segmental motion. Of course their solvent is far less viscous, and their observed activation energies correspond to energy barriers of over 10 kJ mol^{-1}. In poly(2,6-dimethyl-1,4-phenylene oxide) and poly(2-methyl-6-phenyl-1,4-phenylene oxide) the phenylene ring rotations are only slightly slower than in the polycarbonate while the segmental motions are considerably slower.[12] Our cyclohexylene rings thus appear to be especially mobile.

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Spectrum of Light Quasi-elastically Scattered from Dilute Solutions of Very Long and Slightly Bendable Rods. Effect of Hydrodynamic Interaction

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ABSTRACT: The effect of the hydrodynamic interaction on the spectral shape of light quasi-elastically scattered from dilute solutions of very long and slightly bendable rods was considered theoretically on the basis of a spherically averaged interaction tensor. Numerical simulation of the field correlation function of polarized scattered light for dimensions appropriate to fd virus showed a definite effect of the hydrodynamic interaction on the spectral shape. The method presented here will provide an approximate but practical procedure to estimate the flexibility parameter of very long and semiflexible filaments from experimental spectra for dilute solutions.

Introduction

On the basis of the Harris and Hearst (HH) model of polymer dynamics,[1] we have presented a theory of the spectrum of light quasi-elastically scattered from solutions of very long filaments.[2-6] There are two kinds of criticisms to our model. One is that the HH model has some unphysical properties.[7] Another is that our treatment does not include the hydrodynamic interaction. For the first criticism, we would like to stress that the HH model is mathematically tractable and that the model has afforded some valuable insights into semiflexible chain dynamics and should not be dismissed too lightly.[8] For the second criticism, we would like to discuss here approximately the effect of the hydrodynamic interaction on the spectrum of light in the framework of the Hearst, Beals, and Harris (HBH) model.[9]

HBH Model

We adopt the notation used in our previous papers, although it has one-to-one correspondence to that in the HH paper. The operator describing the free-draining force per unit length is $A(s)$, where

$$A(s) = \epsilon(\partial^4/\partial s^4) - \kappa(\partial^2/\partial s^2) \quad (1)$$

The quantity s is a continuous contour parameter whose range is $-L/2 \le s \le L/2$ where L is the contour length of the chain. The quantity ϵ is a bending force constant and κ is the Lagrange multiplier introduced as a means of establishing the constraint that the contour length of the chain be a constant equal to L. HBH treated the hydrodynamic interaction between beads in its spherically averaged form, as was done by Zimm.[10] The interaction tensor has been introduced as

$$H(s,s') = \delta(s - s') + (\zeta/6\pi\eta)f(|s - s'|) \quad (2)$$

The quantity ζ is the friction constant per unit length of the chain, which is assigned the value $3\pi\eta$ throughout by analogy to a string of touching spherical beads. The solvent viscosity is η.

The eigenvalue problem which has to be solved now has the form

$$A(s)\Psi(n,s) + \tfrac{1}{2}\int_{-L/2}^{L/2} f(|s - s'|)A(s')\Psi(n,s')\,ds' = \sigma_n\Psi(n,s) \quad (3)$$

For the function $f(|s - s'|)$, HBH followed the method of Hearst and Stockmayer[11]

$$f(|s - s'|) = (6/\pi)^{1/2}\gamma^{(1-\nu)/2}|s - s'|^{-(1+\nu)/2}$$

where $\gamma|s - s'| > a$ ($\simeq 2$) and

$$f(|s - s'|) = |s - s'|^{-1}(1 + \tfrac{1}{3}\gamma|s - s'| + c\gamma^2|s - s'|^2 + d\gamma^3|s - s'|^3) \quad (4)$$

where $\gamma|s - s'| < a$. The quantity γ is the flexibility pa-

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Table I
11 × 11 Portion of the Matrix M for $\kappa = 0$ and $L/b = 200$[a]

