Dynamics of Wormlike Coils: Amplitudes of Normal Bending Modes

SERGIO R. ARAGÓN

Department of Chemistry and Biochemistry, San Francisco State University, San Francisco, California 94132

Received October 15, 1990;
Revised Manuscript Received December 12, 1990

The dynamics of semistiff polymers in solution is a subject that has attracted great interest over the past two decades but has made only slow progress due to the difficulty of the mathematical treatment. Harris and Hearst[1] were the first to attempt to solve the dynamics using the wormlike chain model of Kratky and Porod,[2] while Soda[3] pointed out the internal inconsistencies of their model a few years later. The model has nevertheless been used by several authors such as Moro and Pecora[4] and Maeda and Fujime[5–7] to describe dynamic light scattering from semiflexible molecules and by Schmidt and Stockmayer[8] to study the first cumulant in dynamic light scattering. Soda[9] has used a Harris–Hearst-like model to describe the dynamic light scattering from circular wormlike chains by generalizing the work of Berg.[10] Yamakawa and Yoshisaki[11] have also presented a theory of the more general helical wormlike chain, but no calculations of dynamic light scattering have been done with this theory to date.

The first theory of the dynamics of the wormlike chain shown to be free of the inconsistencies of the Harris–Hearst theory was presented by Aragón and Pecora[12] (hereafter referred to as AP). The important advance made in this theory was the introduction of the pure bending equation of motion and the procedures for calculating correlation functions for nonstretching chains. The constraint of constant length can be handled exactly by using the proper tangent vector orientational distribution function. This theory was used by Aragón[13] to calculate the electric field correlation functions for forward depolarized light scattering. An important feature of this theoretical framework is that the rigid-rod limits are always correctly obtained, while this is not the case in all the alternate theories presented to date. In the work of Aragón,[13,12] however, hydrodynamic interactions and dynamical couplings between degrees of freedom have been ignored.

Recently, Schurr and co-workers[14,15] have developed a theory for weakly bending rods and applications have been made to dilute DNA and M13 virus suspensions. While this weakly bending theory does include approximate hydrodynamic interactions, it still suffers from inconsistencies. The constraints of constant length have not been included with the result that the theories fail to yield correct behavior in the rigid-rod limit.

One fundamental difficulty encountered by previous authors lies in the proper computation of the average of the products of normal mode amplitudes. When the length constraint is not enforced, the potential energy of the chain looks quadratic in the normal mode amplitudes, with the consequence that the equilibrium probability distribution for the normal modes becomes Gaussian. Yet, a Gaussian probability distribution is only appropriate for very flexible chains, thus introducing an inconsistency. The purpose of this paper is to present a computation of the average of quadratic products of the normal mode amplitudes, for rigorously nonstretching chains, which can be useful in the development of theories of light scattering, fluorescence polarization anisotropy, and other measurements on systems of wormlike chains.

Table I
The Amplitude Function $d_{jk}(a)$ for Arbitrary Persistence Length

$$d_{00}(a) = 1/10a - 1/4a^3 + 3/8a^4 - 3/8a^6 + 3(1+a)^2 e^{-2a}/8a^6$$

$$d_{0k}(a) = -\frac{3^{1/2}(z_k \cot z_k - 1)}{2az_k^4} - \frac{3^{1/2}(1+a)}{4a^2(a^4 - z_k^4)}[(z_k \cot z_k - a) - (z_k \cot z_k + a)e^{-2a}] \qquad k \neq 0, k \text{ even}$$

$$d_{kk}(a) = \frac{a^3[z_k^2 \cot^2 z_k - z_k \cot z_k - z_k^4/a^2]}{4z_k^4(a^4 - z_k^4)} + \frac{a^2[a^2 - z_k^2 \cot^2 z_k + (z_k \cot z_k + a)^2 e^{-2a}]}{2(a^4 - z_k^4)^2} \qquad k \neq 0, k \text{ even}$$

$$d_{kk}(a) = \frac{a^3[z_k^2 \tan^2 z_k + z_k \tan z_k - z_k^4/a^2]}{4z_k^4(a^4 - z_k^4)} + \frac{a^2[a^2 - z_k^2 \tan^2 z_k - (z_k \tan z_k - a)^2 e^{-2a}]}{2(a^4 - z_k^4)^2} \qquad k \neq 0, k$$

