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Dynamics of Wormlike Chains

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Received January 8, 1985

ABSTRACT: The dynamics of free-draining polymers in dilute solution are treated with the Kratky–Porod wormlike chain model. The model consists of differentiable space curves of constant length with bending elasticity. We show that eliminating the stretching elasticity gives an internally consistent model which satisfies the pure bending Langevin equation of motion. The dynamical equation is solved by a normal mode analysis representing the transverse vibrations of an elastic curve with free ends. A time-independent Green's function is used to calculate the pair correlation function, giving all equilibrium properties of the model. The same techniques are applied to the time-dependent case. All properties depend on one parameter, the persistence length, λ^{-1}, of the polymer. As an example, the polarized light scattering from a dilute solution of isotropic random coils is calculated in detail. The model requires the separate treatment of the rotational and the internal flexing degrees of freedom of the polymer. Its main area of application will be in the description of the dynamics of dilute solutions of semiflexible macromolecules.

I. Introduction

The concept of a random flight chain is a key concept in understanding polymer solution properties for very flexible polymers. The model most widely used to describe the dynamics of such flexible chains is the famous "spring and bead" model proposed originally by Rouse[1] and Bueche.[2] The dynamical consequences of this model were developed mainly by Zimm,[3] who applied it to the viscoelasticity, flow birefringence, and dielectric relaxation in dilute polymer solutions. Other properties such as the dynamic light scattering of the optically isotropic Rouse model were given by Pecora[4] and Saito,[5] and for optically anisotropic Rouse polymers (in the forward scattering limit) by Ono and Okano.[6] The success of the Rouse–Zimm model in most of these areas is well-known and a good account is given in Yamakawa's[7] thorough exposition of dilute polymer solution theory.

Nevertheless, the Rouse model, apart from the considerations of excluded volume and hydrodynamic interaction effects, does have limitations. Obviously it is only applicable to very flexible molecules, yet there is great interest in both natural and synthetic polymers with intermediate degrees of flexibility between the random coil and the rigid rod. In addition, as Harris and Hearst[8] have pointed out, the Rouse model, even for very flexible molecules, is inappropriate for high-frequency phenomena since in this case any real molecule looks increasingly rigid and the assumption of Gaussian statistics for the bead separations breaks down. Finally, a related problem is that the number of beads used to model a polymer molecule is arbitrary; thus, only the slow relaxations of a polymer molecule can be treated since the results of any calculations must be independent of the actual number of beads chosen.

With these considerations in mind, Harris and Hearst[8] introduced the Kratky–Porod[9] wormlike chain, treated as a differentiable space curve with bending elasticity, to account for the presence of stiffness in a linear polymer molecule. The wormlike chain model contains one main parameter, the persistence length, λ^{-1}, which is simply related to the bending elasticity constant,[10] ϵ, by $\lambda = kT/2\epsilon$.

Given a polymer of contour length L, the rigid-rod limit corresponds to $\lambda L \rightarrow 0$, whereas the random-coil limit corresponds to $\lambda L \rightarrow \infty$. This model, in addition to covering the whole range of flexibilities, resolves the difficulties of the Rouse model in the high-frequency region because the statistics are not Gaussian. Nevertheless, in our version of this model, we neglect hydrodynamic and

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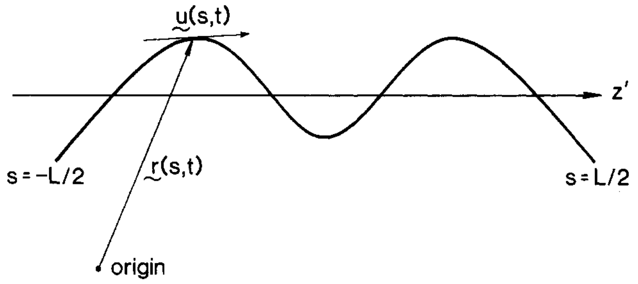

Figure 1. Elastic space curve shown deformed schematically for the $l = 3$ mode. The position vector, $\mathbf{r}(s,t)$, and the tangent vector, $\mathbf{u}(s,t)$, are also shown.

other interactions and consider only the free-draining case.

In sections II and III of this paper we study the previously proposed differential (Langevin) equations for elastic space curves and arrive at the simplest description of a nonstretching curve, the pure bending equation. The normal mode solution to the elastic transverse vibration problem is presented in section IV, while equilibrium properties and time-dependent properties are studied in sections V and VI, respectively. The approximations required in practical applications of the model are reviewed and discussed in the last section.

II. Harris–Hearst and Soda Equations

Harris and Hearst,[8] in addition to the bending elasticity constant, introduced a Lagrange multiplier, κ, in an attempt to make their theory valid for chains of constant length. This had the effect, however, of introducing effective restoring forces with respect to stretching motions of the chain. They subsequently showed[11] that the mean square fluctuation of the contour length, while zero in the coil limit, became large in the rod limit. Hearst et al.[11] nevertheless applied this model to the viscoelastic properties of a polymer solution and later noted, in computing the elastic light scattering, that their results were at variance with the known behavior in the rod limit.

The Harris–Hearst (HH) differential equation for a stochastic Brownian force, $\mathbf{A}(s,t)$

$$\rho\frac{\partial^2\mathbf{r}}{\partial t^2} + \zeta\frac{\partial\mathbf{r}}{\partial t} + \epsilon\frac{\partial^4\mathbf{r}}{\partial s^4} - \kappa\frac{\partial^2\mathbf{r}}{\partial s^2} = \mathbf{A}(s,t) \tag{2.1}$$

describes the dynamics of the position vector $\mathbf{r}(s,t)$ at a point on the chain parameterized by s ($-L/2 \leq s \leq L/2$) with a friction constant ζ and linear mass density ρ. (See Figure 1.) This equation has been used extensively by Fujime and co-workers[12] in the interpretation of polarized light scattering from semiflexible macromolecules in solution. Moro and Pecora[13] have also used this equation to compute the forward depolarized scattering from semiflexible macromolecules and have noted the inconsistencies of the HH equation as first elucidated by Soda.[14] The equation simply does not give the correct behavior in the rod limit.

In fact, Saito et al.[15] were the first to write down the correct potential energy for a space curve with both a bending (ϵ) and stretching (κ) elasticity constant. However, whereas their treatment of the equilibrium properties of the wormlike chain was done correctly and elegantly in both constant-length and variable-length cases, Saito et al. merely quoted the HH result for the equation of motion of the chain.

