Scattering Functions of Wormlike and Helical Wormlike Chains

Takenao Yoshizaki and Hiromi Yamakawa*

Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan.
Received May 14, 1980

ABSTRACT: The scattering function covering the range of light, small-angle X-ray, and neutron scattering is evaluated on the basis of the wormlike and helical wormlike chain models. Evaluation is carried out exactly but numerically by the weighting function method and ϵ method developed previously. Interpolation formulas for the scattering function as a function of scattering angle and chain length are also presented and are useful for various values of the model parameters. The scattering function of the helical wormlike chain may exhibit a maximum and a minimum, but that of the wormlike chain is a monotonically increasing function of scattering angle and does not exhibit a plateau in the transition range.

On the bond-length or somewhat longer scale, any real flexible or stiff chain may be represented by a helical wormlike (HW) chain.[1,2] Therefore, the scattering function covering the range of light, small-angle X-ray, and neutron scattering may be evaluated on the basis of this model[3] as well as on the basis of the rotational isomeric state model.[4] Although the range of its application is limited because of an inevitable continuous-point-scatterer approximation, our model augments our understanding of the general behavior of the scattering function. We initially evaluated it by using a Hermite polynomial expansion[5-7] of the distribution function of the end-to-end distance and presented some preliminary numerical results.[3] Subsequently, we devised two more efficient, complementary approximation methods, i.e., the weighting function method[8,9] and the ϵ method,[9] in order to obtain better convergence at large scattering angles. The object of the present paper is to complete numerical computations by these methods and present empirical interpolation formulas for the scattering function as a function of scattering angle and chain length which are useful for various values of the model parameters.

The Kratky–Porod (KP) wormlike chain[10] is also considered as a special case of the HW chain. It is then pertinent to note that wormlike chain statistics has been introduced only approximately in earlier investigations,[11-13] though the exact evaluation has been carried out for the infinitely long chain[14] and also in the light-scattering range.[15-17]

Methods of Numerical Calculation

All lengths are measured in units of the stiffness parameter λ^{-1} as usual.[1,2] The scattering function, or form factor, $P(\theta) \equiv P(k; L)$, for the general continuous chain of total contour length L and without excluded volume is then given, in the point-scatterer approximation, by

$$P(k; L) = 2L^{-2}\int_0^L (L-t)I(\mathbf{k}; t)\, \mathrm{d}t \qquad (1)$$

where $I(\mathbf{k}; t)$ is the characteristic function, or the Fourier transform of the distribution function $G(\mathbf{R}; t)$ of the end-to-end distance $\mathbf{R}$, for the chain of contour length t, and $\mathbf{k}$ has the meaning of the scattering vector whose magnitude is

$$k = (4\pi/\lambda')\sin(\theta/2) \qquad (2)$$

with θ the scattering angle and λ' the (reduced) wavelength in the scattering medium. For the HW chain, $P(k; L)$ depends also on the three model parameters: the constant curvature κ_0 and torsion τ_0 of the characteristic helix and Poisson's ratio σ. However, for simplicity, we assume that σ is zero as in most of the cases studied previously. For the KP chain, for which $\kappa_0 = 0$, $P(k; L)$ is a function of only k and L.

Now, we give a short sketch of the weighting function method and the ϵ method for the evaluation of $I(\mathbf{k}; t)$. The former provides a least-squares approximation to the distribution function $G(\mathbf{R}; t)$, as given by eq 4 with eq 16 and 20 of ref 9; i.e.