0	0	0.1889	0	−1.971	0	7.271	0	−17.60	0	34.18
0	0	0	1.488	0	−7.925	0	22.25	0	−46.83	0
0	0	1.748	0	4.711	0	−17.37	0	41.29	0	−78.82
0	0	0	12.47	0	9.771	0	−28.86	0	61.34	0
0	0	0.1589	0	44.70	0	17.12	0	−43.42	0	85.13
0	0	0	0.9308	0	114.7	0	27.17	0	−61.48	0
0	0	−0.0961	0	2.805	0	241.7	0	40.23	0	−83.20
0	0	0	−0.6316	0	6.241	0	447.1	0	56.60	0
0	0	0.0661	0	−2.059	0	11.64	0	755.5	0	76.48
0	0	0	0.4590	0	−4.829	0	19.36	0	1191	0
0	0	−0.0490	0	1.568	0	−9.347	0	29.71	0	1781

[a] $10^{-3}M_{km}$ in units of ϵ/L^4.

rameter and ν is the excluded volume parameter. The constants a, c, and d have been tabulated.[12]

Eigenvalue Problem

In order to solve eq 3, we follow a method quite similar to that of Zimm et al.[13] The free-draining eigenfunctions $Q(n,s)$ and eigenvalues λ_n satisfy the following equations:

$$A(s)Q(n,s) = \lambda_n Q(n,s) \qquad (5)$$

$$\lambda_n = \epsilon\beta_n^4 + \kappa\beta_n^2 = \epsilon\alpha_n^4 - \kappa\alpha_n^2$$

They have been given in ref 4. We expand $\Psi(n,s)$ in terms of $Q(n,s)$:

$$\Psi(n,s) = \sum_m a_m(n)Q(m,s) \qquad (6)$$

By substituting eq 6 into eq 3, multiplying both sides by $Q(k,s)$, and integrating over s, we have a set of homogeneous linear simultaneous equations for the expansion coefficients $a_m(n)$

$$\mathbf{Ma}(n) = \sigma_n\mathbf{a}(n) \qquad (7)$$

with

$$M_{km} = G_{km} + \lambda_k\delta_{km}$$

$$G_{km} = (\lambda_m/2)\int\int Q(k,s)f(|s-s'|)Q(m,s')\,ds\,ds'$$

$$\mathbf{a}(n) = \mathrm{col}\,[a_0(n),...,a_m(n),...,a_n(n),...,a_N(n)]$$

where col means a column vector. In terms of the new variables $p = (s+s')/2L$ and $q = (s-s')/2L$ we have

$$G_{km} = (2\lambda_m)L^2\int_0^{0.5} f(2Lq)G(k,m,q)\,dq \qquad (8)$$

where $G(k,m,q)$ is analytically given in Appendix A. To avoid divergence of the integral in eq 8, a lower limit of $|s-s'| = b$ (or a lower limit of $q = b/2L$) is chosen, where b is a measure of the hydrodynamic diameter of the polymer backbone.

We are interested in the case of $\gamma L \leq 0.5$ (i.e., the case of slightly bendable rods). In this case, we can put $\kappa = 0$ into eq 1.[6] In what follows, we mainly consider this case, unless otherwise stated. In this situation, $f(|s-s'|)$ is given by eq 4 without c and d terms. Under these conditions, the matrix elements M_{km} of $\mathbf{M}$ have been computed by use of the Simpson quadrature algorithm (the first 11 × 11 portion is shown in Table I). It is seen that the matrix is almost diagonal, so that perturbation methods may be used to find the eigenvalues. The off-diagonal elements of the secular determinant $|\mathbf{M} - \sigma_n\mathbf{I}|$ are considered as perturbations on the equation formed from the diagonal elements only. The formula including the second-order perturbation is

$$\sigma_n = M_{nn} - \sum_{m\neq n} M_{nm}M_{mn}/(M_{mm} - M_{nn}) \qquad (9)$$

The numerical values of Table I show that contributions to σ_n from the second-order terms in the right-hand side of eq 9 are negligible (at most 2% of M_{nn} as a whole). The first-order formula for the expansion coefficients $a_m(n)$ in eq 6 is, for $m \neq n$

$$a_m(n) = M_{mn}a_n(n)/(\sigma_n - M_{nn}) \qquad (10)$$

The value of $a_n(n)$ is to be determined by the normalization requirement that the integral of $\Psi(n,s)^2$ is to be unity; in fact the numerical values in Table I give $a_n(n)$ to be at most 1% smaller than unity for all cases except $a_0(0)$ and $a_1(1)$, both of which are unity.