The origin of the shortcomings of the HH equation was finally made clear by Soda.[14] He showed, in a very careful derivation, the explicit form that the potential energy must have for a space curve possessing both bending and stretching elasticity. The tangent vector at position s of the polymer is given by $\mathbf{u}(s,t) = \partial\mathbf{r}(s,t)/\partial s$. Soda's potential energy is then

$$V = \frac{\epsilon}{2}\int_{-L/2}^{L/2}\mathrm{d}s\left\{\left(\frac{\partial\mathbf{u}}{\partial s}\right)^2 - \left(\frac{\partial\mathbf{u}}{\partial s}\cdot\hat{u}\right)^2\right\} + \frac{\kappa}{2}\int_{-L/2}^{L/2}\mathrm{d}s\,(u-1)^2 \tag{2.2}$$

The interpretation of this potential energy is clear. When there is no bending, $\partial\mathbf{u}/\partial s$ is parallel to $\hat{u} \equiv (1/u)(\partial\mathbf{r}/\partial s)$, so that the first bracket vanishes. The first term is thus the pure bending energy. When there is no stretching, $u = 1$, which implies that the second term, the pure stretching energy, vanishes. Note that the stretching term is harmonic in the actual stretching displacement; this is not so in the HH equation.

The principle of least action using a Lagrangian constructed with the above potential energy gives the correct equation of motion. Since V is a complicated functional of the position vectors $\mathbf{r}(s,t)$, Soda[14] obtained the equation of motion valid only for small longitudinal deformations (large κ limit). The Langevin equation of motion is then

$$\rho\frac{\partial^2\mathbf{r}}{\partial t^2} + \zeta\frac{\partial\mathbf{r}}{\partial t} + \epsilon\frac{\partial^4\mathbf{r}}{\partial s^4} - \kappa\left\{\left(\frac{\partial^2\mathbf{r}}{\partial s^2}\cdot\hat{u}\right)\hat{u} + (u-1)\frac{\partial^2\mathbf{r}}{\partial s^2}\right\} = \mathbf{A}(s,t) \tag{2.3}$$

The HH equation, by contrast, corresponds to a model in which the natural length is actually zero and is thus basically equivalent to a continuous Rouse model, which is free of inconsistency only when $\epsilon = 0$. This can be appreciated by noting that the mutually contradictory approximations $|\partial\mathbf{u}/\partial s| \gg |(\partial\mathbf{u}/\partial s)\cdot\hat{u}|$ and $u \gg 1$ yield the HH equation when applied to the Soda potential energy.

III. Pure Bending Equation

The Soda equation of motion, eq 2.3, is a nonlinear partial differential equation and cannot be solved with a normal mode analysis. Thus we seek a simpler equation that can represent a real polymer molecule reasonably well. Since we are representing a linear polymer molecule of length L with a space curve of contour length L, any stretching of this curve will involve stretching of individual bonds, or at least bond-angle deformation for zigzag-like configurations. This stretching not only takes considerably more energy than simple flexing, it also relaxes much faster.

Soda pointed out in his original paper that when κ is large and thus $u \approx 1$, the longitudinal relaxation process is very fast and is well separated in time from the transverse relaxation processes arising from pure bending. In fact, estimates of these relaxation times exist for a slightly bendable rodlike molecule. Rosser[16] has shown, based on work by Ookubo[17] et al., that the ratio of longitudinal (τ_L) to flexural (τ_F) relaxation times is given by

$$\tau_L/\tau_F \simeq 2.8(d/L)^2$$

where d is the molecular transverse diameter. The axial ratio of typical polymers of interest can vary from 10 to several hundred, making τ_L 2–5 orders of magnitude faster than the flexing time.

Thus, in most instances, we expect to be able to describe the internal mode dynamics of a linear polymer molecule in terms of only the bending constant ϵ. Apart from being very fast, the longitudinal modes will have a very small amplitude in any experiments sensitive to the total length of the polymer. Light scattering or birefringence experiments that detect the change in polarizability associated with dynamical modes are one example.

The dynamical model proposed here then is that of free-draining space curves of constant length with bending elasticity. The configurational partition function for this case has been obtained by Saito et al.[15] If we write the partition function as a path integral

$$Z = \int e^{-V/kT}\,\mathrm{d}\{\mathbf{r}(s)\} \tag{3.1}$$

and note that the stretching piece is in the infinite κ limit

$$\lim_{\kappa\to\infty}\left[\exp\left(-\kappa/2kT\int|u-1|^2\,\mathrm{d}s\right)\right] = 1, \quad u = 1$$
$$= 0, \quad \text{otherwise} \tag{3.2}$$

the partition function becomes

$$Z = \int_{u=1}\exp\left[-\frac{\epsilon}{2kT}\int\left(\frac{\partial^2\mathbf{r}}{\partial s^2}\right)^2\mathrm{d}s\right]\mathrm{d}\{\mathbf{r}(s)\} \tag{3.3}$$

where the set of configurations considered includes only those with no stretching ($u = 1$, $(\partial\mathbf{u}/\partial s)\cdot\hat{u} = 0$). Z satisfies the differential equation

$$\partial Z/\partial s = \lambda\nabla_u^{\ 2}\,Z, \qquad u = 1 \tag{3.4}$$

so that Green's function associated with this equation can be readily obtained.[7,15]

$$G(\hat{u},\hat{u}';s-s') = \sum_{lm} e^{-\lambda l(l+1)|s-s'|}\,Y_{lm}(\hat{u})\,Y_{lm}{}^{*}(\hat{u}') \tag{3.5}$$

where Y_{lm} is a (complex) spherical harmonic. Green's function can be interpreted as the joint probability that given an orientation $\hat{u}'$ of the curve at position s', the orientation will be $\hat{u}$ at position s.

The dynamical equation for curves of constant length is just the Soda equation with $u = 1$ and $(\partial\mathbf{u}/\partial s)\cdot\hat{u} = 0$. We call this the pure bending equation

$$\rho\frac{\partial^2\mathbf{r}}{\partial t^2} + \zeta\frac{\partial\mathbf{r}}{\partial t} + \epsilon\frac{\partial^4\mathbf{r}}{\partial s^4} = \mathbf{A}(s,t) \tag{3.6}$$

In a molecular frame of reference, we would like the molecule's ends to experience no net force or torque, so that the appropriate boundary conditions are those of free ends

$$\frac{\partial^2\mathbf{r}}{\partial s^2} = \frac{\partial^3\mathbf{r}}{\partial s^3} = 0 \quad \text{at } s = \pm L/2 \tag{3.7}$$

IV. Normal Mode Analysis

The bending equation is a fourth-order, linear partial differential equation and is susceptible to normal mode analysis. In addition, we note that the operator is hermitian with the assumed boundary conditions. This guarantees that its nondegenerate eigenfunctions are orthogonal and that these functions form a complete set. Let the eigenvalue equation for the above differential operator be

$$\epsilon\frac{\mathrm{d}^4 q_l}{\mathrm{d}s^4} = \lambda_l q_l \tag{4.1}$$

Then, expanding the position and force in eq 3.6

$$\mathbf{r}(s,t) = \sum_l \mathbf{P}_l(t)q_l(s)$$
$$\mathbf{A}(s,t) = \sum_l \mathbf{A}_l(t)q_l(s) \tag{4.2}$$

we obtain the dynamical equation

$$\rho\frac{\mathrm{d}^2\mathbf{P}_l}{\mathrm{d}t^2} + \zeta\frac{\mathrm{d}\mathbf{P}_l}{\mathrm{d}t} + \lambda_l\mathbf{P}_l = \mathbf{A}_l(t) \tag{4.3}$$

