

5.24) farther apart along  $b$ . It had been suggested from far infrared studies<sup>9</sup> that the  $C \cdots Cl$  contact between the

(9) A. V. R. Warrier and S. Krimm, *Macromolecules*, **3**, 709 (1970).

above two chains might involve a  $C-H \cdots Cl$  hydrogen-bond-type of interaction. Our results indicate that this is not the case, since this distance is a 4.71 Å, compared to a van der Waals contact distance of 4.1 Å.

## Spectrum of Light Quasielastically Scattered from Linear Macromolecules

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**ABSTRACT:** Based on a simple model of molecular motion, the form factors in the quasielastic scattering of laser light were calculated for flexible and stiff linear macromolecules. This result will play a role of a guiding principle in the analysis of spectra composed of various modes of molecular motion.

Since the pioneering work of Pecora,<sup>2a</sup> quasielastic scattering of laser light has become a powerful tool for the dynamic study of macromolecules.<sup>2b</sup> Under a condition that  $dK < 1$  (where  $d$  is the representative linear dimension of a scatterer such as the root-mean-square end-to-end distance of a chain, the length of a rod, and  $K$  is the absolute value of the scattering vector), the main contribution to the line broadening of light scattered from solutions of macromolecules comes from the center-of-mass motion. Therefore, measurements of spectral densities at  $dK < 1$  give a translational diffusion coefficient.<sup>3</sup> This is one of the most important merits of the technique. On the other hand, if spectral densities can be measured under a condition of large  $dK$ , it will be found that the internal modes of molecular motion (rotational,<sup>4</sup> stretching,<sup>5</sup> bending<sup>6</sup> etc.) contribute to the line broadening of scattered light. Thus there is a possibility that we can obtain the rotational diffusion coefficient of, and elastic constants of stretching and bending of, a macromolecule in solution as well as its translational diffusion coefficient. In decomposition of a spectrum into components due to various modes of motion, numerical values of scattering form factors at various values of  $dK$  must be known.<sup>7–10</sup> Based on a simple model of molecular motion,<sup>11</sup> we present in this paper the scattering form factors of chain molecules.

### The Model

A brief summary of our treatment<sup>6</sup> is at first presented.

Let a chain molecule be represented by a space curve,  $\mathbf{r}(x, t)$ , where  $x$  is the contour length along the chain ( $0 \leq x \leq L$ ) and  $t$  is the time. The Langevin equation for the Brownian motion of the molecule may be written as<sup>11,12</sup>

$$\rho \partial^2 \mathbf{r} / \partial t^2 + \zeta \partial \mathbf{r} / \partial t + \epsilon \partial^4 \mathbf{r} / \partial x^4 - \kappa \partial^2 \mathbf{r} / \partial x^2 = \mathbf{A}(x, t) \quad (1)$$

where  $\rho$  is the linear density,  $\zeta$  is the friction constant per unit length,  $\epsilon$  and  $\kappa$  are, respectively, elastic constants of bending and stretching of a chain and  $\mathbf{A}(x, t)$  is the fluctuating force acting on the molecule. The elastic constants have been given in terms of  $\gamma$  (the inverse of the statistical length) as<sup>11</sup>

$$\epsilon = 3kT/4\gamma \quad \text{and} \quad \kappa = 3kT\gamma\mu(\gamma L) \quad (2)$$

where

$$\begin{aligned} \mu(\gamma L) &= [1 - (1 - e^{-2\gamma L})/2\gamma L]^{-1} \\ &= 1 \quad (\text{for } \gamma L \gg 1) \quad \text{and} \quad 1/\gamma L \quad (\text{for } \gamma L \ll 1) \end{aligned} \quad (3)$$

The end-to-end distance of the chain is given in terms of  $\gamma$  as<sup>11–13</sup>

$$\langle R^2 \rangle = [\exp(-2\gamma L) - 1 + 2\gamma L]/2\gamma^2 \quad (4)$$

When  $\mathbf{r}(x, t)$  and  $\mathbf{A}(x, t)$  are, respectively, expanded by an orthonormal set  $\{Q(n, x)\}$  as

$$\begin{Bmatrix} \mathbf{r}(x, t) \\ \mathbf{A}(x, t) \end{Bmatrix} = \sum_n \begin{Bmatrix} \mathbf{q}(n, t) \\ \mathbf{B}(n, t) \end{Bmatrix} Q(n, x) \quad (5)$$

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(2) (a) R. Pecora, *J. Chem. Phys.*, **40**, 1604 (1964). (b) S. Fujime, *Advan. Biophys.*, **3**, 1 (1972).