$$d_{jk}(a) = \frac{a^3(z_k \cot z_k - z_j \cot z_j)(2a^4 - z_k^4 - z_j^4)}{2(z_j^4 - z_k^4)(a^4 - z_k^4)(a^4 - z_j^4)} + \frac{a^2[e^{-2a}(z_k \cot z_k + a)(z_j \cot z_j + a) + (z_k \cot z_k)(z_j \cot z_j) - a^2]}{2(a^4 - z_k^4)(a^4 - z_j^4)} \qquad j \neq k \neq 0, j, k \text{ even}$$

$$d_{jk}(a) = \frac{a^3(z_j \tan z_j - z_k \tan z_k)(2a^4 - z_k^4 - z_j^4)}{2(z_j^4 - z_k^4)(a^4 - z_k^4)(a^4 - z_j^4)} - \frac{a^2[e^{-2a}(z_k \tan z_k - a)(z_j \tan z_j - a) + (z_k \tan z_k)(z_j \tan z_j) - a^2]}{2(a^4 - z_k^4)(a^4 - z_j^4)} \qquad j \neq k \neq 0, j, k \text{ odd}$$

Theory

The main ingredients required in the calculation have already been presented in AP. While the constraint of constant length is handled exactly, for mathematical simplicity, we will ignore hydrodynamic interactions. When computing equilibrium properties of wormlike chains, this assumption is of no consequence, as demonstrated in AP. When one is interested in dynamical properties, however, hydrodynamic interactions become important, especially as the flexibility increases. These interactions can be incorporated by using the perturbation theory as shown by Maeda and Fujime.[7]

If we position ourselves in the center of mass of a wormlike chain of contour length L and Kuhn length $\lambda^{-1} = 2P$ (P, the persistence length) and we locate a position on the chain by a vector $\mathbf{r}(s,t)$, we can write the pure bending equation as follows:

$$\rho\, \partial^2\mathbf{r}(s,t)/\partial t^2 + \zeta\, \partial\mathbf{r}(s,t)/\partial t + \epsilon\, \partial^4\mathbf{r}(s,t)/\partial s^4 = \mathbf{A}(s,t) \qquad (1)$$

which is to be solved for free-ends boundary conditions

$$\partial^2\mathbf{r}(s,t)/\partial s^2 = \partial^3\mathbf{r}(s,t)/\partial s^3 = 0 \qquad \text{at } s = \pm L/2 \qquad (2)$$

In eq 1, ρ is the linear mass density, ζ is the friction per unit length, and ϵ is the intrinsic elasticity constant of the chain ($\lambda = k_BT/2\epsilon$). The parameter s runs along the

0024-9297/91/2224-3451$02.50/0

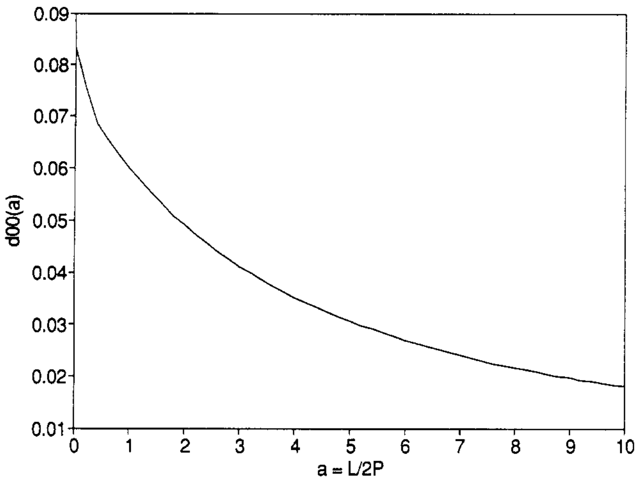

Figure 1. The function $d_{00}(a)$.

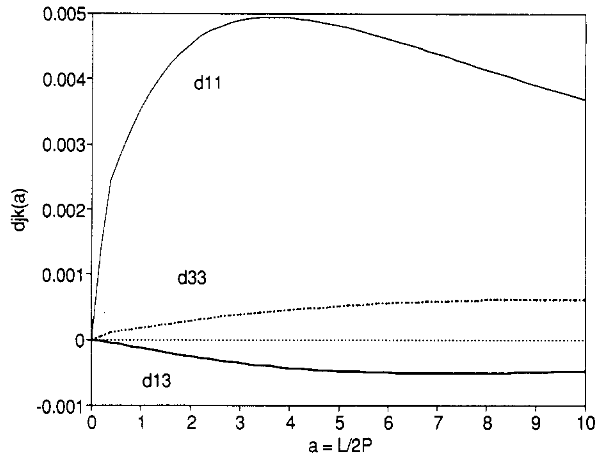

Figure 2. The function $d_{jk}(a)$ for odd j, k.