$$G(\mathbf{R}; t) = \left(\frac{3}{2\langle R^2\rangle}\right)^{3/2} w(\rho)\sum_{m=0}^{s} M_m(t)\rho^{2m} \qquad (3)$$

where $w(\rho)$ is a weighting function defined by

$$w(\rho) = \exp[-a_1\rho^2 - a_2\rho - (b\rho^2)^5] \qquad (4)$$

with

$$\rho = (3/2\langle R^2\rangle)^{1/2}R \qquad (5)$$

The coefficients a_1, a_2, b, and M_m are functions of the contour length t and the model parameters κ_0 and τ_0; the first three are first determined in such a way that the normalized weighting function gives the exact moments $\langle R^2\rangle$, $\langle R^4\rangle$, and $\langle R^6\rangle$, and then M_m (m = 0–s; $s \geq 3$) are determined in such a way that the $G(\mathbf{R}; t)$ given by eq 3 with this w gives the exact moments $\langle R^{2m}\rangle$ (m = 0–s). We note that $w(\rho)$ with $a_2 = 0$ is the weighting function of Fixman and Skolnick[8] and that when $a_2 = b = 0$, eq 3 gives the Hermite polynomial expansion of $G(\mathbf{R}; t)$.[5-7] By Fourier inversion of $G(\mathbf{R}; t)$, we obtain for $I(\mathbf{k}; t)$

$$I(\mathbf{k}; t) = 4\pi k^{-1}\int_0^\infty R\sin(kR)G(\mathbf{R}; t)\, \mathrm{d}R \qquad (6)$$

The determination of the coefficients above and the integration in eq 6 must be carried out numerically.

For very small t, the weighting function method breaks down,[9] and the ϵ method is used. If we define the relative deviation ϵ of R^2 by

$$R^2 = \langle R^2\rangle(1+\epsilon) \qquad (7)$$

we have

$$\langle\epsilon^m\rangle = \langle R^{2m}\rangle/\langle R^2\rangle^m - \sum_{r=0}^{m-1}\binom{m}{r}\langle\epsilon^r\rangle \qquad (8)$$

so that $\langle\epsilon^m\rangle$ ($m \geq 1$) may be expressed successively in terms of $\langle R^{2r}\rangle$ (r = 1–m). Then, we have the sth-order ϵ expansion of I[9,17]

$$I(\mathbf{k}; t) = \sum_{m=0}^{s}\frac{(-x)^m}{2^m m!}j_m(x)\langle\epsilon^m\rangle \qquad (9)$$

with

$$x = \langle R^2\rangle^{1/2}k \qquad (10)$$

where $j_m(x)$ is a spherical Bessel function of the first kind. We note that $\langle\epsilon\rangle = 0$ and $\langle\epsilon^m\rangle = O(t^m)$ for $m \geq 2$. The moments $\langle R^{2m}\rangle$ (m = 1–s) required in both methods may be evaluated by an operational method.[18]

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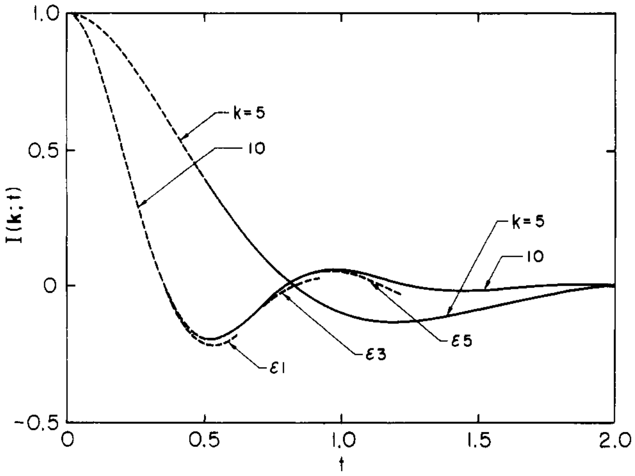

Figure 1. $I(\mathbf{k}; t)$ plotted against the reduced contour length t for the KP chain for $k = 5$ and $k = 10$. The full and broken curves represent the values by the weighting function method ($t \geq 0.5$) and by the ϵ method ($t < 0.5$), respectively, both for $s = 5$. The latter values for $s = 1$ and $s = 3$ are also included for $k = 10$. s is the degree of approximation.