(3) S. B. Dubin, J. H. Lunacek, and G. B. Benedek, *Proc. Nat. Acad. Sci. U. S. A.*, **57**, 1164 (1967).

(4) (a) H. Z. Cummins, F. D. Carlson, J. T. Herbert, and G. Woods, *Bio-phys. J.*, **9**, 518 (1969). (b) A. Wada, N. Suda, T. Tsuda, and K. Soda, *J. Chem. Phys.*, **51**, 31 (1969). (c) S. Fujime, *J. Phys. Soc. Jap.*, **29**, 416 (1970).

(5) (a) R. Pecora, *J. Chem. Phys.*, **43**, 1562 (1965). (b) P.-G. de Gennes, *Physics*, **3**, 37 (1967). (c) E. Dubois-Violette and P.-G. de Gennes, *Physics*, **3**, 181 (1967). (d) N. Saito and S. Ito, *J. Phys. Soc. Jap.*, **25**, 1446 (1968). (e) T. F. Reed and J. E. Frederick, *Macromolecules*, **4**, 72 (1971).

(6) S. Fujime, *J. Phys. Soc. Jap.*, **29**, 751 (1970).

(7) R. Pecora, *J. Chem. Phys.*, **48**, 4126 (1968).

(8) S. Fujime, *J. Phys. Soc. Jap.*, **31**, 1805 (1971).

(9) R. Pecora, *J. Chem. Phys.*, **49**, 1032 (1968).

(10) S. Fujime, M. Maruyama, and S. Asakura, *J. Mol. Biol.*, **68**, 347 (1972).

(11) (a) As to a dynamical model of a linear macromolecule, we adopted the model of R. A. Harris and J. E. Hearst (*J. Chem. Phys.*, **44**, 2595 (1966)), where some of equations in the next section have been given. To avoid unnecessarily complexity in seeing general features of spectra, hydrodynamic interactions were neglected. (b) The following must be mentioned. There is equivalence between the spring force constant of the Rouse model and the Lagrange multiplier of the Harris-Hearst (HH) model if the Lagrange multiplier is evaluated from equilibrium properties of the coil at zero shear. However, the contour length of the original HH model increases infinitely with increasing shear rate. This is a nonphysical property of the model. Nevertheless, we applied the HH model to the light-scattering problem, because light-scattering experiments are usually carried out at zero shear and because this model gives a functional relationship between the spring force constant and the persistence length.

(12) N. Saito, K. Takahashi, and Y. Yunoki, *J. Phys. Soc. Jap.*, **22**, 219 (1967).

(13) L. D. Landau and E. M. Lifshitz, "Statistical Physics," Pergamon Press, London, 1958, p 478.