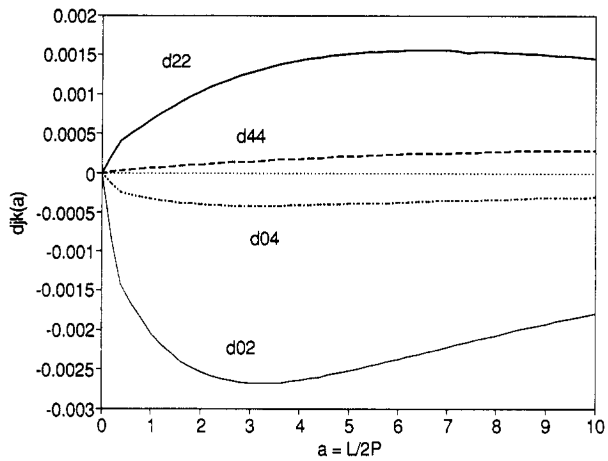

Figure 3. The function $d_{jk}(a)$ for even j, k.

contour of the chain. The solution can be obtained by normal mode analysis, as shown in AP. Both the position vector and the random force, $\mathbf{A}(s,t)$, are expanded in the complete set of eigenfunctions of the quartic bending operator, q_k. Implicit in the use of these eigenfunctions is the absence of hydrodynamic interactions, as well as the neglect of coupling between the center of mass motions and the bending and the neglect of the coupling between the rotational motions and the bending. Work in progress, using Brownian dynamics simulations to investigate the importance of these neglected coupling terms, indicates that these assumptions are not unreasonable.[16] The vectors in eq 1 can be expanded as follows:

$$\mathbf{r}(s,t) = \sum_{k=0}^{\infty} \mathbf{P}_k(t) q_k(s) \tag{3}$$

$$\mathbf{A}(s,t) = \sum_{k=0}^{\infty} \mathbf{A}_k(t) q_k(s) \tag{4}$$

The fundamental quantity that enters into correlation functions of physically measured variables is the correlation function of the normal mode amplitudes

$$\langle \mathbf{P}_k(t)\cdot\mathbf{P}_j(0)\rangle = \langle \mathbf{P}_k(0)\cdot\mathbf{P}_j(0)\rangle \exp[-\lambda_k t/\zeta] \tag{5}$$

where λ_k are the eigenvalues of the bending operator. The relation above is obtained because the normal mode amplitudes are uncorrelated with the amplitudes of the random force, $\mathbf{A}_k(t)$. The objective of this paper is to compute the average of the products of normal mode amplitudes at time zero. For convenience, these can be written as follows:

$$\langle \mathbf{P}_k(0)\cdot\mathbf{P}_j(0)\rangle = L^2 d_{kj}(a) \tag{6}$$

where $a = \lambda L = L/2P$. Changing variables to $x = 2s/L$, we can rewrite the expression given in AP (eq 5.5) for the dimensionless function

$$d_{kj}(a) = (1/4)\int_{-1}^{1}\mathrm{d}x \int_{-1}^{1}\mathrm{d}y\, v_k(y) v_j(x) e^{-a|x-y|} \tag{7}$$

Where the constant-length Green's function, or the distribution function for the tangent vectors, has been used.[12,17] The functions $v_k(y)$ are given by

$$v_k(y) = (1/2)\int_{-1}^{y} q_k(y')\,\mathrm{d}y' \tag{8}$$

Results and Discussion

In order to evaluate d_{kj} we use the expressions for $v_k(x)$ presented in Table I of Aragon.[13] The correctness of the integrals for arbitrary values of a was checked with the aid of Mathematica[18] V. 1.2 on a Sun 4 workstation, and these values are presented in Table I. Figures 1–3 display the behavior of the first few $d_{jk}(a)$ for a up to 10. The only part that requires care is the evaluation of the absolute value in the exponential. The calculation is carried out by symmetrizing the argument and nesting the double integrals. In addition, it is useful to take into account the facts that $v_k(1) = 0$ and the parity of v_k is $(-)^k$. At this point, it is instructive to examine various limits.

