Torsion Dynamics in Linear Macromolecules: Exact Inclusion of Hydrodynamic Interaction

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Received July 20, 1982

ABSTRACT: An equation is derived relating the hydrodynamic torque/unit length to the instantaneous angular velocity along a long, torsionally flexible cylinder. In practice, the hydrodynamic torque at some point is locally determined. This result is incorporated in the dynamical theory of torsion in linear macromolecules to account more exactly for hydrodynamic interaction. In the case of fluorescence depolarization of ethidium bromide bound to DNA, it is shown that the approximate and exact hydrodynamic treatments are in excellent agreement with each other. This is interpreted to mean that fluorescence depolarization primarily monitors the decay of longer wavelength torsional normal modes in DNA.

I. Introduction

In a recent article[1] the hydrodynamic properties of a long torsionally flexible cylinder were considered and the present work can be regarded as its sequel. Specifically the model consists of a long cylinder of length L and radius a lying along the z axis with its ends at $\pm L/2$. It is assumed that the only motion of the cylinder involves twisting or torsional motions about the long axis. What was derived previously[1] was a general equation relating the instantaneous angular velocity at position z, $\dot{\phi}(z)$, to the instantaneous hydrodynamic torque/unit length, $\tau(z')$, acting on the entire chain.

$$\dot{\phi}(z) = \frac{1}{2\pi^2 a^2 \eta} \times \int_0^\infty \mathrm{d}k\, I_1(ka)K_1(ka) \int_{-L/2}^{+L/2} \mathrm{d}z'\, \tau(z') \cos\,[k(z - z')] \quad (1)$$

where η is the viscosity of the solvent, I_1 and K_1 are modified Bessel functions, and a and L are the radius and length of the cylinder, respectively. This result appears to be exact within the limitations of the assumptions about the nature of the solvent and its interaction with the cylinder surface.

It should be noted from eq 1 that it is not generally possible to define a friction coefficient since this implies a one-to-one correspondence between $\tau(z)$ and $\dot{\phi}(z)$. However, in the special case of a torque which varies sinusoidally along the cylinder, it was shown that

$$\dot{\phi}(z) = \frac{\tau(z)}{2\pi a^2 \eta} I_1(qa)K_1(qa) \quad (2)$$

given that

$$\tau(z) = \tau_0 \cos\,(qz + \epsilon) \quad (3)$$

where τ_0 is the amplitude of the hydrodynamic torque, $2\pi/q$ is the distance along the cylinder for a complete cycle of the torque, and ϵ is an arbitrary phase factor. Since the friction coefficient, γ, is given by the relation $\tau = \gamma\dot{\phi}$, we can identify the friction coefficient corresponding to eq 2 and 3

$$\gamma(q) = \frac{2\pi a^2 \eta}{I_1(qa)K_1(qa)} \quad (4)$$

In the case of a rod rotating uniformly about its long axis, $q = 0$ and eq 4 reduces to the Perrin result[2] as it must

$$\gamma(0) = 4\pi a^2 \eta \quad (5)$$

For small qa ($qa \lesssim 0.1$), $\gamma(q)$ does not deviate appreciably from eq 5 but for larger values of qa, the deviation becomes substantial and $\gamma(q)$ increases as q increases. This can be understood physically by considering the following argument. Since stick-boundary conditions are assumed (γ would be zero in the present case for slip-boundary conditions), the velocity of the solvent and that of the cylinder are equal at the point of contact. At large q, there are steep gradients in the solvent velocity near the cylinder surface and hence there is a larger frictional dissipation than at smaller q.

The primary motivation for this work and ref 1 has been the recent interest in the rapid twisting or torsional motions of DNA detected by fluorescence depolarization[3-6] and EPR.[7] The dynamical theory of torsion in linear macromolecules was originally worked out by Barkley and Zimm[8] and Allison and Schurr.[9] More recently, the effect of torsional motions on depolarized light scattering[10] and NMR relaxation[11] have been examined. In the latter work,[11] it has been demonstrated that torsional motions alone can largely account for the relaxation observed in ^{31}P NMR studies of DNA restriction fragments.[12,13]

In the dynamical theories,[8,9] hydrodynamic interaction was accounted for in an approximate way since it was assumed that the Perrin formula (eq 5) was generally valid. From the brief discussion following eq 5 this approximation is a good one provided the wavelength of the relaxing normal modes is large compared to the cylinder radius. A qualitative discussion concerning this point has been given in ref 1 in connection with the fluorescence depolarization of ethidium bromide bound to DNA. It was concluded that at short times (below 5 ns), the above approximation might break down and that there was a need to pursue the problem further.