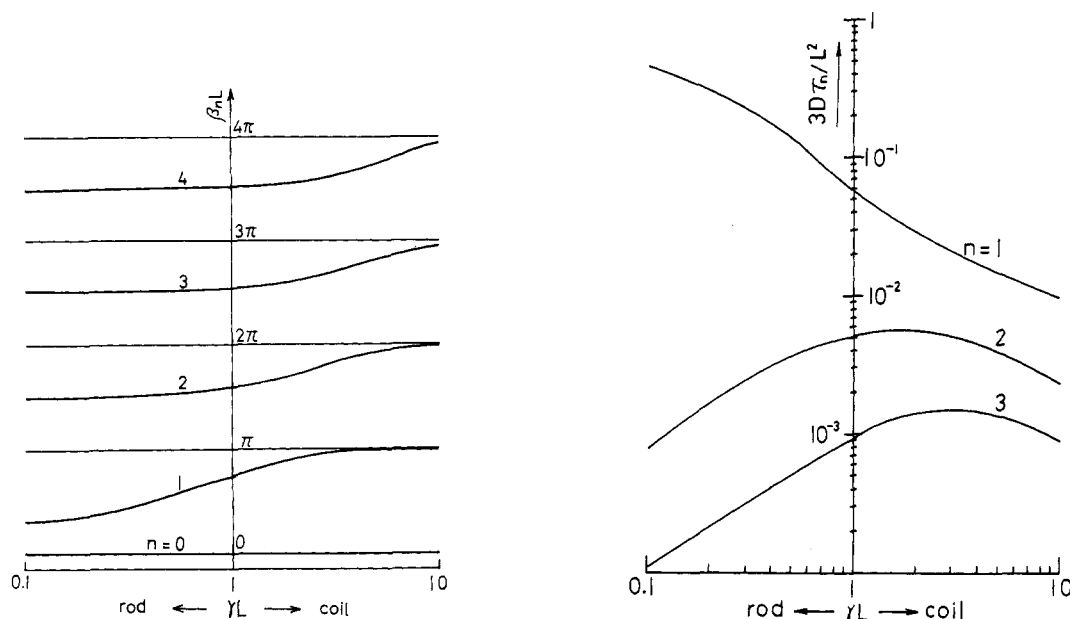


Figure 1. (a, left)  $\beta_n L$  vs.  $\gamma L$ . At  $\gamma L \ll 1$ ,  $\beta_1 L = 0$ . (b, right)  $3D\tau_n/L^2$  vs.  $\gamma L$ .

the following relations hold

$$\epsilon Q^{IV}(n, x) - \kappa Q^{II}(n, x) - \lambda_n Q(n, x) = 0 \quad (6)$$

$$\rho \ddot{q}(n, t) + \zeta \dot{q}(n, t) + \lambda_n q(n, t) = B(n, t) \quad (7)$$

where the Roman numerals mean the  $x$  derivatives and dots the time derivatives. Equation 6 must be solved with the free-end boundary condition

$$Q^{II}(n, x) = \epsilon Q^{III}(n, x) - \kappa Q^I(n, x) = 0 \text{ at } x = 0 \text{ and } L \quad (8)$$

We multiply eq 7 through by  $q(n, 0)$  and take the time average

$$\rho \langle q(n, 0) \ddot{q}(n, t) \rangle + \zeta \langle q(n, 0) \dot{q}(n, t) \rangle + \lambda_n \langle q(n, 0) q(n, t) \rangle = 0 \quad (9)$$

because  $q$  and  $B$  are uncorrelated.<sup>14</sup> Here the angular brackets mean

$$\langle y(0)z(t) \rangle = \langle y(s)z(s+t) \rangle = \lim_{s \rightarrow \infty} \frac{1}{2S} \int_{-S}^S y(s)z(s+t) ds \quad (10)$$

where  $y(t)$  and  $z(t)$  are arbitrary stochastic variables as a function of time  $t$ . Since  $(\zeta/\rho) \gg (\lambda_n/\zeta)$  for a long polymer,<sup>6</sup> we find

$$\langle q(n, 0) q(n, t) \rangle = \langle q(n, 0) q(n, 0) \rangle \exp(-t/\tau_n) \quad (11)$$

$$\tau_n = \zeta/\lambda_n \quad (\lambda_n \neq 0) \quad (12)$$

The mode belonging to  $\lambda_n = 0$  is related to the translational Brownian motion and, for a rod, to the rotational Brownian motion as well (see later). The elastic (potential) energy of the polymer in our model is derived from eq 5, 6, and 8 as

$$\begin{aligned} \langle V \rangle &= \left\langle \frac{1}{2} \int_0^L \{ \epsilon (\partial^2 \mathbf{r} / \partial x^2)^2 + \kappa (\partial \mathbf{r} / \partial x)^2 \} dx \right\rangle \\ &= \frac{1}{2} \sum_n \lambda_n \langle q(n, 0) q(n, 0) \rangle \end{aligned} \quad (13)$$

(14) C. Kittel, "Elementary Statistical Physics," Wiley, New York, N. Y., 1958, p 153.

By equipartition of energy we find from eq 13

$$\langle q(n, 0) q(n, 0) \rangle = \langle q_n^2 \rangle = 3kT/\lambda_n \quad (\lambda_n \neq 0) \quad (14)$$

The spectral density of scattered light is given by<sup>2a, 4, 6</sup>

$$S(K, \omega) = \int_{-\infty}^{\infty} e^{i\omega t} dt \int_0^L J(x, x', t) dx dx' \quad (15)$$

$$J(x, x', t) = e^{-DK^2 t} \exp[-(K^2/6) \langle (\mathbf{r}(x, t) - \mathbf{r}(x', 0))^2 \rangle] \quad (16)^{15}$$

$$K = (4\pi/\lambda) \sin(\phi/2) \quad (17)$$

where  $D$  is the translational diffusion coefficient,  $\lambda$  is the wavelength of the incident light in a medium, and  $\phi$  is the scattering angle.