Dynamic Light Scattering Spectrum

Let $\mathbf{r}(s,t)$ be the position vector of the line element ds at s of the chain. The Langevin equation of motion of the chain is given by

$$\rho(\partial^2\mathbf{r}/\partial t^2) + \zeta(\partial\mathbf{r}/\partial t) + \int H(s,s')A(s')\mathbf{r}(s',t)\,ds' = \mathbf{F}(s,t) \qquad (11)$$

where ρ is the linear mass density of the chain, ζ is the friction factor tensor,[14a] and $\mathbf{F}(s,t)$ is the random force. Equation 11 is an extension of the corresponding equation in the HH model. By mode expansion

$$\mathbf{r}(s,t) = \sum_n \mathbf{q}(n,t)\Psi(n,s)$$

$$\mathbf{F}(s,t) = \sum_n \mathbf{B}(n,t)\Psi(n,s)$$

eq 11 is written in the decoupled form as

$$\rho\mathbf{q}''(n,t) + \zeta_1\mathbf{q}'(n,t) + \sigma_n\mathbf{q}(n,t) = \mathbf{B}(n,t)$$

from which we have under the usual approximations[2-6]

$$\langle\mathbf{q}(n,t)\mathbf{q}(n',t')\rangle = \langle q_n^2\rangle \exp(-\tau/\tau_n)\delta_{nn'} \qquad (12)$$

$$1/\tau_n = \sigma_n/\zeta_1 \qquad (n \geq 2) \qquad (13)$$

where $\tau = |t-t'|$. The friction factor ζ_1 is assumed in eq 13, because we are considering the lateral bending motion.[14] The elastic potential energy of the chain in the HH model (for $\kappa = 0$) is given by

$$V = (\epsilon/2)\int[\partial^2\mathbf{r}(s,t)/\partial s^2]^2\,ds = (1/2)\sum_n\sum_{n'}\sum_m \lambda_m a_m(n)a_m(n')\mathbf{q}(n,t)\mathbf{q}(n',t')$$

from which we have

$$\langle V\rangle = (1/2)\sum_n \lambda_n\langle q_n^2\rangle a_n(n)^2[1 + \Phi(n)]$$

where use was made of eq 12 and $\Phi(n) = \sum_{m\neq n}(\lambda_m/\lambda_n)[a_m(n)/a_n(n)]^2$. Since $\lambda_0 = \lambda_1 = 0$ and $\lambda_n \propto (n - {}^1/_2)^4$ for $n \geq 2$, the numerical values in Table I give $\Phi(n) < 0.005$. Then, the equipartition theorem of the thermal energy gives[14b]

$$\langle q_n^2\rangle a_n(n)^2 = 2k_BT/\lambda_n \qquad (14)$$

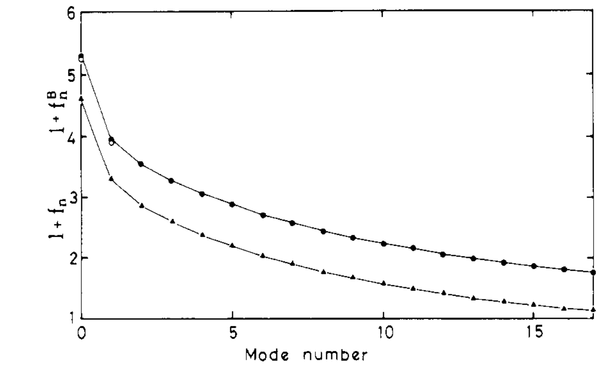

Figure 1. Hydrodynamic interaction factor f_n. $1 + f_n(b)$ for L/b = 200 (●) and 100 (▲). $1 + f_0^B$ and $1 + f_1^B$ are also shown by open symbols for L/d = 100.

Since $a_n(n)^2 \simeq 1$ as mentioned before, eq 14 is essentially the same as that in the free-draining limit. From the normal mode expansion, we have

$$\mathbf{r}(s,t) = \mathbf{R}(t) + s\mathbf{t}(t) + \sum_n{}'' \mathbf{q}(n,t)\Psi(n,s) \qquad (\kappa = 0)$$

$$= \mathbf{R}(t) + \sum_n{}' \mathbf{q}(n,t)\Psi(n,s) \qquad (\kappa \neq 0)$$

where $\mathbf{R}(t)$ is the position vector of the center of resistance of, and $\mathbf{t}(t)$ is the unit vector parallel to the "mean" axis of, the slightly bendable rod. In order to formulate an expression of the field correlation function, we need an explicit form of $C(\tau) = \langle \sum \mathbf{q}(n,t)\Psi(n,s) \sum \mathbf{q}(n',t')\Psi(n',s')\rangle$. From eq 6 and 12, we have

$$C(\tau) = \sum_n \langle q_n^2 \rangle a_n(n)^2 \exp(-\tau/\tau_n) \times [Q(n,s)Q(n,s') + \sum_m{}' \sum_{m'}{}' \Phi(m,m')Q(m,s)Q(m',s')]$$