In the present article, eq 1 is first inverted to obtain an expression relating $\tau(z)$ to the instantaneous angular velocity of the entire chain. This is a more convenient form of the equation since one is usually interested in the resultant torque, $\tau(z)$, given $\dot{\phi}(z)$ and not the other way around. Following the inversion, a particularly simple special case is examined to learn how "long range" the torsional hydrodynamic interaction turns out to be. Following this, torsional hydrodynamic interaction is incorporated into the dynamical theories[8,9] and its effect is explicitly evaluated by using known experimental parameters. We conclude with a short discussion of our findings.

II. Hydrodynamic Torque

We begin by inverting eq 1 for a long, but finite chain. Although the inversion is simpler for an infinite chain, the finite chain must be considered here since the dynamical theory that we shall apply it to pertains to a finite linear

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0024-9297/83/2216-0421$01.50/0

chain. Since $I_1(-x)K_1(-x) = I_1(x)K_1(x)$, eq 1 can be written

$$\dot{\phi}(z) = \frac{1}{4\pi^2a^2\eta}\int_{-\infty}^{\infty}\mathrm{d}k\ I_1(ka)K_1(ka)\int_{-L/2}^{+L/2}\mathrm{d}z'\ \tau(z')e^{ik(z-z')} \tag{6}$$

Multiply both sides of eq 6 by e^{-iqz} and integrate with respect to z from $-L/2$ to $+L/2$ to obtain

$$\int_{-L/2}^{+L/2}\mathrm{d}z\ \dot{\phi}(z)e^{-iqz} = \frac{1}{2\pi^2a^2\eta}\int_{-L/2}^{+L/2}\mathrm{d}z'\ \tau(z') \times \int_{-\infty}^{+\infty}\mathrm{d}k\ e^{-ikz'}I_1(ka)K_1(ka)\left\{\frac{\sin\ [L/2(k-q)]}{k-q}\right\} \tag{7}$$

The quantity in braces is a representation of the δ function in the limit $L \rightarrow \infty$.[14]

$$\lim_{L\rightarrow\infty}\frac{\sin\ [L/2(k-q)]}{k-q} = \pi\delta(k-q) \tag{8}$$

For long but finite chains, it is permissible to use eq 8 in eq 7 for finite L as long as the remainder of the integrand is a slowly varying function of k compared to the quantity in braces. This is true if the remainder of the integrand does not vary appreciably over $\Delta k \approx 1/L$. Making this approximation (which is exact in the $L = \infty$ limit), it is straightforward to show that

$$\int_{-L/2}^{+L/2}\mathrm{d}z'\ \tau(z')e^{-iqz'} = \frac{2\pi a^2\eta}{I_1(qa)K_1(qa)}\int_{-L/2}^{+L/2}\mathrm{d}z'\ \dot{\phi}(z')e^{-iqz'} \tag{9}$$

Finally, multiply both sides of eq 9 by e^{iqz} and integrate with respect to q from $-\infty$ and $+\infty$. Making use of the representation[14]

$$\delta(z-z') = \frac{1}{2\pi}\int_{-\infty}^{+\infty}\mathrm{d}q\ e^{iq(z-z')} \tag{10}$$

yields

$$\tau(z) = a^2\eta\int_{-\infty}^{+\infty}\frac{\mathrm{d}q}{I_1(qa)K_1(qa)}\int_{-L/2}^{+L/2}\mathrm{d}z'\ \dot{\phi}(z')e^{iq(z'-z)} \tag{11}$$

This can also be written

$$\tau(z) = a^2\eta\int_{0}^{\infty}\frac{\mathrm{d}q}{I_1(qa)K_1(qa)}\int_{-L/2}^{+L/2}\mathrm{d}z'\ \dot{\phi}(z')e^{iq(z'-z)} + \mathrm{cc} \tag{12}$$

where cc stands for complex conjugate.