### Eigenvalue Problem

We define

$$\begin{Bmatrix} \alpha \\ i\beta \end{Bmatrix} = [\kappa/2\epsilon \pm \{(\kappa/2\epsilon)^2 + \lambda_n/\epsilon\}^{1/2}]^{1/2} \quad (18)$$

where  $\pm\alpha$  and  $\pm i\beta$  are the roots of the characteristic equation to eq 6. Using eq 2 and 3, we find a relation

$$\alpha^2 - \beta^2 = (2\gamma)^2 \mu(\gamma L) \quad (19)$$

Then the eigenfunction may be written as

$$Q(n, x) = c_1 \cos(\beta x) + c_2 \sin(\beta x) + c_3 \cosh(\alpha x) + c_4 \sinh(\alpha x) \quad (20)$$

where  $c_i$ 's are constants. Insertion of eq 20 into eq 8 gives

(15) For simplicity, complete separation was assumed between the translational diffusive mode and the internal ones. Let  $\mathbf{z}$  be  $\mathbf{r}(x, t) - \mathbf{r}(x', 0)$ , the correlation function  $J(x, x', t)$  contains a factor,  $\langle \exp(i\mathbf{K}\mathbf{z}) \rangle_{\Omega}^{1/2}$ . If we assume that the polymer does not appreciably change its orientation within the time interval of interest (see Discussion), the average over orientation  $\Omega$  results in  $\langle \sin(K|\mathbf{z}|)/K|\mathbf{z}| \rangle_{\Omega}$ . By expanding  $\sin(K|\mathbf{z}|)/K|\mathbf{z}|$  into a Taylor series and taking a Gaussian average with respect to  $|\mathbf{z}|$ , we finally obtain

$$J(x, x', t) = \exp(-DK^2 t) \exp(-K^2 \langle \mathbf{z}^2 \rangle / 6)$$

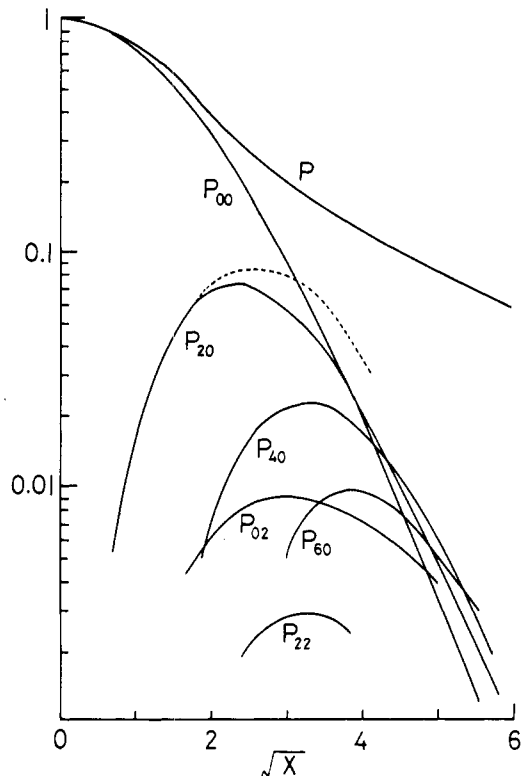


Figure 2.  $P_{NM}(X)$  vs.  $X^{1/2}$  at  $\gamma L \gg 1$ .  $X = K^2 L^2 / 6 \gamma L = K^2 \langle R^2 \rangle / 6$ , - - -;  $P_{20} + P_{40}$ .

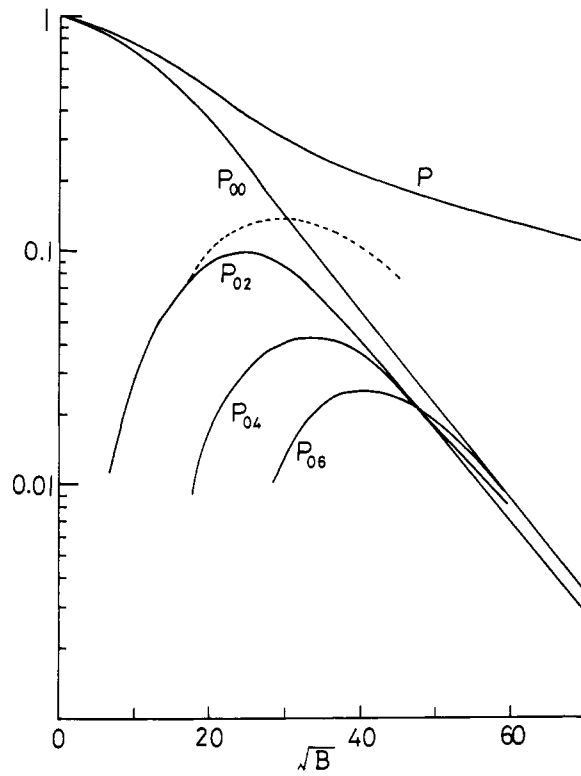


Figure 3.  $P_{0M}(B)$  vs.  $B^{1/2}$  at  $\gamma L \ll 1$ .  $B = K^2 L^2 (\gamma L)$ , - - -;  $P_{02} + P_{04} + P_{06}$ .