Table I
Eigenvalues of the Bending Equation

l	x_l	l	x_l
0	0	6	20.4204
1	4.73004	7	23.5619
2	7.85320	8	26.7035
3	10.9956	9	29.8451
4	14.1372	10	32.9867
5	17.2788		

Since we are interested in the time scale when frictional forces dominate, we neglect the inertial term and obtain the formal solution as

$$\mathbf{P}_l(t) = \mathbf{P}_l(0)e^{-\lambda_l t/\zeta} + \frac{1}{\zeta}e^{-\lambda_l t/\zeta}\int_0^t e^{\lambda_l t'/\zeta}\mathbf{A}_l(t')\,\mathrm{d}t' \tag{4.4}$$

The above expansion coefficient will appear in ensemble averages over all possible configurations of the system. However, the stochastic variable $\mathbf{A}_l(t')$ is uncorrelated with any component of the vector amplitudes $\mathbf{P}_l(t)$. This implies that configurational averages containing products of $\mathbf{A}_l$ and $\mathbf{P}_k$ will vanish. Thus, for example

$$\langle\mathbf{P}_l(t)\cdot\mathbf{P}_k(0)\rangle = e^{-\lambda_l t/\zeta}\langle\mathbf{P}_l(0)\cdot\mathbf{P}_k(0)\rangle \tag{4.5}$$

The eigenvalue equation (eq 4.1) is easily solved and in fact corresponds to the slightly bendable rod model of Landau and Lifschitz[18] and to the $\kappa = 0$ limit in the HH equation.[13] If we put the origin in the center of the molecule, ($-L/2 \le s \le L/2$), the eigenfunctions have even or odd parity and are given by

$$q_l(s) = L^{-1/2}\frac{\cos(\nu_l s)}{\cos(x_l/2)} + \frac{\cosh(\nu_l s)}{\cosh(x_l/2)}, \qquad l = 1, 3, 5, 7, \ldots$$
$$q_l(s) = L^{-1/2}\frac{\sin(\nu_l s)}{\sin(x_l/2)} + \frac{\sinh(\nu_l s)}{\sinh(x_l/2)}, \qquad l = 2, 4, 6, 8, \ldots \tag{4.6}$$

where $\nu_l \equiv (\lambda_l/\epsilon)^{1/4}$, $x_l \equiv \nu_l L \simeq (2l + 1)(\pi/2)$, $l > 0$ and $x_0 = 0$. The eigenvalue equation is

$$\cos x_l \cosh x_l = 1, \qquad i = 0, 1, 2, 3, \ldots \tag{4.7}$$

which is satisfied approximately by the relation given above. More precise values for the x_l are given in Table I.

Note, however, that the $x_0 = 0$ eigenvalue is doubly degenerate. This can be seen as follows. The general solution of $\mathrm{d}^4q/\mathrm{d}s^4 = 0$ with the given boundary conditions is of the form

$$q(s) = A + Bs \tag{4.8}$$

where A and B are arbitrary constants. Thus we could choose two orthogonal solution simply as $q_* = A$ and $q_{**} = Bs$ or in normalized form

$$q_* = L^{-1/2}$$
$$q_{**} = (12/L)^{1/2}(s/L) \tag{4.9}$$

so that the full set given by eq 4.6 and 4.9 is a complete orthonormal set.

In any applications of the present model, when the expansion in normal modes is used, one will have to consider configurational averages over products of Cartesian components of the expansion vectors $\mathbf{P}_l$. A specific example, the pair correlation function, is computed in the next section. The calculations of these configurational averages can be done with the aid of Green's function $G(\hat{u},\hat{u}';s - s')$ provided the $\mathbf{P}_l$ can be expressed in terms of the tangent vectors $\mathbf{u}(s)$. The required relations can be obtained as follows.

The normal mode expansion, eq 4.2, can be rewritten in terms of the complete set of functions obtained above

$$\mathbf{r}(s,t) = \mathbf{P}_*(t)q_* + \mathbf{P}_{**}(t)q_{**}(s) + \sum_{l=1}^{\infty}\mathbf{P}_l(t)q_l(s)$$

$$\mathbf{A}(s,t) = \mathbf{A}_*(t)q_* + \mathbf{A}_{**}(t)q_{**}(s) + \sum_{l=1}^{\infty}\mathbf{A}_l(t)q_l(s) \tag{4.10}$$

When (4.2) is written in this way one cannot express $\mathbf{P}_*$ and $\mathbf{P}_{**}$ in terms of a tangent vector. However, if we position the origin of the coordinate system at the center of mass of the polymer, we can obtain the desired relation. As shown in the Appendix, doing this eliminates the function q_* so that we can define $q_0(s) = q_{**}$ and the motion of the center of mass is eliminated from the problem. The new normal mode expansion is

$$\mathbf{r}(s,t) = \sum_{l=0}^{\infty}\mathbf{P}_l(t)q_l(s)$$

$$\mathbf{A}(s,t) = \sum_{l=0}^{\infty}\mathbf{A}_l(t)q_l(s) \tag{4.11}$$

The set of functions $\{q_l(s)\}$, $l = 0, 1, 2, ...$ is an orthonormal set; thus the relations above can be inverted to obtain

$$\mathbf{P}_l(t) = \int_{-L/2}^{L/2}\mathbf{r}(s,t)q_l(s)\,\mathrm{d}s = -\int_{-L/2}^{L/2}\mathbf{u}(s,t)v_l(s)\,\mathrm{d}s \tag{4.12}$$

The second equality is obtained by performing an integration by parts and noting that all $v_l(L/2) = 0$. This is the relation we wanted to obtain. The first integrals $v_l(s)$ are defined in the Appendix.

Before any examples are considered, it is important to state the completeness relations for our sets of functions

$$\delta(s - s') = \sum_{l=1}^{\infty}q_l(s)q_l(s') + q_*q_* + q_{**}(s)q_{**}(s')$$

or

$$\delta(s - s') = \sum_{l=0}^{\infty}q_l(s)q_l(s') + 1/L \tag{4.13}$$

where $\delta(s - s')$ is a Dirac δ-function.

Finally, note that the characteristic time constant appearing in equations such as eq 4.5 can be written as

$$\tau_l \equiv \zeta/\lambda_l = \frac{\zeta L^4}{x_l^{\,4}\epsilon} = \frac{2\lambda L^3}{Dx_l^{\,4}} \tag{4.14}$$

where the translational diffusion coefficient is $D = kT/L\zeta$, and we have used the definition of $x_l = \nu_l L$ and of $\lambda = kT/2\epsilon$.