The factor $\Phi(m,m') = a_m(n)a_{m'}(n)/a_n(n)^2$ is small, i.e., those for $m = m' = n - 2$ with n = 2, 3, and 4 are smaller than 0.015 and those for other combination of m and m' are extremely small. Since $a_n(n)^2 \simeq 1$, we have

$$C(\tau) \simeq \sum_n{}'' \langle q_n^2 \rangle \exp(-\tau/\tau_n) Q(n,s)Q(n,s') \qquad (15)$$

which is again very close to that in the free-draining limit except that τ_n is given by eq 13. Then, the spectrum can be computed by use of eq 65 in ref 6, eq 49 in ref 5, or eq D7 in ref 4, if we adopt unperturbed eigenfunctions $Q(n,s)$ and average amplitudes $\langle q_n^2 \rangle$, and the first-order eigenvalues $\sigma_n = \lambda_n + G_{nn}$ for evaluation of τ_n. (Schmidt and Stockmayer have adopted the same procedure as above without proving eq 14 and 15.[8])

Results

The first-order eigenvalues are given by

$$\sigma_n = \lambda_n(1 + f_n) \quad \text{with} \quad f_n = G_{nn}/\lambda_n \qquad (16)$$

The effect of hydrodynamic interaction on the normal modes n = 0 and 1 cannot be discussed on the basis of eq 16, because λ_0 (for any value of κ) and λ_1 (for κ = 0) are zero. We consider first the translational diffusion coefficient D[11]

$$D_1 = D_1^\circ(1 + f_0) \qquad (17)$$

$$f_0 = \ln(L/b) - 1 + (1/6)\gamma L + b/L + O(\gamma b) \qquad (18)$$

where $D_1^\circ = k_BT/\zeta_1 L$ with $\zeta_1 = 4\pi\eta$ is the sideways translational diffusion coefficient in the free-draining limit. For the rotational diffusion coefficient Θ, we have to start from eq 1 with $\kappa \neq 0$. In the stiff limit $\gamma L \ll 1$, we have $\beta_1 L = (48\gamma L)^{1/4} \rightarrow 0$ but $\lambda_1 \rightarrow 36k_BT/L^3$. In this limit, we have $Q(1,s) = (12/L^3)^{1/2}s$ and $\tau_1^{-1} = \lambda_1/\zeta_1 = 36k_BT/\zeta_1 L^3 = 3\Theta^\circ$, where $\Theta^\circ = 12k_BT/\zeta_1 L^3$ is the rotational diffusion coefficient in the free-draining limit.[4] Then, we easily have

$$\Theta = \Theta^\circ(1 + f_1) \qquad (19)$$

$$f_1 = \ln(L/b) - 7/3 + 3(b/L) + O(\gamma b) \qquad (20)$$

When we consider the case of $L/b \gtrsim 100$ and $\gamma L \leq 0.5$, we may ignore terms proportional to γL and b/L in eq 18 and 20. Then, eq 17 and 19 in the present framework of the theory can be compared with corresponding ones of, for example, Broersma's formula[15]

$$D_1^B = (k_BT/4\pi\eta L)(1 + f_0^B) = D_1^\circ(1 + f_0^B) \qquad (21)$$

$$\Theta^B = (3k_BT/\pi\eta L^3)(1 + f_1^B) = \Theta^\circ(1 + f_1^B) \qquad (22)$$

where we have for a rod diameter d and $p = L/d$[16]

$$1 + f_0^B = \ln(2p) - 0.19 + 4.2[1/\ln(2p) - 0.39]^2$$

$$1 + f_1^B = \ln(2p) - 1.45 + 7.5[1/\ln(2p) - 0.27]^2$$

By equating eq 17 and 21 and eq 19 and 22, we have

$$f_0(b) = f_0^B \quad \text{and} \quad f_1(b) = f_1^B$$

These relationships can be used to determine an appropriate value of b which is not known a priori. For a long rod, it is evident that we have to take $b = d/2$. The cylinder model gives this relation naturally.[17] The quantity f_n ($n \geq 2$) can be computed easily. The results are shown in Figure 1 by closed symbols. The values of $1 + f_0^B$ and $1 + f_1^B$ for L/d = 100 are also shown in Figure 1 by open circles.