the following transcendental equation

$$1 - \cos(\beta L) \cosh(\alpha L) + (1/2)(y - 1/y) \sin(\beta L) \sinh(\alpha L) = 0 \quad (21)$$

where  $y \equiv (\beta/\alpha)^3$ . The  $n$ th root of eq 21,  $\beta_n$ , gives the eigenvalue

$$\lambda_n = \varepsilon \beta_n^4 + \kappa \beta_n^2 \quad (22)$$

Figure 1a shows  $\beta_n L$  as a function of  $\gamma L$ . It must be noted that the doubly degenerated eigenvalue  $\lambda_0 = 0$  for  $\gamma L \ll 1$  (rod) splits into two different values: one is  $\lambda_0 = 0$  and the other  $\lambda_1 \neq 0$ . From eq 2, 3, 12, and 22 the relaxation time,  $\tau_n$ , of the internal mode of motion is given by

$$D \tau_n / L^2 = (4\gamma L / 3) / [(\beta_n L)^4 + (2\gamma L)^2 (\beta_n L)^2 \mu(\gamma L)] \quad (23)$$

where  $D = kT/\zeta L$  is assumed because  $\zeta$  is defined as the friction constant per unit length (Figure 1b). Eigenfunctions will be

$$Q(0, x) = (1/L)^{1/2} \quad (24)$$

$$Q(n, x) = (c_n/L)^{1/2} \left\{ [\cos(\beta_n x) + (\beta_n/\alpha_n)^2 \cosh(\alpha_n x)] - \frac{\cos(\beta_n L) - \cosh(\alpha_n L)}{\sin(\beta_n L) - (\alpha_n/\beta_n)^3 \sinh(\alpha_n L)} [\sin(\beta_n x) + (\alpha_n/\beta_n) \sinh(\alpha_n x)] \right\} \equiv (c_n/L)^{1/2} h(n, x) \quad (25)$$

where  $c_n$  is the normalization constant. The eigenfunction  $Q(0, x)$  belonging to the eigenvalue  $\lambda_0 = 0$  is not in the present interest, because this mode is related to the diffusive motion of the center of mass of the molecule and has been considered in eq 16 as  $\exp(-DK^2 t)$ .

The following two limiting cases are of interest.

i.  $\gamma L \gg 1$  (Coil). In this limit eq 22, 23, and 25 become

$$\lambda_n = \kappa (n\pi/L)^2 \quad (n: 1, 2, 3, \dots) \quad (26)$$

$$\tau_n = \langle R^2 \rangle / 3D\pi^2 n^2 \quad (27)$$

$$Q(n, x) = (2/L)^{1/2} \cos(n\pi x/L) \equiv (2/L)^{1/2} f(n, x) \quad (28)$$

ii.  $\gamma L \ll 1$  (Rod). In this limit we have

$$\lambda_1 = 0 \quad (29)$$

$$\lambda_n = \varepsilon [(n - 1/2)\pi/L]^4 \quad (n: 2, 3, 4, \dots) \quad (30)$$

$$\tau_n = 4L^2(\gamma L) / 3D\pi^4 (n - 1/2)^4 \quad (31)$$

$$Q(1, x) = (12/L^3)^{1/2} (L/2 - x) \quad (32)$$

$$Q(n, x) = (\text{eq 25 with } c_n = 1, \alpha_n = \beta_n) \equiv (1/L)^{1/2} g(n, x) \quad (33)$$

The eigenfunction  $Q(1, x)$  belonging to  $\lambda_1 = 0$  is also not in the present interest, because it should be related to the rotational Brownian motion of a rod. This mode was ignored so that only the initial random distribution of orientation was taken into account in eq 16.