V. Pair Correlation Function

The pair correlation function $C(s,s')$ contains a wealth of information regarding the equilibrium properties of the model. We will outline the computation of this function as an example of the use of the machinery developed above. The pair correlation function is defined by

$$C(s,s') \equiv \langle\mathbf{r}(s)\cdot\mathbf{r}(s')\rangle = \sum_{l=0}^{\infty}\sum_{k=0}^{\infty}q_l(s)q_k(s')\langle\mathbf{P}_l\cdot\mathbf{P}_k\rangle \tag{5.1}$$

where the second equality is obtained by using the expansion of eq 4.11 and the angular brackets signify an average over all configurations. Using the expression of eq 4.12 for a $\mathbf{P}_l$ in terms of $\mathbf{u}(s)$, we can evaluate the required average

$$\langle\mathbf{P}_l\cdot\mathbf{P}_k\rangle = \int_{-L/2}^{L/2}\mathrm{d}s_1\int_{-L/2}^{L/2}\mathrm{d}s_2\; v_l(s_1)v_k(s_2)\langle\mathbf{u}(s_1)\cdot\mathbf{u}(s_2)\rangle \tag{5.2}$$

and Green's function (eq 3.5) yields the average over cos $\theta_{12} = \mathbf{u}(s_1)\cdot\mathbf{u}(s_2)$

$$\langle\mathbf{u}(s_1)\cdot\mathbf{u}(s_2)\rangle = \int\cos\theta_{12}G(\Omega_{12},0;s_1 - s_2)\,\mathrm{d}\Omega_{12} = e^{-2\lambda|s_1-s_2|} \tag{5.3}$$

The final expansion of the pair correlation function is

$$C(s,s') = L^3\sum_{l=0}^{\infty}\sum_{k=0}^{\infty}q_l(s)q_k(s')d_{lk}(\lambda) \tag{5.4}$$

where the dimensionless coefficient is given by

$$d_{lk}(\lambda) = \frac{1}{L^3}\int_{-L/2}^{L/2}\mathrm{d}s_1\int_{-L/2}^{L/2}\mathrm{d}s_2\; v_l(s_1)v_k(s_2)e^{-2\lambda|s_1-s_2|} \tag{5.5}$$

The expansion of eq 5.4 has a simple form in the rigid-rod limit, $\lambda \rightarrow 0$

$$d_{lk}(0) = \frac{1}{L^3}\int_{-L/2}^{L/2}\mathrm{d}s_1\int_{-L/2}^{L/2}\mathrm{d}s_2\; v_l(s_1)v_k(s_2) = \frac{1}{12}\delta_{l0}\delta_{k0} \tag{5.6}$$

The simplest way to verify the above integrations for l, $k \neq 0$ is by noting that the integral of v_l is proportional to the second derivative of q_l and it vanishes at the end points in view of our boundary conditions. The rigid-rod correlation function is simply

$$C_{\mathrm{R}}(s,s') = ss' \tag{5.7}$$

A bilinear expansion of unity can be obtained from eq 5.4 by noting that $\mathbf{u}(s)\cdot\mathbf{u}(s) = 1$ and that

$$\langle\mathbf{u}(s)\cdot\mathbf{u}(s)\rangle = \lim_{s'\rightarrow s}\frac{\mathrm{d}}{\mathrm{d}s}\frac{\mathrm{d}}{\mathrm{d}s'}C(s,s') = L^3\sum_{l,k}\frac{\mathrm{d}q_l(s)}{\mathrm{d}s}\frac{\mathrm{d}q_k(s)}{\mathrm{d}s}d_{lk}(\lambda) = 1 \tag{5.8}$$

Integrating this relation we obtain

$$\sum_{l=0}^{\infty}\sum_{k=0}^{\infty}A_{lk}d_{lk}(\lambda) = 1 \tag{5.9}$$

where

$$A_{lk} \equiv L^2\int_{-L/2}^{L/2}\mathrm{d}s\;\frac{\mathrm{d}q_l(s)}{\mathrm{d}s}\frac{\mathrm{d}q_k(s)}{\mathrm{d}s}$$

These expansions of unity will be useful in the study of the properties of the model in the coil limit where divergences can occur when we take the limit $\lambda \rightarrow \infty$.

The pair correlation function can also be obtained in closed form by converting the expansion into simple integrations using the completeness relation (eq 4.13) $C(s,s')$ can be rewritten by interchanging summations and integrations in eq 5.4

$$C(s,s') = \int_{-L/2}^{L/2}\mathrm{d}s_1\int_{-L/2}^{L/2}\mathrm{d}s_2\; e^{-2\lambda|s_1-s_2|}\int_{-L/2}^{s_1}\mathrm{d}x\sum_{l=0}^{\infty}q_l(s)q_l(x)\int_{-L/2}^{s_2}\mathrm{d}y\sum_{k=0}^{\infty}q_k(s')q_k(y) \tag{5.10}$$

Upon insertion, the completeness relation yields

$$C(s,s') = \int_{-L/2}^{L/2}\mathrm{d}s_1\int_{-L/2}^{L/2}\mathrm{d}s_2\; e^{-2\lambda|s_1-s_2|}[\theta(s_1 - s) - s_1/L - 1/2][\theta(s_2 - s') - s_2/L - 1/2] \tag{5.11}$$

where we have used

$$\int_{-L/2}^{s_1}\mathrm{d}x\;[\delta(s - x) - 1/L] = \theta(s_1 - s) - s_1/L - 1/2$$

and $\theta(x - y)$ is the Heaviside step function.

The integrations required in eq 5.11 are simple but they must be done carefully to account correctly for the absolute value in the exponential. The result is best presented by defining the following quantities:

$$I(s,s') = \frac{1}{4\lambda^2}[2\lambda(L - 2s')\theta(s' - s) + 2\lambda(L - 2s)\theta(s - s') + e^{-\lambda(L-2s')} + e^{-\lambda(L-2s)} + e^{-2\lambda|s-s'|}] \quad (5.12)$$

$$B(s) = \frac{1}{8\lambda^3 L}[4\lambda^2 s(s + L) - e^{-\lambda(L+2s)} - (1 + 2\lambda L)e^{-\lambda(L-2s)}] \quad (5.13)$$

$$C = \frac{1}{4\lambda^2}\left[\frac{1}{\lambda L} - \frac{5}{3}\lambda L + \frac{1}{2\lambda^2 L^2} - \frac{e^{-2\lambda L}}{2\lambda^2 L^2}\right] \quad (5.14)$$

Then the pair correlation function is

$$C(s,s') = I(s,s') + B(s) + B(s') + C \quad (5.15)$$

As complex as this function is, it is gratifying that the rod limit does agree with eq 5.7. The coil limit is more easily obtained. Keeping terms to order λ^{-1} when λ goes to infinity, we obtain

$$C_c(s,s') = \frac{1}{2\lambda}\left[(L - 2s')\theta(s' - s) + (L - 2s)\theta(s - s') + \frac{1}{2L}[s(s + L) + s'(s' + L)] - \frac{5}{12}L\right] \quad (5.16)$$