When we put $\kappa = 0$ for $\gamma L \leq 0.5$, we have $\beta_0 L = \beta_1 L = 0$ and $\beta_n L = (n - 1/2)\pi$ for $n \geq 2$ (ref 6, see also Appendix A) and $\epsilon = k_BT/2\gamma$ (ref 14b). Then, we have the following relationships for the relaxation time τ_n of the n-th normal mode ($n \geq 2$) of bending motion:

$$\begin{aligned}\tau_n^{-1} = \sigma_n/\zeta_1 &= (\lambda_n/\zeta_1)(1 + f_n) \\ &= (\pi^4/2\gamma L)(n - 1/2)^4(k_BT/\zeta_1 L^3)(1 + f_n) \\ &= (\pi^4/24\gamma L)(n - 1/2)^4(12D_1^\circ/L^2)(1 + f_n) \\ &= (\pi^4/24\gamma L)(n - 1/2)^4\Theta^\circ(1 + f_n) \qquad (23)\end{aligned}$$

In our previous papers, we assumed $D_1^\circ(1 + f_n) = D_1^B$ or $\Theta^\circ(1 + f_n) = \Theta^B$, i.e., $k_BT/(\zeta L)_n = D_1^B$ or $12k_BT/(\zeta L)_n L^2 = \Theta^B$, independently of n in eq 23 in order to obtain an appropriate value of ζ for normal modes ($n \geq 2$). From the results in Figure 1, this assumption seems not to be good.

To see the effect of the hydrodynamic interaction on the spectrum of scattered light, we simulated the spectra by use of our formulation given above. The simulated correlation functions were least-squares fitted to the second-order cumulant expansion formula, and the resultant $\bar{\Gamma}/K^2$ vs. K^2 relationships are shown in Figure 2. In this computation, the b value was determined from the relationship $\Theta^\circ(1 + f_1(b)) = \Theta$ where Θ is the observed value for fd virus (L = 0.895 μm, d = 9 nm, and L/d = 100),[16] and by using this b value, we computed f_n's for $n \geq 2$ (cf. Figure 1).

Discussion

We have shown that the matrix **M** for the eigenvalue problem of the HBH model is almost diagonal over the whole range of the flexibility parameter γL (see Appendix B). Thus, the first-order perturbation results are accurate enough to evaluate various quantities. Using this result, we have examined the effect of hydrodynamic interaction on the relaxation times of flexing motions of a slightly bendable rod (Figure 1; see also Appendix B). Since our treatment of the hydrodynamic interaction started with

Table II
11 × 11 Portion of the Matrix M for $\gamma L = 1.0$ and $L/b = 200$[a]

0	0	0.0140	0	−1.635	0	6.776	0	−16.96	0	33.40
0	0.3286	0	1.631	0	−7.466	0	19.42	0	−38.33	0
0	0	2.987	0	4.685	0	−15.86	0	35.45	0	−63.83
0	0.0293	0	14.94	0	9.403	0	−26.13	0	52.64	0
0	0	0.2482	0	48.65	0	15.91	0	−38.35	0	71.48
0	−0.0146	0	1.024	0	120.3	0	24.43	0	−52.74	0
0	0	−0.1456	0	2.757	0	249.3	0	35.03	0	−69.25
0	0.0090	0	−0.6717	0	5.768	0	457.1	0	47.69	0
0	0	0.0956	0	−1.952	0	10.29	0	767.5	0	62.33
0	−0.0061	0	0.4672	0	−4.299	0	16.47	0	1206	0
0	0	−0.0673	0	1.422	0	−7.952	0	24.37	0	1798

[a] $10^{-3}M_{km}$ in units of ϵ/L^4.