### Scattering Form Factors

Equation 16 may be expanded in a Taylor series

$$J(x, x', t) = e^{-DK^2 t} \exp[-(K^2/6) \sum_n' \langle q_n^2 \rangle (Q(n, x)^2 + Q(n, x')^2) \sum_N (1/N!) [2(K^2/6) \times \sum_n' \langle q_n^2 \rangle Q(n, x) Q(n, x') \exp(-t/\tau_n)]^N] \quad (34)$$

where the prime in the summation sign means the sum over all  $n$ 's except for  $n = 0$  (for  $\gamma L \gg 1$ ) or for  $n = 0$  and 1 (for  $\gamma L \ll 1$ ).

i.  $\gamma L \gg 1$ . When only  $n = 1$  and 2 are retained in  $[\dots]^N$  in eq 34, we obtain

$$J(K, t) = \int_0^L \int_0^L J(x, x', t) dx dx' \\ = L^2 \sum_{N, M: \text{even}} P_{NM}(X) \exp[-(DK^2 + N/\tau_1 + M/\tau_2)t] \quad (35)^{16}$$

$$P_{NM}(X) = \frac{1}{N!M!} (4X/\pi^2)^N (X/\pi^2)^M \times$$

$$\left[ \int_0^1 f(1, x)^N f(2, x)^M \exp\{-(2X/\pi^2) \sum_n f(n, x)^2/n^2\} dx \right]^2 \quad (36)$$

$$X = K^2 L^2 / 6\gamma L \quad (= K^2 \langle R^2 \rangle / 6) \quad (37)$$

where eq 2, 3, 4, 26, and 28 were used and the integration range was transformed to  $[0, 1]$ . The total scattering factor,  $P(X)$ , has been given by Debye as<sup>17</sup>

$$P(X) = 2[\exp(-X) - 1 + X]/X^2 \quad (38)$$

A machine computation of  $P_{NM}$ 's was carried out, taking  $n$  in eq 36 up to 10 (Figure 2). Numerical values of  $P_{00}$  and  $P_{20}$  below  $X^{1/2} = 2.6$  completely coincide with Pecora's results.<sup>9</sup> The present calculation suggests that the terms involving only  $\tau_1$  are important.

ii.  $\gamma L \ll 1$ . Since  $\lambda_n$  is proportional to  $(n - 1/2)^4$ , only the lowest mode ( $n = 2$ ) is important.<sup>8</sup> Therefore, the terms involving only  $\tau_2$  in eq 34 were retained

$$J(K, t) = L^2 \sum_{M: \text{even}} P_{0M}(B) \exp[-(DK^2 + M/\tau_2)t] \quad (39)$$

$$P_{0M} = (1/M!)(2BS(2))^M \times$$

$$\left[ \int_0^1 g(2, x)^M \exp\{-B \sum_n S(n) g(n, x)^2\} dx \right]^2 \quad (40)$$

$$B = K^2 L^2 (\gamma L) \text{ and } S(n) = 2/3\pi^4 (n - 1/2)^4 \quad (n \geq 2) \quad (41)^{18}$$

Equation 40 was calculated, taking  $n$  up to 5. The total scattering form factor,  $P(B)$ , was calculated by use of

$$P(B) = \int_0^1 \int_0^1 \exp \times \\ [-B \sum_n S(n) \{g(n, x) - g(n, x')\}^2] dx dx' \quad (42)$$

Figure 3 shows the calculated values of  $P(B)$  and  $P_{0M}(B)$ 's.

iii. **Intermediate Range of  $\gamma L$ .** From Figure 1, we can see that the rotational motion (the lowest order bending motion) of a rod tends to the lowest order internal mode (the next lowest order mode) of a Gaussian chain as  $\gamma L$

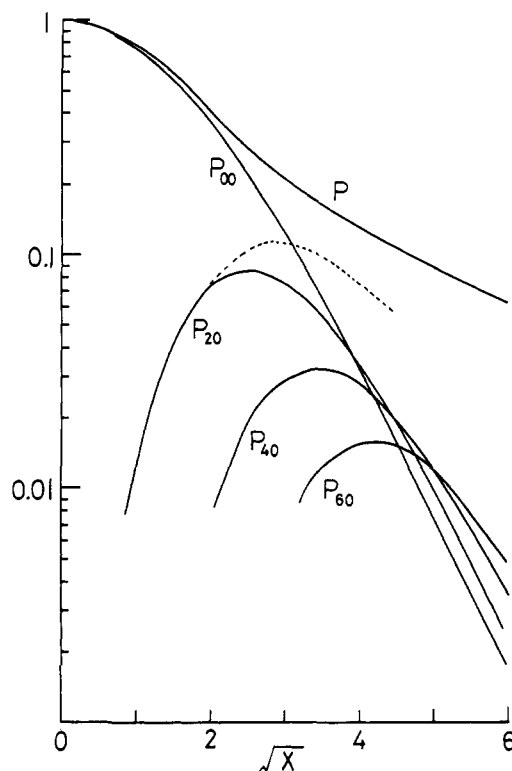


Figure 4.  $P_{N0}(X)$  vs.  $X^{1/2}$  at  $\gamma L = 10$ . - - - :  $P_{20} + P_{40}$ .