Two properties of $C(s,s')$ are worth checking at once. The differential property

$$\frac{\mathrm{d}}{\mathrm{d}s}\frac{\mathrm{d}}{\mathrm{d}s'}C(s,s') = \langle \mathbf{u}(s)\cdot\mathbf{u}(s')\rangle = e^{-2\lambda|s-s'|} \quad (5.17)$$

is satisfied by eq 5.15. In addition, the well-known mean square distance from s to s' can be computed. By definition

$$\langle[\mathbf{r}(s) - \mathbf{r}(s')]^2\rangle = C(s,s) + C(s',s') - 2C(s,s') \quad (5.18)$$

Evaluation according to eq 5.15 gives the correct result[11]

$$\langle[\mathbf{r}(s) - \mathbf{r}(s')]^2\rangle = \frac{1}{2\lambda^2}[2\lambda|s - s'| - 1 + e^{-2\lambda|s-s'|}] \quad (5.19)$$

The mean square end-to-end distance corresponds to evaluation of the above function at $s = L/2$ and $s' = -L/2$.

The following are examples of properties that can be computed directly from $C(s,s')$:

(i) Average Contour Length

$$\langle L\rangle = \int_{-L/2}^{L/2}\mathrm{d}s \lim_{s\to s'}\frac{\mathrm{d}}{\mathrm{d}s}\frac{\mathrm{d}}{\mathrm{d}s'}C(s,s') = \int_{-L/2}^{L/2}\mathrm{d}s\ \langle\mathbf{u}(s)\cdot\mathbf{u}(s)\rangle = L \quad (5.20)$$

It is constant as required in the model.

(ii) Mean Square Curvature

$$\langle\kappa^2\rangle = \frac{1}{L}\int_{-L/2}^{L/2}\mathrm{d}s \lim_{s'\to s}\frac{\mathrm{d}^2}{\mathrm{d}s^2}\frac{\mathrm{d}^2}{\mathrm{d}s'^2}C(s,s') = \frac{1}{L}\int_{-L/2}^{L/2}\mathrm{d}s \lim_{s'\to s}\frac{\mathrm{d}}{\mathrm{d}s}\frac{\mathrm{d}}{\mathrm{d}s'}\langle\mathbf{u}(s)\cdot\mathbf{u}(s')\rangle \quad (5.21)$$

so that with eq 5.17 we obtain $\langle\kappa^2\rangle = 4\lambda^2$.

(iii) Radius of Gyration

$$\langle R_G{}^2\rangle = \frac{1}{L}\int_{-L/2}^{L/2}\mathrm{d}s\ C(s,s) = \frac{1}{L}\int_{-L/2}^{L/2}I(s,s)\ \mathrm{d}s + \frac{2}{L}\int_{-L/2}^{L/2}B(s)\ \mathrm{d}s + C$$

Evaluation gives the correct expression[7]

$$\langle R_G{}^2\rangle = \frac{L}{6\lambda} - \frac{1}{4\lambda^2} + \frac{1}{4\lambda^3 L} + \frac{e^{-2\lambda L} - 1}{8\lambda^4 L^2} \quad (5.22)$$

VI. Time-Dependent Correlation Functions

The application of the dynamical model presented above to problems in dynamic light scattering, flow and transient electric birefringence, and viscoelasticity requires the consideration of a variety of time correlation functions of polymer properties. These can usually be written in terms of basic correlation functions involving the tangent vectors $\mathbf{u}(s,t)$ and the position vectors $\mathbf{r}(s,t)$. For example, the fundamental correlation function that occurs in forward depolarized light scattering[19] and in the decay of transient electric birefringence (of nonpolar molecules) is

$$\langle(\mathbf{u}(s,t)\cdot\hat{y})(\mathbf{u}(s,t)\cdot\hat{z})(\mathbf{u}(s',0)\cdot\hat{y})(\mathbf{u}(s',0)\cdot\hat{z})\rangle$$

whereas that occurring in polarized light scattering (of optically isotropic molecules) is

$$\langle[\mathbf{q}\cdot[\mathbf{r}(s,t) - \mathbf{r}(s',0)]]^j\rangle, \qquad j = 1, 2, \ldots$$

where $\mathbf{q}$ is the scattering vector. Since the computation of correlation functions such as these can be a rather involved process, we will present such calculations in separate communications. In this section, however, we will illustrate the general procedures involved with a simpler example.

Consider the simple time-dependent pair correlation function

$$C(s,s';t) = \langle\mathbf{r}(s,t)\cdot\mathbf{r}(s',0)\rangle \quad (6.1)$$

At $t = 0$, it reduces to the pair correlation function considered before. Using eq 4.5, 5.2, and 5.3, we obtain immediately

$$C(s,s';t) = L^3\sum_{l=0}^{\infty}\sum_{k=0}^{\infty}q_l(s)q_k(s')e^{-\lambda_l t/\zeta}d_{lk}(\lambda) \quad (6.2)$$

The sum over k can be carried out by the same technique as in eq 5.11 to yield

$$C(s,s';t) = L^3\sum_{l=0}^{\infty}q_l(s)D_l(s',\lambda)e^{-\lambda_l t/\zeta} \quad (6.3)$$

where

$$D_l(s,\lambda) = \frac{1}{L^3}\int_{-L/2}^{L/2}\mathrm{d}s_1\ v_l(s_1)\int_{-L/2}^{L/2}\mathrm{d}s_2\ e^{-2\lambda|s_1-s_2|}[\theta(s_2 - s) - s_2/L - 1/2] \quad (6.4)$$

The rod and coil limits of the $D_l(s,\lambda)$ coefficient are easily obtained (primed quantities are differentiated with respect to the argument)

$$D_l(s,0) = \frac{1}{2(3L)^{1/2}}(s/L)\delta_{l0}, \quad \text{rod}$$

$$D_l(s,\infty) = \frac{-1}{\lambda x_l{}^4}[-Lq_l''(s) + q_l'(L/2) - q_l'(-L/2)], \qquad \text{coil, } l > 0$$

$$D_0(s,\infty) = \frac{2s/L}{8\lambda L(3L)^{1/2}}[3 - (2s/L)^2], \qquad \text{coil, } l = 0 \quad (6.5)$$

Note that in the rod case, the correlation function is time independent: $C(s,s';t) = ss' = C(s,s')$.