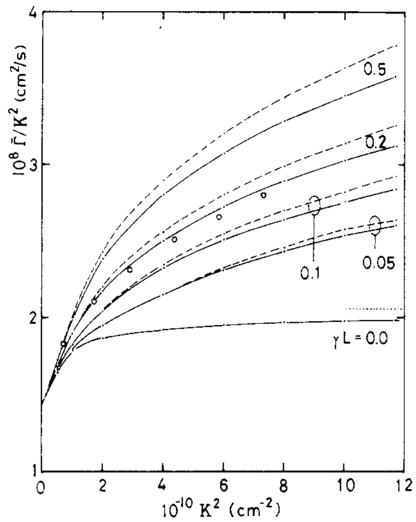

Figure 2. $\bar{\Gamma}/K^2$ vs. K^2 relationships for fd virus: (O) Experimental results for a solution of 0.088 mg/mL fd virus (part of our unpublished results). Simulation was made by use of eq 65 in ref 6 for internal normal modes up to 8. Diffusion coefficients at 5 °C were assumed to be $D = 1.41$, $D_1 = 1.19$, and $D_3 = 1.87$ in units of 10^{-8} cm²/s and $\Theta = 13.1$ s⁻¹. $L = 0.895$ μm, $d = 9.0$ nm, and temperature = 5 °C. (—) With the hydrodynamic interaction, where f_n's ($n \geq 2$) were computed for the b value determined from $\Theta°[1 + f_1(b)] = \Theta$. (- - -) Without the hydrodynamic interaction, where the ζL value has determined from $k_BT/\zeta L = L^2\Theta/12$ for any $n \geq 2$. (···) Asymptote for a rigid rod, $D_1 + L^2\Theta/12$.

the spherically averaged tensor $H(s,s')$ in eq 2, a trick had to be introduced, i.e., the friction factor tensor ζ in eq 11 and hence the friction factor ζ_1 for the lateral motion in eq 13. If we have a more appropriate form of $H(s,s')$, we will be able to avoid this kind of trick. In such a situation, too, the present method will be equally applicable.

We have shown that, in the framework of the HBH model, the field correlation function of light scattered from dilute solutions of long filaments can be computed by our formulation[4-6] with $Q(n,s)$ and $\langle q_n^2\rangle$ in the free-draining limit and τ_n of the first-order perturbation result. These features will remain unchanged for any other form of the interaction tensor $H(s,s')$.

Our simulation of the field correlation functions for dimensions appropriate to fd virus clearly showed that even for $\gamma L = 0.05$, the $\bar{\Gamma}/K^2$ vs. K^2 relationship deviates from that for a rigid rod at $K^2 \gtrsim 2 \times 10^{10}$ cm⁻² (Figure 2). Since our previous method determined the friction factor $(\zeta L)_n$ for $n \geq 2$ from $k_BT/(\zeta L)_n = L^2\Theta/12$, the effect of hydrodynamic interaction is not very large for $\gamma L \leq 0.1$. However, the effect is definitely observed, and if one wants to estimate the value of the flexibility parameter in two digits, one has to take account of the hydrodynamic interaction explicitly even in a crude model as has been discussed. For cases where γL values are larger than unity and higher normal modes are involved (i.e., for very long and flexible filaments), the effect of the hydrodynamic interaction will be very large. In such cases, the present method will provide an approximate but practical procedure for analyzing experimental spectra.

In our previous papers,[4-6] we have shown a relationship

$$\bar{\Gamma}/K^2 = D_1 + L^2\Theta/12 + D_1{\sum_n}''1 \qquad (KL \gg 1)$$

where $\sum_n''1$ stands for the number of internal normal modes involved in the scattering process. This relationship should read

$$\bar{\Gamma}/K^2 = D_1 + L^2\Theta/12 + D_1°{\sum_n}''(1 + f_n) \qquad (KL \gg 1) \tag{24}$$

A detailed account of our experimental result and an application of the present method to solutions of fd virus will be given in the near future.