increases. Since we do not take into account the rotational Brownian motion of a rod, we encounter a difficult problem how to treat  $\lambda_1$  and  $Q(1, x)$  for  $\gamma L < 1$  (see Discussion).

In calculating form factors, we have two possibilities in choosing the parameter,  $B$  or  $X$

$$(K^2/6)\langle q_n^2 \rangle = BY(n)L \text{ or } XZ(n)L \quad (43)$$

$$\left\{ \frac{Y(n)}{Z(n)} \right\} = \left\{ \frac{2/3}{(2\gamma L)^2} \right\} / [(\beta_n L)^4 + (2\gamma L)^2 (\beta_n L)^2 \mu(\gamma L)] \quad (44)$$

Since the normalization constant,  $c_n$ , in eq 25 depends on  $\gamma L$ , the form factors will be written as (cf. eq 36)

$$P_{NM}(B) = \frac{1}{N!M!} (2Y(1)c_1 B)^N (2Y(2)c_2 B)^M \times \\ \left[ \int_0^1 h(1, x)^N h(2, x)^M \exp\{-B \sum_n c_n Y(n) h(n, x)^2\} dx \right]^2 \quad (45)$$

For  $P_{NM}(X)$ ,  $Y(n)B$  in eq 45 should be replaced by  $Z(n)X$ , that is,  $B/X = 6(\gamma L)^2$ . The total scattering factor can be calculated by use of eq 42, provided that  $g(n, x)$  and  $S(n)B$  are replaced, respectively, by  $h(n, x)$  and by  $c_n Y(n)B$  or  $c_n Z(n)X$ . A machine computation was carried out for  $\gamma L = 10$  and 0.1 (Figures 4 and 5). It must be noted that the relative difference

$$|Q(1, x)_{\gamma L=0.1} - Q(1, x)_{\gamma L \ll 1}| / |Q(1, x)|$$

amounts to 0.04% at most, where  $Q(1, x)_{\gamma L=0.1}$  is given by eq 25 with  $\gamma L = 0.1$  and  $Q(1, x)_{\gamma L \ll 1}$  by eq 32. This means that  $Q(1, x)$  at  $\gamma L = 0.1$  may practically be regarded as that of the rotational mode. Therefore, the  $n = 1$  mode was omitted in the calculation of form factors at  $\gamma L = 0.1$ .

(16) Around  $x = 1/2$ ,  $f(n, x)$ 's are odd (even) functions for odd (even)  $n$ 's and further  $\exp[\dots]$  in eq 36 is an even function. Therefore  $P_{NM}(X)$ 's with odd  $N$ 's are zero, whereas those with even  $N$ 's are non-zero. However  $P_{NM}(X)$ 's with even  $N$ 's and odd  $M$ 's are usually small compared to those with even  $N$ 's and  $M$ 's of the present interest. These statements are also valid for eq 39 and 45 below.

(17) A. Peterlin in "Electromagnetic Scattering," M. Kerker, Ed., Pergamon Press, London, 1963, p 358.

(18) Parameter  $B$  in ref 10 is different from the present  $B$  by a factor of  $(2/3\pi^4)$ .