Light Scattering from Gaussian Coils. As a specific example in which $C(s,s';t)$ appears, we will compute the electric field correlation function for a dilute solution of N optically isotropic Gaussian coils of polarizability α. The correlation function is given simply by[19]

$$C_{\rm vv}(t) = \frac{N\alpha^2}{L^2}\int_{-L/2}^{L/2}{\rm d}s\int_{-L/2}^{L/2}{\rm d}s'\,\langle e^{i\mathbf{q}\cdot[\mathbf{x}(s,t)-\mathbf{x}(s',0)]}\rangle \qquad (6.6)$$

where the angular brackets signify an orientational and a configurational average. The position vectors $\mathbf{x}(s,t)$ can be written in terms of the location of the center of mass, $R(t)$, in the laboratory frame

$$\mathbf{x}(s,t) = \mathbf{R}(t) + \mathbf{r}(s,t) \qquad (6.7)$$

Substituting this into eq 6.6 and making the assumption that the translation of the center of mass is statistically independent of rotation and internal motions, the center-of-mass correlation function factors as the well-known translational diffusive part.[19] We have then

$$C_{\rm vv}(t) = \frac{N\alpha^2e^{-q^2Dt}}{L^2}\int_{-L/2}^{L/2}{\rm d}s\int_{-L/2}^{L/2}{\rm d}s'\,\langle e^{i[\mathbf{q}(t)\cdot\mathbf{r}(s,t)-\mathbf{q}(0)\cdot\mathbf{r}(s',0)]}\rangle \qquad (6.8)$$

where, for convenience, we have now gone over into the molecule frame of reference in which a suitable coordinate system is fixed to the molecule at time $t = 0$ and has its origin at the center of mass. The time dependence of the position vectors $\mathbf{r}(s,t)$ arises now only from the internal flexing modes and that of $\mathbf{q}(t)$ arises from the rigid-body rotation of the molecule frame with respect to the laboratory frame. This crucial point will be discussed further below.

When the normal modes of flexing obey Gaussian statistics (which is true for the wormlike coil in the limit of large λ), the configurational average operates on the argument of the exponential factor as was shown by Pecora.[4] Keeping track of the time-dependent scattering vectors, we obtain

$$C_{\rm vv}(t) = \frac{N\alpha^2e^{-q^2Dt}}{L^2}\int_{-L/2}^{L/2}{\rm d}s\int_{-L/2}^{L/2}{\rm d}s'\,\langle e^{-q^2[C(s,s)+C(s',s')-2\hat{q}(t)\cdot\hat{q}(0)C(s,s';t)]/6}\rangle \qquad (6.9)$$

where the remaining average corresponds to the orientational average describing the polymer rigid-body rotation. The implicit assumption in obtaining the above equation is that the rigid-body reorientation and internal mode dynamics are uncoupled. In a real polymer molecule this may actually not be the case—we make the assumption here for simplicity. The required orientational average is of the form

$$\langle e^{(q^2/3)C(s,s';t)\cos\theta_t}\rangle = \sum_{k=0}^{\infty}\frac{\left[\dfrac{q^2C(s,s';t)}{3}\right]^k}{k!}\langle\cos^k\theta_t\rangle \qquad (6.10)$$

If we model the reorientation dynamics in the simplest possible way, taking the polymer to be, on the average, an effective cylindrically symmetric body with average rotational diffusion coefficient Θ for tumbling of its major axis, we can write (by choosing $\Omega_0 = 0$)

$$\langle\cos^k\theta_t\rangle = \int G(\Omega_t,\Omega_0,t)\cos^k\theta_t\,{\rm d}\Omega_t = \frac{1}{4\pi}\sum_{l=0}^{\infty}(2l+1)e^{-l(l+1)\Theta t}\int P_l(\cos\theta_t)\cos^k\theta_t\,{\rm d}\Omega_t = k!\sum_{\substack{l=0\\ l+k,\text{even}}}^{\infty}\frac{2^l(2l+1)[(k+l)/2]!}{(l+k+1)![(k-l)/2]!}e^{-l(l+1)\Theta t} \qquad (6.11)$$

The correlation function can be written as

$$C_{\rm vv}(t) = N\alpha^2e^{-q^2Dt}\sum_{l=0}^{\infty}(2l+1)e^{-l(l+1)\Theta t}F_l(t) \qquad (6.12)$$

where

$$F_l(t) = \frac{2^l}{L^2}\int_{-L/2}^{L/2}{\rm d}s\int_{-L/2}^{L/2}{\rm d}s'\; e^{(-q^2/6)[C(s,s)+C(s',s')]}\sum_{\substack{k=0\\ k+l,\text{even}}}^{\infty}\frac{[q^2C(s,s';t)]^k[(l+k)/2]!}{3^k(l+k+1)![(k-l)/2]!} \qquad (6.13)$$

The time dependence of $F_l(t)$ comes from the internal mode dynamics through the pair correlation function $C(s,s';t)$. Since this function is very complex, we need to expose its most important parts. Noting that the second normal mode relaxes nearly 10 times faster than the first one (independent of λ; see eq 4.14), we can keep terms up to the first normal mode in the expansion for $C(s,s';t)$. We can then write

$$C(s,s';t)^k \simeq L^{3k}\left[q_0{}^k(s)D_0{}^k(s') + kq_0(s)^{k-1}D_0(s')^{k-1}q_1(s)D_1(s')e^{-t/\tau_1} + \frac{k(k-1)}{2}q_0(s)^{k-2}D_0(s')^{k-2}q_1(s)^2D_1(s')^2e^{-2t/\tau_1} + \ldots\right] \qquad (6.14)$$

and

$$F_l(t) = B_l + B_l'e^{-t/\tau_1} + B_l''e^{-2t/\tau_1} + \ldots \qquad (6.15)$$

where the constants are

$$B_l = e^{-q^2L/36\lambda}\frac{2^l}{L^2}\int_{-L/2}^{L/2}{\rm d}s\int_{-L/2}^{L/2}{\rm d}s'\,e^{-q^2(s^2+s'^2)/6\lambda L}\times\sum_{k=l}^{\infty}\frac{[q^2L^3q_0(s)D_0(s')]^k[(l+k)/2]!}{3^k(l+k+1)![(k-l)/2]!},\qquad l,k\text{ even} \qquad (6.16a)$$

$$B_l' = e^{-q^2L/36\lambda}\frac{2^l}{L^2}\int_{-L/2}^{L/2}{\rm d}s\int_{-L/2}^{L/2}{\rm d}s'\,e^{-q^2(s^2+s'^2)/6\lambda L}q_1(s)D_1(s)\times\sum_{k=l}^{\infty}\frac{k(q^2L^3)^k(q_0(s)D_0(s'))^{k-1}[(l+k)/2]!}{3^k(l+k+1)![(k-l)/2]!},\qquad l,k\text{ odd} \qquad (6.16b)$$

$$B_l'' = e^{-q^2L/36\lambda}\frac{2^l}{L^2}\int_{-L/2}^{L/2}{\rm d}s\int_{-L/2}^{L/2}{\rm d}s'\,e^{-q^2(s^2+s'^2)/6\lambda L}q_1(s)^2D_1(s')^2\times\sum_{k=l}^{\infty}\frac{k(k-1)(q^2L^3)^k(q^0(s)D_0(s'))^{k-2}[(l+k)/2]!}{2(3^k)(l+k+1)![(k-l)/2]!},\qquad l,k\text{ even} \qquad (6.16c)$$