Before investigating the dynamical problem through normal coordinates, we shall apply eq 12 to a specific example. In order to gain insight into what effect a large and sudden change in $\dot{\phi}$ (instantaneous angular velocity) at some point has on τ (hydrodynamic torque/unit length) and how far down the cylinder that effect persists, consider the case

$$\begin{aligned}\dot{\phi}(z') &= -\omega \qquad z' < 0\\ \dot{\phi}(z') &= +\omega \qquad z' > 0\end{aligned} \tag{13}$$

Substituting eq 13 into eq 12 leads after a few steps to

$$\tau(\gamma) = 4a^2\eta\omega\int_0^{\infty}\frac{\mathrm{d}p\ \sin\ (py)}{pI_1(p)K_1(p)}\left[1-\cos\left(\frac{pL}{2a}\right)\right] \tag{14}$$

where $y = z/a$. The cos $(pL/2a)$ term accounts for end effects. Provided that $L/a \gg 1$ and z is not located near the end of the cylinder, this term can be ignored since it is a rapidly oscillating function of p and goes to zero. The remaining term can be integrated numerically using polynomial approximations for I_1 and K_1.[15] The results are summarized in Figure 1. The dotted line in the figure represents $\tau = \pm 4\pi a^2\eta\omega$, the asymptotic value of τ far from the point where $\dot{\phi}$ changes from $-\omega$ to $+\omega$. Note that τ deviates significantly from this asymptotic value only for positions within a distance of about $\pm 3a$ from the point of change in $\dot{\phi}$. Assuming a hydrodynamic radius of 12 Å for DNA, this corresponds to ±36 Å or ±11 base pairs. On the basis of this example then, it appears that the instantaneous *hydrodynamic* torque in the direction of the helix at some position is determined primarily by the instantaneous angular velocity of the immediate neighborhood. This, in turn, suggests that the use of the approximate eq 5 in the dynamical theory is valid provided gradients in $\dot{\phi}(z)$ are not large compared to a. Finally, it justifies the use of a straight cylinder in treating torsional hydrodynamic interactions. Although there is still disagreement regarding the actual persistence length of DNA in solution,[16-20] the smallest cited value is around 300 Å in high salt and substantially higher values in low salt. Over a distance of 75 Å, DNA can be accurately approximated as a straight cylinder.

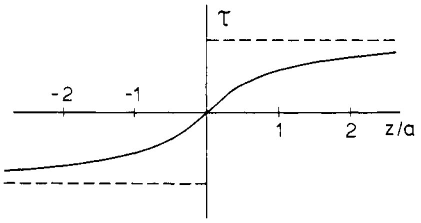

Figure 1. Variation in τ along z given that $\dot{\phi}$ changes from $-\omega$ to $+\omega$ at $z = 0$. The dotted lines represent the asymptotic values of $\tau = \pm 4\pi a^2\eta\omega$ far from $z = 0$.

III. Normal Coordinates

The instantaneous angular velocity can be related to the set of complex normal coordinates, $\{\sigma_j\}$, by the Fourier series

$$\dot{\phi}(z') = \sum_{j=-N}^{+N}\dot{\sigma}_j e^{2\pi iz'/L_j'} \tag{15}$$

where

$$L_j' = \frac{2(N+1)}{j}l_0 \tag{16}$$

and l_0 is the basic unit length, which can be taken to be one base pair. The normal mode $\dot{\sigma}_0$ accounts for overall axial rotation of the cylinder. Since $\dot{\phi}$ is real

$$\dot{\sigma}_j = \dot{\sigma}_{-j}^* \tag{17}$$

so the number of linearly independent normal coordinates is $N + 1$. Substituting these in eq 12 leads to

$$\tau(z) = 2\pi a^2\eta\left[2\dot{\sigma}_0 + \sum_{j=1}^{N}\frac{\dot{\sigma}_j e^{izq_j'} + \dot{\sigma}_j^* e^{-izq_j'}}{I_1(q_j'a)K_1(q_j'a)}\right] \tag{18}$$

where $q_j' = 2\pi/L_j'$.