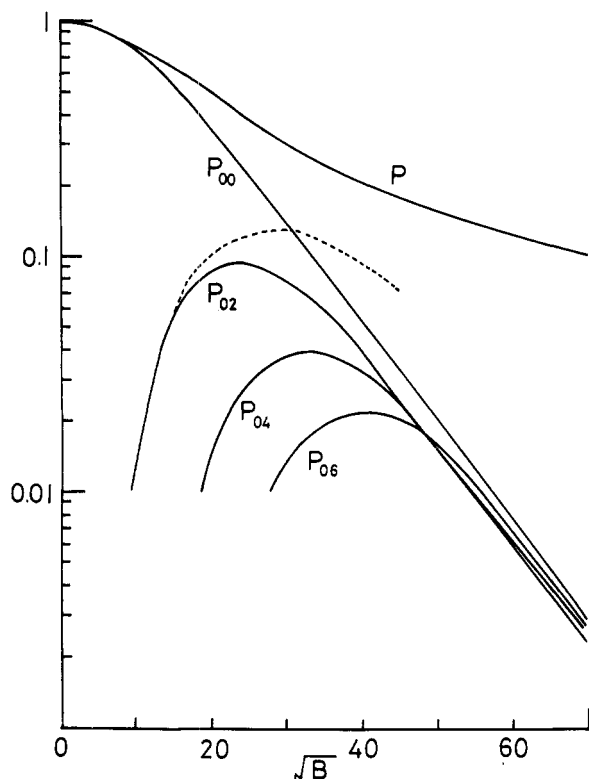


Figure 5.  $P_{0M}(B)$  vs.  $B^{1/2}$  at  $\gamma L = 0.1$ . In this case, the  $n = 1$  mode was omitted (see text). - - -;  $P_{02} + P_{04} + P_{06}$ .

### Discussion

We have calculated the scattering form factors based on a simple model. The limiting case of  $\gamma L \gg 1$  (coil) of our model is equivalent to the so-called Rouse model (a bead-and-spring model for a Gaussian chain). We find from eq 2, 3, 13, and 22 that the ratio of elastic energies due to bending and stretching is given by

$$R_n = \epsilon \beta_n^4 / \kappa \beta_n^2 = (\beta_n L)^2 / (2\gamma L)^2 \mu(\gamma L) \quad (46)$$

Thus one sees that  $R_1 \leq 0.1$  for  $\gamma L \geq 5$ . This suggests that the results in Figure 2 will qualitatively be valid for  $\gamma L$  down to 5, although they were calculated for  $\gamma L \gg 1$ . In fact, form factors for  $\gamma L = 10$  (Figure 4) are very similar to those for  $\gamma L \gg 1$  (Figure 2). The present results will play a role of a guiding principle in the analysis of spectra from linear aggregates as stiff as DNA, for example, whose

$\gamma$  value has been reported to be about  $15 \mu\text{m}^{-1}$ .<sup>19</sup> For DNA with length  $L = 2 \mu\text{m}$ ,  $X^{1/2}$  will amount to 3 and 4, respectively, at  $\phi = 65$  and  $100^\circ$ .

On the other hand, the limiting case of  $\gamma L \ll 1$  (rod) of our model is equivalent to the so-called Kratky-Porod model for a stiff chain. In this case, the spontaneous bending motion of a rod contributes to the broadening of scattered light. Our results (Figure 3) will play a role of a guiding principle in the analysis of spectra from long, stiff chain molecules. An experimental example will be found in a previous paper,<sup>10</sup> where the  $\gamma L$  and  $L$  of the polymer are, respectively, of the order of  $10^{-2}$  and  $10 \mu\text{m}$ . In the limit of  $\gamma L \ll 1$ , the  $n = 1$  mode is the rotational one. For a very long rod, it may hold that  $\tau_r > \tau_c \gg \tau_n$  ( $n \geq 2$ ) ( $\tau_r$ , rotational relaxation time,  $\tau_c$  coherence time of laser light,  $\tau_c \approx 100$  msec at best<sup>20</sup>). Within the time interval  $T$  of our interest ( $\tau_c \gg T \gg \tau_n$  ( $n \geq 2$ )), orientation of the rod is considered to be fixed. Therefore the neglect of the  $n = 1$  mode in eq 40 may be justified. From eq 46, it holds that  $R_2 \geq 10$  for  $\gamma L \leq 0.5$ . This suggests that the results in Figure 3 will qualitatively be valid for  $\gamma L$  up to 0.5. Since  $\tau_1 > \tau_c \gg \tau_n$  ( $n \geq 2$ ) for a very long polymer with small  $\gamma L$  (Figure 1b), the same consideration as above may allow us to neglect the  $n = 1$  mode in eq 45. The results in Figure 5 ( $\gamma L = 0.1$ ) are similar to those in Figure 3. Our calculations for small  $\gamma L$  are valid only for very long polymers. Because of the weakness of the model, we can say little about the scattering factors for  $\gamma L$  near unity.

The results presented here have been used as a guiding principle in the analysis of spectra from solutions of bacterial flagella,<sup>10</sup> and of muscle- and plasmodium-actin polymers under various environmental conditions.<sup>2b,6,21-24</sup> The present calculations qualitatively support the previous treatments. For a quantitative study of dynamics of linear macromolecules by quasielastic light scattering, a theoretical approach based on a more realistic model is still necessary.

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