Rigid Rod. In this case, $a \rightarrow 0$, and we can use the fact that the integrals of v_k, for $k > 0$, are proportional to the second derivative of the eigenfunctions q_k. These vanish when evaluated at the end points. The result is then

$$d_{kj}(0) = \delta_{k0}\delta_{j0}/12 \tag{9}$$

Weakly Bending Rod. Expanding the exponential to first order in a and performing the integrals over $|x - y|$ yield coefficients inversely proportional to the persistence length:

$$d_{00} = 1/12 \tag{10}$$

$$d_{0k} = -a \cot(z_k)/(3^{1/2} z_k^{3}) \qquad k \neq 0 \tag{11}$$

$$d_{jk} = a/(4 z_k^{4})\delta_{jk} \qquad j, k \neq 0 \tag{12}$$

The quantity $z_k \approx (2k + 1)\pi/4$ is related to the eigenvalues $x_k = 2z_k$ given in Table I of AP. Expanding the general results of Table I using the Series function of Mathematica yields results in agreement with eqs 10–12. It is interesting to note that when $j \neq k \neq 0$, the first nonzero terms of d_{jk} start with a^3 for j, k even, whereas for j, k odd it is quadratic in a:

$$d_{jk} = -a^2 \tan(z_j) \tan(z_k)/z_j^3 z_k^3 \quad (13)$$

Random Coil. The persistence length of the random coil tends to zero, so $a \to \infty$. In this case, the exponential behaves like a Dirac δ function, and we obtain

$$d_{kj}(\infty) = (1/2a)\int_{-1}^{1}dx \int_{-1}^{1}dy\, v_k(y)v_j(x) = 6ab_{kj}(\infty) \quad (14)$$

where the function $b_{kj}(\infty)$ is given in Table III of Aragón.[13] Due to parity, this integral is zero unless k+j is even. The results can also be obtained from Table I by a suitable limit. Note that the function is proportional to the persistence length P since $1/a = P/L$. By use of the fact that $\cot(z_k) \approx 1$ (for k even) and $\tan(z_k) \approx -1$ (for k odd), the coil results can be summarized as follows

$$d_{00} = 1/10a \quad (15)$$

$$d_{0k} \approx -3^{1/2}(z_k - 1)/(2az_k^4) \qquad k \neq 0 \quad (16)$$

$$d_{kk} \approx (z_k - 1)/(4az_k^3) \qquad k \neq 0 \quad (17)$$

$$d_{jk} \approx (z_k - z_j)/(a(z_j^4 - z_k^4)) \qquad j \neq k \neq 0 \quad (18)$$

It is noteworthy that the d_{jk} functions decrease rather rapidly with increasing index, due to the large powers of the eigenvalue they contain in the denominators, but that they decrease more rapidly for rigid chains than for flexible chains.

Comparison with Other Works. Moro and Pecora[4] calculated the depolarized dynamic light scattering from semiflexible chains, while Maeda and Fujime[5-7] calculated the polarized light scattering from semiflexible filaments, both using the Harris–Hearst[1] theory. The Harris–Hearst theory uses a quadratic expression for the potential energy and the distribution function for the normal modes is a Gaussian.[4] As a result, the expression for the average of the square of a normal mode amplitude is

$$\langle \mathbf{P}_j(0)\mathbf{P}_j(0)\rangle = k_BT/\lambda_j = L^2 2a(\epsilon/\kappa)/x_j \quad (19)$$

where ϵ/κ is the ratio of the bending to the stretching force constants, $a = L/2P$, and x_j is a dimensionless eigenvalue, typically of magnitude greater than 1. This expression is proportional to a, as in the weakly bending rod case presented above, but contains only one power of the dimensionless eigenvalue in the denominator. There is a general agreement on the lack of applicability of the Harris–Hearst theory to stiff systems, since it yields the wrong rigid-rod limits. Schmidt and Stockmayer[8] have shown this limitation very graphically in their study of the first cumulant of the dynamic light scattering from semiflexible chains.

The case of the circular semiflexible chain treated by Soda[9] is very similar to the above. Soda used the equipartition theorem to evaluate the square of the normal mode amplitudes from a potential that is quadratic in both flexing and chain stretching deformations. As such, it is not a model of wormlike chains but rather an implementation of the Harris–Hearst theory for closed chains. The expression obtained for the normal modes amplitudes does not differ significantly from eq 19.