In order to make the present work compatible with the dynamical theory of Allison and Schurr,[9] it is necessary to discretize the cylinder into $N + 1$ identical rods or disks linked end-to-end by Hookean torsion springs. It shall be assumed that N is even and that the centers of disks 1 and $N + 1$ lie at $z = -L/2$ and $+L/2$, respectively. N, L, and l_0 are related by $L = Nl_0$. Letting $z = l_0m - l_0(N + 2)/2$, eq 18 becomes

$$\tau_m = 2\pi a^2\eta\left[\dot{\sigma}_0 + \sum_{j=1}\frac{\dot{\sigma}_j e^{-\pi ij/2}e^{+\pi ij(2m-1)/2(N+1)} + \text{cc}}{I_1(q_j'a)K_1(q_j'a)}\right] \tag{19}$$

An objection could be made to applying eq 18 to a discrete model since it was derived on the assumption $\dot{\phi}(z)$ varies continuously with z and not in jumps as in the discrete model. However, if the amplitudes of the shortest σ_j modes are small compared to longer modes as is the case in DNA torsional motions, this is not expected to cause problems.

The complex normal modes, $\{\sigma_j\}$, introduced previously can be related to the conventional Rouse–Zimm normal modes of a linear chain, $\{\rho_l\}$, by comparing their relationship to $\dot{\phi}_m$

$$\dot{\phi}_m = \sum_{l=1}^{N+1} Q_{ml}\dot{\rho}_l$$

$$Q_{ml} = \left(\frac{2-\delta_{l,1}}{N+1}\right)^{1/2}\cos\left[\frac{(2m-1)(l-1)\pi}{2(N+1)}\right] \tag{20}$$

to the corresponding expression (eq 15) for $\{\dot{\sigma}_j\}$. After some straightforward algebra, it can be shown

l even:

$$\dot{\sigma}_l^{(\mathrm{r})} = (-)^{l/2}\dot{\rho}_{l+1}/((2-\delta_{l,1})(N+1))^{1/2}; \qquad \dot{\sigma}_l^{(\mathrm{i})} = 0$$

l odd:

$$\dot{\sigma}_l^{(\mathrm{i})} = (-)^{(l-1)/2}\dot{\rho}_{l+1}/((2-\delta_{l,1})(N+1))^{1/2}; \qquad \dot{\sigma}_l^{(\mathrm{r})} = 0 \tag{21}$$

where the r and i superscripts refer to real and imaginary parts, respectively. Consequently

$$\dot{\sigma}_j e^{izq_j'} + \text{cc} = Q_{m,j+1}\dot{\rho}_{j+1} \tag{22}$$

Making the following final substitutions

$$q_j \equiv q_{j-1}' = \frac{\pi(j-1)}{(N+1)l_0} \tag{23}$$

$$\gamma_j = \frac{2\pi a^2\eta}{I_1(q_ja)K_1(q_ja)} \tag{24}$$

Equations 20–24 can be used in eq 18 to obtain

$$\tau_m = \sum_{l=1}^{N+1} Q_{ml}\gamma_l\dot{\rho}_l \tag{25}$$

In matrix notation, this can be written

$$\tau_{\text{hydro}} = \mathbf{Q}\gamma\dot{\rho} = \mathbf{Q}\gamma\mathbf{Q}^{-1}\dot{\mathbf{\Phi}} \tag{26}$$

where τ_{hydro} and $\dot{\mathbf{\Phi}}$ are $N + 1$ dimensional column vectors, $\mathbf{Q}$ is the $N + 1 \times N + 1$ matrix that diagonalizes the Rouse–Zimm matrix, and γ is the diagonal friction matrix: $(\gamma)_{lm} = \delta_{lm}\gamma_l$.