We have examined the convergence of $I(\mathbf{k}; t)$ obtained by the weighting function method for $s = 3$–5 and by the ϵ method for $s = 1$–5, where s is the degree of approximation. If k is increased at constant κ_0 and τ_0, the radius t of convergence becomes small for the ϵ method, and the convergence of the weighting function method becomes bad over the whole range of t. If the helical nature[9,19] of the chain becomes strong, the radius t of convergence again becomes small for the ϵ method, but the convergence of the weighting function method becomes good even for small t and large k. Thus, it has been found that if k is not very large, we may obtain accurate values of $I(\mathbf{k}; t)$ over the whole range of t, using the values from the ϵ method for t smaller than some small value and from the weighting function method for t larger than that value, both for $s = 5$, for any of those values of κ_0 and τ_0 for which the latter method has the solution. Note that the stronger the helical nature of the chain, the wider the range of k over which the values of $I(\mathbf{k}; t)$ are available. For the KP chain ($\kappa_0 = 0$), for example, they are available for $k \lesssim 10$. Figure 1 shows plots of $I(\mathbf{k}; t)$ against t for this chain for $k = 5$ and $k = 10$. The full and broken curves represent the values from the weighting function method ($t \geq 0.5$) and from the ϵ method ($t < 0.5$), respectively, both for $s = 5$, the latter values for $s = 1$ and $s = 3$ also being included to indicate the convergence for $k = 10$. For this k, the ϵ method is seen to be convergent for $t \lesssim 0.6$ (when $\kappa_0 = 0$).

Finally, the values of the scattering function $P(k; L)$ are obtained from eq 1 with the values of $I(\mathbf{k}; t)$ above by carrying out the integration over t numerically as before.[3] All numerical work has been carried out with a FACOM M-200 digital computer in this university.

Empirical Equations

In order to construct empirical equations for the scattering function, it is convenient to use instead of κ_0 and τ_0 the parameters μ and ν defined by[19]

$$\mu = \tau_0(\kappa_0{}^2 + \tau_0{}^2)^{-1/2}$$

$$\nu = (\kappa_0{}^2 + \tau_0{}^2)^{1/2} \qquad (11)$$

and also to consider instead of $P(k; L)$ the function $F(k; L)$ defined by

$$F(k; L) = Lk^2P(k; L) \qquad (12)$$

Note that $F(k; L)$ corresponds to the quantity usually plotted in small-angle X-ray and neutron scattering experiments. For the present purpose, we have obtained the numerical values of $F(k; L)$ for $\kappa_0 = 0$ ($|\mu| = 1$), the values of κ_0 and τ_0 indicated by the filled points in the (κ_0, τ_0) plane of Figure 3 of ref 19 (except $\mu = 0.5$ and $\nu = 8$) and also $\mu = 0$, 0.2, and 0.4 with $\nu = 1$, and for various values of L ranging from 0.05 to 10 000 over the range of k of convergence.

It has been found that $F(k; L)$ may well be approximated by

$$F(k; L) = F_0(k; L)\Gamma(k; L) \qquad (13)$$

$F_0(k; L)$ is given by

$$F_0(k; L) = [1 - \chi(k, L)]F_{(\mathrm{C}*)}(k; L) + \chi(k, L)F_{(\mathrm{R})}(k; L) \qquad (14)$$

where $F_{(\mathrm{C}*)}(k; L)$ is the Debye scattering function for a random coil[20] having the same mean-square radius of gyration $\langle S^2 \rangle$ as that of the HW chain under consideration

$$F_{(\mathrm{C}*)}(k; L) = 2k^2Lu^{-2}(e^{-u} + u - 1) \qquad (15)$$

with

$$u = \langle S^2 \rangle k^2 \qquad (16)$$

$F_{(\mathrm{R})}(k; L)$ is the scattering function for the rod[20,21]

$$F_{(\mathrm{R})}(k; L) = 2k\ \mathrm{Si}\ (kL) - 4L^{-1} \sin^2 (\tfrac{1}{2}kL) \qquad (17)$$