Appendix A

Evaluation of $G(k,m,q)$ in Eq 8. From the previous results,[4] we have

$$Q(n,s) = S_n \sin[B_n(p + q)] + S_n' \sinh[A_n(p + q)]$$
$$Q(n,s') = S_n \sin[B_n(p - q)] + S_n' \sinh[A_n(p - q)]$$

for odd n, and

$$Q(0,s) = Q(0,s') = (1/L)^{1/2}$$
$$Q(n,s) = C_n \cos[B_n(p + q)] + C_n' \cosh[A_n(p + q)]$$
$$Q(n,s') = C_n \cos[B_n(p - q)] + C_n' \cosh[A_n(p - q)]$$

for even n, where

$$S_n = (c_n/L)^{1/2}/\sin(B_n/2)$$
$$S_n' = (c_n/L)^{1/2}(B_n/A_n)^2/\sinh(A_n/2)$$
$$C_n = (c_n/L)^{1/2}/\cos(B_n/2)$$
$$C_n' = (c_n/L)^{1/2}(B_n/A_n)^2/\cosh(A_n/2)$$
$$B_n = \beta_n L \quad \text{and} \quad A_n = \alpha_n L$$

The quantity c_n is the normalization constant, and β_n and α_n are the n-th root of (note $y \equiv (\beta/\alpha)^3$ and $\alpha^2 - \beta^2 = \kappa/\epsilon$)

$$1 - \cos(\beta L)\cosh(\alpha L) + (1/2)(y - 1/y)\sin(\beta L)\sinh(\alpha L) = 0$$

In the stiff limit, $\kappa/\epsilon \to 0$ or $\gamma L \to 0$, we have

$$\beta_1 L = (48\gamma L)^{1/4}$$
$$Q(1,s) = (12/L^3)^{1/2}s$$

By the aid of mathematical formulas in a standard textbook, we easily have expressions for $G(k,m,q)$ in eq 8

$$G(k,m,q) = S_kS_m[-G_1(B_k,B_m,x_k,x_m,u_k,u_m) + G_1(B_k,-B_m,x_k,-x_m,u_k,-u_m)] + S_kS_m'[\cos(x_k)\cosh(y_m)G_2(-B_k,A_m,u_k,v_m) - \sin(x_k)\sinh(y_m)G_2(A_m,B_k,u_k,v_m)] + S_k'S_m[\cos(x_m)\cosh(y_k)G_2(-B_m,A_k,u_m,v_k) - \sin(x_m)\sinh(y_k)G_2(A_k,B_m,u_m,v_k)] + S_k'S_m'[G_3(A_k,A_m,y_k,y_m,v_k,v_m) - G_3(A_k,-A_m,y_k,-y_m,v_k,-v_m)] \quad (A1)$$

for odd k and odd m, and

$$G(k,m,q) = C_kC_m[G_1(B_k,B_m,x_k,x_m,u_k,u_m) + G_1(B_k,-B_m,x_k,-x_m,u_k,-u_m)] + C_kC_m'[\cos(x_k)\cosh(y_m)G_2(A_m,B_k,u_k,v_m) + \sin(x_k)\sinh(y_m)G_2(-B_k,A_m,u_k,v_m)] + C_k'C_m[\cos(x_m)\cosh(y_k)G_2(A_k,B_m,u_m,v_k) + \sin(x_m)\sinh(y_k)G_2(-B_m,A_k,u_m,v_k)] + C_k'C_m'[G_3(A_k,A_m,y_k,y_m,v_k,v_m) + G_3(A_k,-A_m,y_k,-y_m,v_k,-v_m)] \quad (A2)$$

for even k and even m (k, $m \geq 2$), where x_k, y_k, u_k, and v_k are defined as

$$x_k = B_kq, \quad y_k = A_kq$$

$$u_k = B_k(1/2 - q), \quad v_k = A_k(1/2 - q)$$

and functions G_1, G_2, and G_3 are defined as

$$G_1(B,B',x,x',u,u') = \sin(u + u')\cos(x - x')/(B + B')$$

$$G_2(A,B,u,v) = 2[A\cos(u)\sinh(v) + B\sin(u)\cosh(v)]/(A^2 + B^2)$$

$$G_3(A,A',y,y',v,v') = \sinh(v + v')\cosh(y - y')/(A + A')$$

Note that $G_i(a,y,z) = ay^2 + z$, for example, means $G_i(y,b,c) = yb^2 + c$, $G_i(b,c,d) = bc^2 + d$, etc. For $k = m$ (≥ 1), care should be taken for G_1 and G_3; $G_1(B,-B,x,-x,u,-u) = (u/B)\cos(2x)$ and $G_3(A,-A,y,-y,v,-v) = (v/A)\cosh(2y)$. It is obvious that $G(k,m,q) = 0$ for mixed k and m (≥ 1), $G(k,0,q)$ for any k including $k = 0$ is not required because of $\lambda_0 = 0$, $G(0,m,q) = 0$ for odd m, and

$$G(0,m,q) = 2(L)^{-1/2}[(C_m/B_m)\cos(x_m)\sin(u_m) + (C_m'/A_m)\cosh(y_m)\sinh(v_m)] \quad (A3)$$

for even m.