Equation 26 is a discrete analog of eq 11 and 12 and shows how τ acting on a particular disk is related to $\dot{\mathbf{\Phi}}$ of the entire chain although in practice only disks in the neighborhood of the one in question have a large effect. Previously,[8,9] eq 26 was approximated with $\tau_{\text{hydro}} = \gamma_1\dot{\mathbf{\Phi}}$, which can be obtained from (26) by substituting γ_1 for all γ_l in the diagonal friction matrix. As discussed in ref 1, this is only valid for the longer normal modes.

IV. Dynamics

The dynamics of a torsion-disk model are isomorphic with the corresponding dynamics of a Rouse–Zimm chain.[9] The reader unfamiliar with the Rouse–Zimm chain and Langevin theory is referred to a number of detailed treatments in the literature.[21,22] The equation of motion of the torsion-disk model can be written

$$J\ddot{\mathbf{\Phi}} + \mathbf{Q}\gamma\mathbf{Q}^{-1}\dot{\mathbf{\Phi}} + \alpha\mathbf{A}\mathbf{\Phi} = \mathbf{T}(t) \tag{27}$$

where J is the disk moment of inertia for axial rotation, $\mathbf{A}$ is the Rouse–Zimm matrix for a linear chain, α is the Hookean torsional force constant between adjacent disks, and the elements of the column vector $\mathbf{T}(t)$ are independent stochastic torques acting on the individual disks. In terms of normal coordinates defined by eq 20, this can be written

$$J\ddot{\rho} + \gamma\dot{\rho} + \alpha\Lambda\rho = \mathbf{G}(t) \tag{28}$$

where $\Lambda = \mathbf{Q}^{-1}\mathbf{A}\mathbf{Q}$ is the diagonal Rouse–Zimm eigenvalue matrix, with $\Lambda_{ll} = \lambda_l = 4\sin^2[\pi(l-1)/2(N+1)]$ and $\mathbf{G}(t) = \mathbf{Q}^{-1}\mathbf{T}(t)$. The only difference between eq 28 and its approximate predecessor is the replacement of γ in eq 28 by $\gamma_1 = 4\pi a^2\eta$. Since eq 28 still represents a set of $N + 1$ uncoupled stochastic differential equations, its solution along with the standard conditional probabilities and hence correlation functions that are related to experimental observables can be written down immediately. This shall be demonstrated with a particular example.

The fluorescence polarization anisotropy at time t is defined

$$r(t) = [I_\parallel(t) - I_\perp(t)]/[I_\parallel(t) + 2I_\perp(t)] \tag{29}$$

where $I_\parallel(t)$ and $I_\perp(t)$ are the emitted fluorescence intensities parallel and perpendicular, respectively, to the polarization of the exciting light pulse, which was delivered at time $t = 0$. The emitted light is observed at an angle of 90° with respect to both the propagation and polarization vectors of the exciting light. In the case of ethidium bromide bound to DNA, the connection between $r(t)$ and molecular parameters is given by[8,9]

$$r(t) = 0.4[a + b\langle e^{i(\phi(t)-\phi(0))}\rangle + c\langle e^{2i(\phi(t)-\phi(0))}\rangle] \tag{30}$$

where $\phi(t) - \phi(0)$ is the net change in the torsion angle of a disk or rod in time t and angular brackets denote an average over all equilibrium initial conditions and dynamical torsion trajectories of the rod and over all disks that comprise the DNA. a, b, and c are related to the dye–DNA geometry

$$a = (\tfrac{3}{2}\cos^2\epsilon - \tfrac{1}{2})^2$$
$$b = \tfrac{3}{4}\sin^2 2\epsilon \tag{31}$$
$$c = \tfrac{3}{4}\sin^4\epsilon$$

where ϵ is the angle between the dye transition moment and the local helix axis. The solution of the correlation functions in eq 30 can be written (see eq 9 of ref 9)

$$\langle e^{ik(\phi(t)-\phi(0))}\rangle = \frac{1}{N+1}e^{-k^2k_\mathrm{B}Tt/(N+1)\gamma_1}\sum_{m=1}^{N+1} e^{-k^2S(t)} \tag{32}$$

$$S(t) = \sum_{l=2}^{N+1} d_l^2 Q_{ml}^2(1 - e^{-t/\tau_l}) \tag{33}$$

where k_B is Boltzmann's constant, T is the absolute temperature,

$$d_l^2 = k_\mathrm{B}T/\left[4\alpha\sin^2\left(\frac{\pi(l-1)}{2(N+1)}\right)\right] \tag{34}$$

is the mean-squared angular displacement, or amplitude, of normal mode l,

$$\tau_l = \gamma_l/[4\alpha\sin^2(\pi(l-1)/2(N+1))] \tag{35}$$

is the relaxation time of normal mode l, and γ_l is its friction coefficient given by eq 24.