with Si the sine integral

$$\mathrm{Si}\ (x) = \int_0^x t^{-1} \sin t\ \mathrm{d}t \qquad (18)$$

and χ is defined by

$$\chi = \exp(-\xi^{-5}) \qquad (19)$$

with

$$\xi = \pi\langle S^2 \rangle k/2L \qquad (20)$$

$\Gamma(k; L)$ is given by

$$\Gamma(k; L) = 1 + (1 - \chi) \sum_{i=2}^{5} A_i\xi^i + \chi \sum_{i=0}^{2} B_i\xi^{-i} \qquad (21)$$

where

$$A_i = \sum_{j=0}^{2} a_{1,ij}L^{-j}e^{-40/(4+\nu)L} + \sum_{j=1}^{2} a_{2,ij}L^je^{-2L} \qquad (22)$$

$$B_i = \sum_{j=0}^{2} b_{1,ij}L^{-j} + \sum_{j=1}^{2} b_{2,ij}L^je^{-2L} \qquad (23)$$

with $a_{1,ij}$, $a_{2,ij}$, $b_{1,ij}$, and $b_{2,ij}$ being numerical coefficients dependent on μ and ν.

The mean-square radius of gyration $\langle S^2 \rangle$ of the HW chain in eq 16 and 20 is given by eq 56 of ref 2 with $t = L$ and $\sigma = 0$, i.e.

$$\langle S^2 \rangle = \mu^2\langle S^2 \rangle_{\mathrm{KP}} + (1 - \mu^2)\left[\frac{2L}{3r^2} - \frac{1}{r^2}\cos(2\phi) + \frac{2}{r^3L}\cos(3\phi) - \frac{2}{r^4L^2}\cos(4\phi) + \frac{2}{r^4L^2}e^{-2L}\cos(\nu L + 4\phi)\right] \quad (\sigma = 0) \qquad (24)$$

where

$$r = (4 + \nu^2)^{1/2} \qquad (25)$$

$$\phi = \cos^{-1}(2/r) \qquad (26)$$

and $\langle S^2 \rangle_{\mathrm{KP}}$ is the $\langle S^2 \rangle$ of the KP chain with the same λ^{-1}

as that of the HW chain under consideration and is given by

$$\langle S^2\rangle_{KP} = \frac{L}{6} - \frac{1}{4} + \frac{1}{4L} - \frac{1}{8L^2}(1 - e^{-2L}) \qquad (27)$$

(Note that eq 27 was originally derived by Benoit and Doty.[22])

The numerical coefficients in eq 22 and 23 have been determined by the method of least squares for the respective pairs of values of μ and ν (κ_0 and τ_0) above, and the results are given in Tables I–IV. It is difficult to construct empirical equations for these coefficients as functions of μ and ν. The application of eq 13 is limited to the range of k

$$k \leq 10 \qquad \text{for } \kappa_0 = 0 \text{ (KP)}$$
$$k \leq 10 + 2.5\nu \qquad \text{for } \kappa_0 \neq 0 \qquad (28)$$

In this range of k, the solution obtained by the weighting function method and the ϵ method is convergent, and the continuous model itself may be regarded as valid. Within the range of its application, the error in the value of F calculated from eq 13 does not exceed 1% except for $\mu = 0$ and $\nu = 5$ and for $\mu = 0.1$ and $\nu = 6$, in which cases the maximum possible error is 2% for $0.4 \lesssim L \lesssim 50$ and $k \gtrsim 5$.

We note that for very small L, we may also use eq 42 with eq 43 of ref 17 derived for $P(k; L)$ by the ϵ method near the rod limit in the light-scattering range.