For a slightly bendable rod, i.e., for $\gamma L \leq 0.5$, we can put $\kappa = 0$ into eq 1. In this case, we have $\alpha_n = \beta_n$ or $A_n = B_n$ and $c_n = 1$,[6] and hence $x_k = y_k$ and $u_k = v_k$. Then, we have a little simpler expressions for $G(k,m,q)$. Note that we have in this case

$$\lambda_1 = 0$$

$$Q(1,s) = (12/L^3)^{1/2}s$$

Thus, $G(k,1,q)$ is not required because of $\lambda_1 = 0$, $G(1,m,q) = 0$ for even m and

$$G(1,m,q) = (12/L)^{1/2}(2/B_m^2) \times [S_m\{\cos(x_m)[\sin(u_m) - u_m\cos(u_m)] - x_m\sin(x_m)\sin(u_m)\} + S_m'\{\cosh(x_m)[-\sinh(u_m) - u_m\cosh(u_m)] - x_m\sinh(x_m)\sinh(u_m)\}] \quad (A4)$$

for odd m.

To obtain the correct sign of the matrix elements, the factor $(-1)^{(k+m)/2}$ for even k and m or the factor $-(-1)^{(k+m)/2}$ for odd k and m has to be multiplied.

Appendix B

Matrix M of the HH Model. Since we are interested in the case of a slightly bendable rod which undergoes anisotropic translational diffusion ($D_3 \neq D_1$),[5,6] we considered in the text the case of $\kappa = 0$ for $\gamma L \leq 0.5$. Even if we adopt the original HH model, the situation is not very different from that discussed in the text. Only appreciable difference appears, of course, for nonzero matrix elements M_{k1} for odd k because of $\lambda_1 \neq 0$. For our discussion to be complete, we computed the matrix **M** for various values of the flexibility parameter γL of the original HH model. Table II shows an example of the matrix elements ($\gamma L = 1.0$). We can easily observe that eq 14 and 15 still hold with a high accuracy in this case too. Since the flexible limit ($\gamma L \gg 1$) of the HH model tends toward the Zimm model,[10] and since Zimm et al. have shown that the matrix **M** is almost diagonal,[13] the statements in the text hold over the whole range of the γL values. Apart from some inconsistency in the HH model, therefore, the HBH model can be applied to evaluation of the light scattering spectrum as discussed in the text.

The f_n values for $L/b = 200$ were computed for $\gamma L = 1 \times 10^{-6}$ to 1.0 and found to be the same for each n within 1% over this range of γL values, for example, $f_1 = 2.98$, 2.98, 2.99, and 3.00 for $\gamma L = 1 \times 10^{-6}$, 0.1, 0.5, and 1.0, respectively.

References and Notes

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(14) (a) The friction factor tensor ζ in eq 11 has the diagonal elements ζ_1, $\zeta_2 = \zeta_1$, and ζ_3, where $\zeta_1 = 4\pi\eta$ and $\zeta_3 = 2\pi\eta$ for the overall friction factor $\zeta = 3\pi\eta$ (note that $D = (2D_1 + D_3)/3$ or $\zeta^{-1} = [2\zeta_1^{-1} + \zeta_3^{-1}]/3$). (b) The vector $\mathbf{q}(n,t)$ has three mutually perpendicular components $[q_1(n,t), q_2(n,t), q_3(n,t)]$. In the original HH model,[1] therefore, the elastic constant is given by $\epsilon = 3k_BT/4\gamma$. If we assume $\kappa = 0$ for $\gamma L \leq 0.5$, the component $q_3(n,t)$, which is parallel to the long axis of the rod, should be zero. In such a situation, we have to put $\epsilon = 2k_BT/4\gamma = k_BT/2\gamma$.[6]
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