A detailed analysis of eq 32 and 33 subject to the approximation $\gamma_l = \gamma_1$ can be found elsewhere.[9] Briefly, the total time course of the decay of eq 32 can be divided into several time zones. At long times, end effects become important and the decay of eq 32 becomes sensitive to the total chain length. For long DNA molecules, however, the nanosecond decay of the fluorescence polarization anisotropy is attributed to local motions so that only times that are substantially less than the longest relaxation times ($t \ll \tau_{11}$, for example) need be considered here.

Consider, then, the case of a long chain where the contribution to the decay of eq 32 due to disks near the ends of the chain can be ignored. The first exponential on the right-hand side of eq 32 can be set equal to one since it represents the contribution of the uniform ($l = 1$) mode. Q_{ml}^2 can also be set equal to its average value of $1/(N + 1)$ since each disk in the interior of the chain decays identically. Then eq 32 and 33 can be written

$$\langle e^{ik(\phi(t)-\phi(0))}\rangle = e^{-k^2 S(t)} \tag{36}$$

$$S(t) = \frac{1}{N+1}\sum_{l=2}^{N+1} d_l^2(1 - e^{-t/\tau_l}) \tag{37}$$

As discussed in ref 9, it is possible to break the short-time behavior for which eq 36 and 37 are valid, down further into the Initial Exponential Decay Zone and the Intermediate Zone. On the basis of recent experiments,[4,6] it has been concluded that the overwhelming decay of eq 37 occurs in the Intermediate Zone, which carries the interpretation that the disks (taken to be one base pair in length) are strongly coupled to one another and indistinguishable from an infinitely long continuum elastic cylinder. Shortly, the Intermediate Zone is reconsidered, but not subject to the approximation $\gamma_l = \gamma_1$. First, however, it shall prove instructive to contrast the $t \rightarrow 0$ limiting behavior of eq 37 with and without the $\gamma_l = \gamma_1$ approximation.

Since the bulk of the decay of eq 36 occurs at "intermediate" times, it is more meaningful to consider the time derivative of $S(t)$ rather than $S(t)$ itself in the $t = 0$ limit. Differentiating eq 37 with respect to t

$$\frac{\partial S(0)}{\partial t} = \frac{k_B T}{\gamma_1(N+1)}\sum_{l=2}^{N+1} f_l \tag{38}$$

where

$$f_l = 2I_1\left(\frac{\pi l a}{(N+1)l_0}\right)K_1\left(\frac{\pi l a}{(N+1)l_0}\right) \tag{39}$$

Replacing the sum by an integral and changing variables, this reduces to

$$\frac{\partial S(0)}{\partial t} = \frac{k_B T}{\gamma_1}\left[\frac{1}{z}\int_0^z \mathrm{d}x\, f(x)\right] \tag{40}$$

where $z = \pi a/l_0$ and $f(x) = 2I_1(x)K_1(x)$. The integral in eq 40 is not difficult to solve and yields

$$\int_0^z \mathrm{d}x\, f(x) \simeq 0.661 + \ln z \tag{41}$$

which is valid for z greater than about 8. Assuming a = 12 Å and l_0 = 3.4 Å gives z = 11.088. Equation 40 then becomes

$$\frac{\partial S(0)}{\partial t} \simeq \frac{k_B T}{\gamma_1}(0.277) \tag{42}$$

On the other hand, the same quantity evaluated in the $\gamma_l = \gamma_1$ approximation gives $k_B T/\gamma_1$. Hence, the $\gamma_l = \gamma_1$ approximation predicts an initial decay rate of eq 36 that is more than 3 times the rate predicted by eq 42. A physical interpretation of this is that the initial decay rate is dominated by the shortest, most rapidly decaying torsion modes and the friction coefficient of these modes is substantially greater than γ_1 (eq 24). Hence, a substantially slower decay rate results. We now turn to a study of the Intermediate Zone, which is of more practical importance than the $t = 0$ limit since it corresponds to actual experimental observables.