In the above equations we have used the fact that the parity of both $q_l(s)$ and $D_l(s) = D_l(s,\infty)$ is $(-)^{l+1}$ in determining the restrictions on the indices in eq 6.16. These B coefficients are functions of q and are thus form factors for the problem. When the indicated sums are performed, closed-form expressions can be obtained in terms of finite range double integrals for these form factors as a function of $z = q^2\langle R_G{}^2\rangle$. From eq 5.22 we see that the mean square radius of gyration of a coil is $\langle R_G{}^2\rangle = L/6\lambda$. The final expressions (which can be easily evaluated numerically) are

$$B_l = e^{-z/6}\int_0^1{\rm d}x\int_0^1{\rm d}y\,e^{-(z/4)(x^2+y^2)}a^l\left(\frac{1}{a}\frac{\rm d}{{\rm d}a}\right)^l\frac{\sinh a}{a},\qquad l\text{ even} \qquad (6.17a)$$

$$B_l' = e^{-z/6}\int_0^1 \mathrm{d}x \int_0^1 \mathrm{d}y \; e^{-(z/4)(x^2+y^2)}\left[\frac{q^2L^3}{3}q_1(x)D_1(y)\right]\frac{\mathrm{d}}{\mathrm{d}a}\left[a^l\left(\frac{1}{a}\frac{\mathrm{d}}{\mathrm{d}a}\right)^l\frac{\sinh a}{a}\right], \quad l \text{ odd} \qquad (6.17\text{b})$$

$$B_l'' = \frac{e^{-z/6}}{2}\int_0^1 \mathrm{d}x \int_0^1 \mathrm{d}y \; e^{-(z/4)(x^2+y^2)}\left[\frac{q^2L^3}{3}q_1(x)D_1(y)\right]^2\frac{\mathrm{d}^2}{\mathrm{d}a^2}\left[a^l\left(\frac{1}{a}\frac{\mathrm{d}}{\mathrm{d}a}\right)^l\frac{\sinh a}{a}\right], \quad l \text{ even} \qquad (6.17\text{c})$$

where $a = (z/4)xy(3 - y^2)$, $x = 2s/L$, and $y = 2s'/L$. From these expressions one can see that the behavior of the form factors at $z = 0$ is $B_l = \delta_{l0}$ and $B_l'' = B_l' = 0$.

The general structure of the correlation function can be appreciated by exhibiting the first few terms

$$C_{\mathrm{vv}}(t) = N\alpha^2 e^{-q^2Dt}\{[B_0 + B_0''e^{-2t/\tau_1} + ...] + e^{-2\Theta t}[B_1'e^{-t/\tau_1} + ...] + e^{-6\Theta t}[B_2 + B_2''e^{-2t/\tau_1} + ...] + ...\} \qquad (6.18)$$

We will discuss the main features of this correlation function here, leaving numerical details to a forthcoming communication on the polarized light scattering of chains of arbitrary flexibility. It is immediately obvious that there are terms that correspond to pure translational diffusion (B_0), translation plus pure rigid body rotation (B_2...), and translation plus internal modes (B_0''...) as well as terms where all three dynamical variables contribute. The relative magnitudes of these terms depend on the value of $z = q^2\langle R_G^2\rangle$ and it is clear from eq 6.17 that for $z < 1$, the B_l will dominate, making the internal modes practically invisible. For $z > 1$, however, flexing modes may gain a dominant intensity as the pure translational term decreases in intensity.

The most striking feature of eq 6.18, as compared to the equivalent calculation for the Rouse chain, is the presence of the rigid body rotation terms. Pecora's result[4] for the Rouse chain contains only the equivalent of B_0 and B_0'', thus being a much simpler expression. However, truncation of eq 6.18 by eliminating all terms containing rotations is not equivalent to Pecora's previous calculation. This is due to the fact that the time constants in the wormlike chain vary as $(2l + 1)^{-4}$, whereas those of the Rouse chain vary as l^{-2}, making the set of numbers much more widely separated in the wormlike coil case. This is related to the fact that the variables in the spring-and-bead model represent, in an average way, the dynamical variables of flexing and rotating of a segment of polymer. This interpretation is consistent with the fact that the Rouse model contains only one eigenfunction with zero eigenvalue. This eigenfunction represents the motion of the center of mass of the polymer, while the remaining eigenfunctions represent the reorientation and flexing motions of the chain.

By contrast, the eigenvalue problem for the wormlike coil contains two degenerate eigenfunctions with zero eigenvalue. Fujime[20] has shown, in a brief consideration of the pure bending equation, that these two degenerate eigenfunctions represent translation and rotation of the rodlike polymer. As we show in the Appendix, the center of mass system leaves a function $q_0(s)$ that is never accompanied by a time-dependent factor and thus must represent a fixed orientation for the polymer molecule. This implies that the normal mode expansion obtained in section IV must be applied in the molecule frame as done above.

Furthermore, the hypothetical case of a rigid but randomly coiled polymer corresponds to eq 6.18 in the limit of $\tau_l \rightarrow \infty$, where only rotation and translation terms appear. We must emphasize, however, that the rigid body rotation has been treated in an approximate way. It is well-known[21] that the instantaneous shape of a random coil is a general triaxial hydrodynamic body; nevertheless, given the difficulty of analyzing correlation functions that are multiexponential, to introduce the rotational diffusion splittings due to the three different components of the rotational diffusion tensor is unwarranted. This point is discussed further in a forthcoming paper on the forward depolarized scattering from semiflexible macromolecules.

Finally, we also emphasize that this calculation has been done mainly for illustrative purposes and as such has disregarded all couplings between dynamical variables. The disregard of the coupling between rotation and flexing in the very flexible case may not be accurate. As a result, for this case, the Rouse–Zimm model may be a more convenient choice, especially if it is necessary to include hydrodynamic interactions in the model. In spite of this, our calculation demonstrates clearly the features that a dynamical model of the wormlike chain presents and shows how we may calculate observable properties for the crucial cases of intermediate flexibility.

Acknowledgment. This work was supported by NSF Grants CHE82-00512 and CHE85-11178, NIH Grant 2R01-GM22517 and the NSF MRL Program through the Center of Materials Research at Stanford University. One of us (SRAS) would like to acknowledge support from a Fulbright–Hayes Fellowship during the course of this work.

Appendix. Translation and Rotation in the Bending Equation

Here we wish to discuss what degrees of freedom can be described by the normal mode expansion obtained in section IV.

