\nu(t)$.

$$\int_0^\infty \nu(t) dt = (kv_{eq})^{-1}. \quad (166)$$

Equation (166) serves as a very important criterion for the goodness of an approximate expression for $\hat{\nu}(s)$. Failure to satisfy Eq. (166) automatically insures an unphysical behavior for $\phi(t)$ as $t \rightarrow \infty$. Equation (51) for $\hat{\nu}(s)$, the zeroth approximation, is seen to satisfy Eq. (166) while Eq. (55) or (164) does not, unless by some fortuitous cancellation of terms Eqs. (163) will equal zero for $s = 0$.

It thus appears that the zeroth order expressions given in Eqs. (51) and (52) are the best to be obtained in this approximation scheme. It does not appear likely that higher order terms would alleviate the difficulties that have been mentioned, and in any case this is not subject to easy verification.

VI. DISCUSSION

The application of the formalism of DCR to describe intrachain reactions of macromolecules has been presented. Following a closure approximation, it was suggested that the integral equations arising in the theory

could be solved exactly by a sum of simple exponential functions. Despite the simplicity of this result, the approximation scheme does not readily lead to any useful higher order corrections, yet in zeroth order it does have two other outstanding features. It has the merit of qualitatively reproducing the behavior of the distribution function in the regions of configuration space where the reactions are highly favored. It also has the virtue of giving exactly the value of the integral of $\nu(t)$ [or $\nu(t)$] which is very important if the long time behavior of $\phi(t)$ is to be qualitatively correct.

APPENDIX: THE HARMONIC SPRING MODEL

With inclusion of the reaction term the Smoluchowski equation for a harmonically bound particle reads

$$(\partial\psi/\partial t) - D\nabla \cdot (\nabla\psi + (3/2L^2)\psi\nabla|\mathbf{r}|^2) = -kS\psi. \quad (A1)$$

Here, D is the relative diffusion constant characteristic of small molecules, and L is the root mean square length of the spring. The harmonic potential is supposed to be a crude approximation to the mean potential acting on the two molecules because of the intervening polymer chain. The operator on the left hand side can be formally obtained from Eq. (1) by specializing to $N=1$ in the free draining limit [$\mathbf{T}(\mathbf{r}_i) = 0$ in Eq. (2)] with $U = S^\infty$ as the backbone potential, setting $b = L$ and transforming to relative coordinates. An operator of this form can also be obtained by integrating Eq. (1) over the coordinates of segments internal to the chain ends; several of the resulting integrals cannot be done exactly, but simple approximations lead to the desired result.

With the substitution

$$\psi = \psi_0 \rho, \quad (A2)$$

$$\psi_0 = (2\pi L^2/3)^{-3/2} \exp[-3|\mathbf{r}|^2/(2L^2)], \quad (A3)$$

Eq. (A1) becomes

$$(\partial\rho/\partial t) - D(\nabla^2\rho - (3/L^2)\mathbf{r} \cdot \nabla\rho) = -kS\rho. \quad (A4)$$

The coordinate operator on the left-hand side of Eq. (A4) possesses the Hermite polynomials, $H_n(u)$, as eigenfunctions. Thus,

$$D\nabla^2 h_{\mathbf{n}} - (3D/L^2)\mathbf{r} \cdot \nabla h_{\mathbf{n}} = -\lambda_{\mathbf{n}} h_{\mathbf{n}}, \quad (A5)$$

where

$$\lambda_{\mathbf{n}} = \lambda_{n_x} + \lambda_{n_y} + \lambda_{n_z} \quad (A6)$$

and

$$\lambda_{n_x} = 2n_x(3D/2L^2). \quad (A7)$$

The normalized eigenfunctions, $h_{\mathbf{n}}(\mathbf{r})$, are given as

$$h_{\mathbf{n}}(\mathbf{r}) = h_{n_x}(x) h_{n_y}(y) h_{n_z}(z), \quad (A8)$$

where

$$h_n(x) = (2^n n!)^{-1/2} H_n((3/2)^{1/2}(x/L)). \quad (A9)$$

The operator of Eq. (A5) is also self-adjoint when the function ψ_0 , defined in Eq. (A3), is used as a weight.

The eigenfunction expansion of the Green's function of Eq. (A1) is given as

$$W(\mathbf{r}, \mathbf{r}^0, t) = \psi_0(\mathbf{r}) \sum_{\mathbf{n}} h_{\mathbf{n}}(\mathbf{r}) h_{\mathbf{n}}(\mathbf{r}^0) e^{-\lambda_{\mathbf{n}} t}, \quad (\text{A10})$$

which can be shown¹⁴ in a variety of ways to be equivalent to

$$W(\mathbf{r}, \mathbf{r}^0, t) = [1 - \exp(-6Dt/L^2)]^{3/2} \exp\{- (3/2)L^{-2} \times |\mathbf{r} - \mathbf{r}^0 \exp(-3Dt/L^2)|^2 / [1 - \exp(-6Dt/L^2)]\}. \quad (\text{A11})$$

Equation (A1) can be solved in terms of this Green's function using the same approximation that was made for its more complicated analog in Sec. III. The results are formally the same, the only difference residing in the altered time dependence of $D(t)$. We have

$$\hat{v}(s) = [s + s(k/v_{\text{eq}}) \hat{H}(s) + kv_{\text{eq}}]^{-1} \quad (\text{A12})$$

and

$$\hat{\phi}(s) = [1 + (k/v_{\text{eq}}) \hat{H}] \hat{v}, \quad (\text{A13})$$

where

$$\phi(t) = \int \psi d\mathbf{r},$$

$$v(t) = \int \psi \mathbf{s} d\mathbf{r} / v_{\text{eq}},$$

$$v_{\text{eq}} = \int \psi_0 \mathbf{s} d\mathbf{r},$$

\hat{H} is defined by Eq. (50) and, finally,

$$D(t) = \int d\mathbf{r} d\mathbf{r}^0 \mathbf{s}(\mathbf{r}) W(\mathbf{r}, \mathbf{r}^0, t) \mathbf{s}(\mathbf{r}^0) \psi_0(\mathbf{r}^0). \quad (\text{A14})$$

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