Table I
Comparison of Approximate (S_0, r_0) and Exact (S, r) Hydrodynamic Treatments of Torsional Brownian Motion in DNA

t, ns	$S_0(t) \times 10^2$	$\delta S(t) \times 10^2$	$S(t) \times 10^2$	$r_0(t)$	$r(t)$
0.2	2.276	0.243	2.033	0.377	0.379
0.4	3.219	0.212	3.007	0.368	0.370
0.6	3.942	0.193	3.749	0.361	0.363
0.8	4.553	0.181	4.372	0.355	0.357
1.0	5.090	0.170	4.920	0.350	0.352
1.5	6.233	0.153	6.080	0.341	0.342
2.0	7.199	0.142	7.057	0.332	0.334
2.5	8.047	0.133	7.914	0.326	0.327
3.0	8.816	0.126	8.690	0.320	0.321
4.0	10.179	0.117	10.062	0.309	0.310
5.0	11.382	0.103	11.279	0.301	0.301

In the Intermediate Zone, defined by $\tau_{11} \gg t \gg \gamma_1/\alpha$, it is permissible to approximate $\sin^2[\pi(l-1)/2(N+1)]$ in eq 34 and 35 with $[\pi(l-1)/2(N+1)]^2$. Replacing the sum in eq 37 by an integral and extending the upper limit to ∞, one can show that

$$S(t) = \frac{k_B T a}{\pi \alpha l_0}\int_0^\infty \frac{\mathrm{d}x}{x^2}(1 - e^{-Bf(x)x^2 t}) \tag{43}$$

where

$$B = \alpha l_0^2/\gamma_1 a^2 \tag{44}$$

$$f(x) = 2I_1(x)K_1(x) \tag{45}$$

It is convenient to rewrite this as

$$\begin{aligned} S(t) &= \frac{k_B T a}{\pi \alpha l_0}\left\{(\pi B t)^{1/2} - \int_0^\infty \frac{\mathrm{d}x}{x^2}(e^{-Bf(x)x^2 t} - e^{-Bx^2 t})\right\} \\ &= S_0(t) - \delta S(t) \end{aligned} \tag{46}$$

where $S_0(t)$ denotes the first ($t^{1/2}$) term on the right-hand side of eq 46 and $\delta S(t)$ denotes the integral term. The quantity $S_0(t)$ represents the $\gamma_l = \gamma_1$ approximation and $\delta S(t)$ represents the correction to this approximation. In order to determine the relative magnitude of the correction term, $S_0(t)$, $\delta S(t)$, and $S(t)$ are calculated with the parameters determined by Thomas et al.[4] Assuming T = 25 °C, a = 12 Å, and l_0 = 3.4 Å, they obtained $\gamma_1 = 5.47 \times 10^{-23}$ dyn cm s and $\alpha = 3.8 \times 10^{-12}$ dyn cm. The quantity $\delta S(t)$ was determined numerically and the results are summarized in Table I. Also listed in the table are the actual fluorescence polarization anisotropies, $r_0(t)$ and $r(t)$, using $S_0(t)$ and $S(t)$, respectively, in eq 30, 31, and 37. In eq 31, a value of ϵ = 70.5° has been used.[23]