Translation. The center of mass is located at

$$\mathbf{R}_{\mathrm{cm}} = \frac{1}{L}\int_{-L/2}^{L/2}\mathrm{d}s\ \mathbf{r}(s,t) = \mathbf{P}_*(t)\upsilon_*(L/2) + \mathbf{P}_{**}(t)\upsilon_{**}(L/2) \qquad (\mathrm{A.1})$$

where $\upsilon(s) \equiv \int_{-L/2}^{s} q(s)\ \mathrm{d}s$ for any q function and $\upsilon_l(L/2) = \int_{-L/2}^{L/2} q_l(s)\ \mathrm{d}s = 0$, for $l \geq 1$. The last equality in eq A.1 is obtained by substituting the normal mode expansion, eq 4.10, into the integral. The fact that $\upsilon_l(L/2) = 0$ can be verified by noting that the first integral of $q_l(s)$ is proportional to the third derivative of q_l and vanishes at the end points due to our boundary conditions. In addition, since q_{**} is proportional to s, $\upsilon_{**}(L/2) = 0$.

The total stochastic force on the molecule at time t is obtained in a similar way

$$\mathbf{F}(t) = \int_{-L/2}^{L/2}\mathrm{d}s\ \mathbf{A}(s,t) = \mathbf{A}_*(t)\upsilon_*(L/2) \qquad (\mathrm{A.2})$$

If we substitute the expansion into the bending equation and integrate over s, we obtain

$$0 = [\rho\ddot{\mathbf{P}}_*(t) + \zeta\dot{\mathbf{P}}_*(t) - \mathbf{A}_*(t)]\upsilon_*(L/2) \qquad (\mathrm{A.3})$$

or, incorporating the expressions for $\mathbf{R}_{\mathrm{cm}}$ and $\mathbf{F}(t)$, we can write

$$M\ddot{\mathbf{R}}_{\mathrm{cm}}(t) + L\zeta\dot{\mathbf{R}}_{\mathrm{cm}}(t) = \mathbf{F}(t) \qquad (\mathrm{A.4})$$

which is just the Langevin equation of motion for a particle of mass M, friction coefficient $L\zeta$, located at $\mathbf{R}_{\mathrm{cm}}(t)$. Thus one of the zero eigenvalue eigenfunctions, q_*, gives us the translational motion of the center mass.

If we choose the origin of our molecule-fixed coordinate system at $\mathbf{R}_{\mathrm{cm}}$, then we can eliminate q_* since $\mathbf{R}_{\mathrm{cm}} = 0$ implies $\mathbf{P}_*(t) = 0$ and $\mathbf{A}_*(t) = 0$. Thus we may define $\mathbf{P}_0 = \mathbf{P}_{**}$, $\mathbf{A}_0 = \mathbf{A}_{**}$, $q_0 = q_{**}$, and $v_0(s) = v_{**}(s)$. In addition, eq A.4 tells us that when we sit at the center of mass, the net force felt by the polymer is zero. This implies that the normal mode expansion in eq 4.11 cannot represent the translational degrees of freedom.

Rotation. The total angular momentum of the polymer can be written as the sum of the angular momenta of all of its segments

$$\mathbf{L}(t) = \frac{\rho}{L}\int_{-L/2}^{L/2} \mathrm{d}s\ \mathbf{r}(s,t) \times \dot{\mathbf{r}}(s,t) \tag{A.5}$$

and the total stochastic torque is similarly

$$\mathbf{T}(t) = \frac{1}{L}\int_{-L/2}^{L/2} \mathrm{d}s\ \mathbf{r}(s,t) \times \mathbf{A}(s,t) \tag{A.6}$$

Now note that

$$\int_{-L/2}^{L/2} \mathrm{d}s\ \mathbf{r}(s,t) \times \frac{\partial^4 \mathbf{r}(s,t)}{\partial s^4} = \sum_{l=0}^{\infty} \lambda_l \mathbf{P}_l \times \mathbf{P}_l = 0 \tag{A.7}$$

This implies that the bending force does not directly contribute to the torque equation. Substituting the bending equation into the torque integral and using eq A.6 and A.7, we obtain

$$\mathbf{T}(t) = \frac{\mathrm{d}}{\mathrm{d}t}\mathbf{L}(t) + \frac{\zeta}{\rho}\mathbf{L}(t) \tag{A.8}$$

which is the expected torque in a viscous medium. If we substitute the normal mode expansion (eq 4.11) into the above relation, we get

$$\mathbf{T}(t) = \frac{1}{L}\left[\rho \frac{\mathrm{d}}{\mathrm{d}t}\sum_{l=0}^{\infty} \mathbf{P}_l \times \dot{\mathbf{P}}_l + \zeta \sum_{l=0}^{\infty} \mathbf{P}_l \times \dot{\mathbf{P}}_l\right] \tag{A.9}$$

Thus, a given mode will contribute angular momentum if the cross product $\mathbf{P}_l \times \dot{\mathbf{P}}_l$ does not vanish. It is easy to see that every nonzero mode is double degenerate in space because the oscillations can occur in two perpendicular planes. These two degenerate modes can be combined to give a "pseudorotation" around the elongation axis of the molecule and give an effective parallel axis rotation to the polymer. It is just these rotations that we have considered as averaging out our polymer structure into an effective cylindrically symmetric body.

Rotations of the elongation axis, however, cannot be reproduced by the above mechanism. Thus the major conclusion is that perpendicular rotations, or tumbling of the elongation axis, are independent dynamical variables that cannot be expressed by the bending dynamics.

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Statistical Thermodynamic Theory for the Melting of *n*-Alkanes from Their Rotator Phases[†]

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Received January 3, 1985

ABSTRACT: Most liquid *n*-alkanes comprised of 9–43 carbons freeze to an equilibrium "rotator" phase a few degrees above the temperatures at which they fully crystallize. We develop statistical mechanical theory to account for the thermodynamic properties of melting from this rotator phase. Chain configurations are taken into account through the rotational isomeric state approximation. Volume-dependent interactions are approximated through adaptation of a classical equation of state for liquid alkanes. The anisotropy of the short-range repulsive forces, which must be the principal source of ordering in alkanes, is taken into account through appropriate modification of a chain pair potential. We also present a critical study of available experimental data. With a minimum of free parameters, the theory predicts enthalpies, volume changes, and temperatures of melting for the alkanes that have rotator phases at atmospheric pressure. For alkanes from 44 carbons to poly(methylene), which have no stable rotator phases at 1 atm, the theory predicts rotator-phase melting temperatures that are nearly identical with the experimentally observed crystalline melting temperatures.

Many liquid paraffins freeze to stable "rotator" phases a few degrees above the temperatures at which they undergo phase transitions to form fully ordered crystals. First observed by Müller,[1] these are partially disordered states in which the chains form layered arrays; however, unlike the chains in fully ordered crystal phases, the chains in rotator phases exhibit some degree of rotational freedom. For *n*-alkane chains having odd numbers of carbons (n_c),

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[†] We dedicate this paper to the memory of Professor Paul J. Flory.

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0024-9297/85/2218-1875$01.50/0 © 1985 American Chemical Society