Song et al.[14] have developed a theory of the weakly bending rod by trying to limit the deviations from a rigid rod shape to fairly small values. The validity of their theory was studied by comparison with Brownian dynamics simulations and reasonable agreement was found for $L/P \leq 0.53$. However, these authors have also evaluated $\langle \mathbf{P}_j(0)\cdot\mathbf{P}_j(0)\rangle$ from an assumed Gaussian probability distribution for the normal modes, which ignores the constraints of constant length. They obtain (when normalization of their eigenvectors is taken into account)

$$\langle \mathbf{P}_j(0)\cdot\mathbf{P}_j(0)\rangle = h^3/P\Lambda_j = L^3/Pz_j^4, \qquad j > 0 \quad (20)$$

where h is the bond distance and the contour length $L = Nh$. This expression is proportional to a and is in accord with our weakly bending rod results since $\Lambda_j = N^{-3}z_j^4$ when the eigenfunctions are normalized.[19] This theory nevertheless leads to incorrect values for some properties, such as the mean-square radius of gyration,[15] because the length constraints have not been properly enforced. It is clear from the above that without the constant length the theory is limited to very small values of a, as is the intent of the authors.

Final Comments on the Dynamics of Wormlike Chains. Of the various distinct effects that must be considered in the dynamics of wormlike chains, the most important effect that one must take into account correctly is the constraint of constant length. Without this, not even the equilibrium properties of the wormlike chain are correctly reproduced. This note has been devoted to that aspect of the problem. Following this is the inclusion of hydrodynamic interactions. Our studies with Brownian dynamics simulations[16] demonstrate that there is a significant difference between free-draining simulations and those containing hydrodynamic interactions, while the difference between full and preaveraged hydrodynamic interactions is small (about 5%). An improved version of the theory containing hydrodynamic interactions explicitly is being pursued.

Other effects, whose relative importance is not yet known, are the dynamical couplings between the degrees of freedom. The various normal modes of bending will become coupled by the hydrodynamic interaction,[7] except in the case of extremely weakly bending rods.[14] Maeda and Fujime[7] have made a preliminary investigation of this coupling and did not find it to be very large. The coupling of flexing with other degrees of freedom (center of mass motion, rotation, and torsion) has not yet received significant attention in the semiflexible case.

Acknowledgment. I thank Nan Wang for assistance in checking the integrations with Mathematica. This work was supported in part by a grant from The Research Corp.

References and Notes

(1) Harris, R. A.; Hearst, J. E. *J. Chem. Phys.* **1966**, *44*, 2595.
(2) Kratky, O.; Porod, G. *Recl. Trav. Chim. Pays-Bas* **1949**, *68*, 1106.
(3) Soda, K. *J. Phys. Soc. Jpn.* **1973**, *35*, 866.
(4) Moro, J.; Pecora, R. *J. Chem. Phys.* **1978**, *69*, 3254.
(5) Maeda, T.; Fujime, S. *Macromolecules* **1981**, *14*, 809.
(6) Maeda, T.; Fujime, S. *Macromolecules* **1984**, *17*, 1157, 2381.
(7) Fujime, S.; Maeda, T. *Macromolecules* **1985**, *18*, 191.
(8) Schmidt, M.; Stockmayer, W. H. *Macromolecules* **1984**, *17*, 509.
(9) Soda, K. *Macromolecules* **1984**, *17*, 2365.
(10) Berg, O. *Biopolymers* **1979**, *18*, 2861.
(11) Yamakawa, H.; Yoshisaki, T. *J. Chem. Phys.* **1981**, *75*, 1016.
(12) Aragón, S. R.; Pecora, R. *Macromolecules* **1985**, *18*, 1868.
(13) Aragón, S. R. *Macromolecules* **1987**, *20*, 370.
(14) Song, L.; Allison, S. A.; Schurr, J. M. *Biopolymers*, in press.
(15) Song, L.; Kim, U.; Wilcoxon, J.; Schurr, J. M., preprint.
(16) Aragón, S. R.; Luo, L., unpublished work.
(17) Saito, N.; Takahashi, K.; Yunoki, Y. *J. Phys. Soc. Jpn.* **1967**, *22*, 219.
(18) Wolfram, S. *Mathematica*; Addison-Wesley: New York, 1988.
(19) Schurr, J. M., private communication.