Qualitatively, these results are not surprising since at short times, depolarization results from the relaxation of shorter torsion modes on the average than at later times and it is the shorter modes that are affected most by the $\gamma_l = \gamma_1$ approximation. The behavior of $S_0(t)$ and $\delta S(t)$ with time bear this out. It is rather surprising, however, that the effect is as small as it is. At 1 ns, for example, it might be expected that depolarization would result primarily from those normal modes with a relaxation time of about 1 ns, which corresponds to around 30 base pairs (eq 24 and 35). For a 30 base pair normal mode, γ_l is larger than γ_1 by 30% (eq 24) so a fairly large difference might be expected on the basis of the above argument. However, Table I shows a 3.3% difference between $S_0(1)$ and $S(1)$ and only a 0.6% difference between $r_0(1)$ and $r(1)$. The explanation of this paradox most likely has to do with the fact that the *amplitude* of the shorter modes is small compared to the longer ones according to eq 34. On the nanosecond time scale, the shorter modes do make a contribution to fluorescence depolarization but they are overwhelmed by the larger amplitude contributions of longer modes. The behavior in the $t = 0$ limit of $\mathrm{d}S(t)/\mathrm{d}t$ also supports this. The *initial* decay rate is dominated by the shortest modes but because of their low amplitude, they contribute little to the net decay.

V. Conclusions

Even though the response $\tau(z)$ depends rigorously on the state (given by $\dot{\phi}(z)$) of the entire cylinder, it is determined locally in practice. Modeling DNA as a continuous elastic cylinder, $\tau(z)$ at some position is determined primarily by the $\dot{\phi}$'s of the 11 nearest-neighbor base pairs on either side of the one in question. This in itself cannot be taken as justification for using the Perrin result (eq 5) to accurately account for torsional hydrodynamic interaction since it is valid only if the local gradient in $\dot{\phi}$ along the cylinder is small. In terms of normal coordinates, the gradient in $\dot{\phi}$ is small provided the amplitudes of the long-wavelength normal modes are collectively large compared to those of the short-wavelength normal modes.

In experiments like fluorescence depolarization,[2–6,8,9] EPR,[7] depolarized light scattering,[10] and NMR[11–13] the measurements are related to time autocorrelation functions of the form $\langle e^{ik(\phi(t)-\phi(0))}\rangle$ ($k = 1, 2$). From eq 34–37, it can thus be seen that these experiments monitor the decay of torsion normal modes weighted by their thermal equilibrium amplitudes. Since the short modes have small amplitudes, the above experiments are dominated by the long-wavelength modes, which means replacing γ_l with eq 5 is justified. It should be emphasized, however, that this justification is a consequence of the limited resolution of the experiments. Although these conclusions were arrived at by considering the particular case of DNA, they would also be true for long, stiff, wormlike chains in general.

Acknowledgment. The author thanks Professor John Schellman for encouragement and support. Thanks are also due to Professor Jeff Skolnick for helpful input into this problem. This research was funded in part by grants from the U.S. Public Health Service (Grant GM 20195) and the National Science Foundation (Grant PCM 8104339) (both to J.A.S.) and by Fellowship No. 1 F32 GM 08090-01 from the National Institutes of Health.

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Particle Scattering Factor of Polymer Chains with Excluded Volumes

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ABSTRACT: Particle scattering factors of polystyrenes having high molecular weights and narrow molecular weight distributions in light scattering were experimentally determined for comparison with the theories so far published. None of the theories satisfactorily agree with experiments over a wide range of scattering angle. An empirical equation is presented.

Introduction

The particle scattering factor, $P(\theta)$, for Gaussian chains in light scattering was calculated by Debye[2] to be

$$P(\theta) = 2u^{-2}[\exp(-u) - 1 + u] \qquad (1)$$

where $u = q^2\langle s^2\rangle$, $q = 4\pi/\lambda \sin(\theta/2)$, $\langle s^2\rangle$ is the mean square radius of gyration of the polymer, λ is the wavelength of the incident light in the solution, and q is the magnitude of the wave vector. It has been confirmed that $P(\theta)$ for nonionic polymers[3] and $P(\theta)$ for polyelectrolytes[4,5] in Θ solvents agree well with eq 1 if the samples have sharp molecular weight distributions.

As the thermodynamic interaction between segments increases or as the solvent becomes better, polymer chains expand and become non-Gaussian on account of the excluded volume effect. Theoretical calculations of $P(\theta)$ for non-Gaussian chains were presented by Peterlin[6] and integration forms by Ptitsyn[7] and Benoit.[8] They introduced

0024-9297/83/2216-0425$01.50/0