Numerical Results and Discussion

In this section, we examine the behavior of the scattering function $F(k; L)$ calculated as a function of k from eq 13, taking as examples two HW chains, code 1 ($\mu = 0.2$ and $\nu = 4$) and code 2 ($\mu = 0.2$ and $\nu = 3$), and the KP chain ($\kappa_0 = 0$ or $|\mu| = 1$). For comparison, we also consider the first Daniels approximation $F_{(D1)}$ to F, which is given by eq 76 of ref 23

$$F_{(D1)}(k; L) = F_{(C)}(k; L) + \frac{12c_0}{c_\infty{}^2L}[(u + 1)e^{-u} - 1] + \frac{6c_1}{c_\infty L}[(u + 2)e^{-u} + u - 2] \qquad (29)$$

with

$$u = \tfrac{1}{6}c_\infty Lk^2 \qquad (30)$$

and

$$c_\infty = (4 + \tau_0{}^2)/(4 + \nu^2) \qquad (31)$$

$$c_0 = -\tfrac{1}{2}c_\infty{}^2 + 2\kappa_0{}^2(4 - \tau_0{}^2)/(4 + \nu^2)^2 \qquad (32)$$

$$c_1 = \tfrac{4}{15} - \tfrac{4}{5}\kappa_0{}^2[1 + (101 + \kappa_0{}^2)/(4 + \tau_0{}^2) + 3(160 + 7\kappa_0{}^2)/(4 + \tau_0{}^2)^2]/(9 + \nu^2)(36 + \nu^2) \qquad (33)$$

In eq 29, $F_{(C)}(k; L)$ is given by eq 15 with eq 30 instead of with eq 16. Note that when $\kappa_0 = 0$, $F_{(D1)}(k; L)$ given by eq 29 reduces to the scattering function of Sharp and Bloomfield[24] with $c_\infty = 1$, $c_0 = -1/2$, and $c_1 = 4/15$.

The values of $F(k; L)$ for codes 1 and 2 and the KP chain in the range of convergence are represented by the full curves 1, 2, and KP in Figures 2–4 for L = 5, 80, and 10000, respectively. The chain curves represent the corresponding values of $F_{(D1)}$ calculated from eq 29, the dotted curves R the values of $F_{(R)}$ calculated from eq 17 for the rods with the respective L, and the broken curves C(1) and C(KP) the values of $F_{(C*)}$ calculated from eq 15 for the random coils with the same model parameters as those of code 1 and the KP chain, respectively. We have already found that for the KP chain in the light-scattering range of small

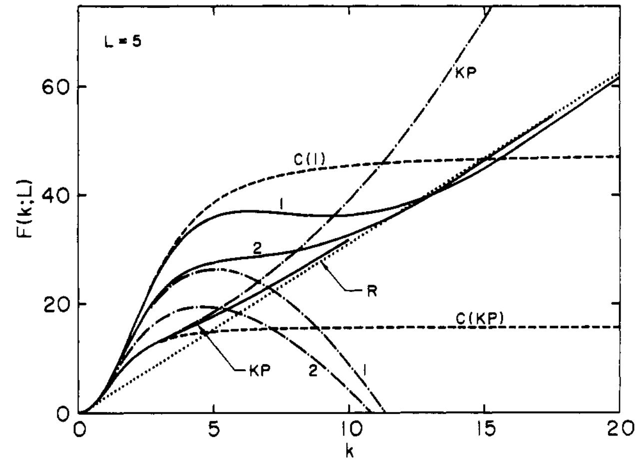

Figure 2. Scattering functions F plotted against the reduced magnitude k of the scattering vector for code 1 ($\mu = 0.2$, $\nu = 4$), code 2 ($\mu = 0.2$, $\nu = 3$), and the KP chain, indicated by the attached numbers and symbol, each with reduced contour length $L = 5$. The chain curves represent the corresponding values of $F_{(D1)}$ for the first Daniels approximation, the dotted curve R the values of $F_{(R)}$ for the rod, and the broken curves C(1) and C(KP) the values of $F_{(C*)}$ for the random coils having the same mean-square radii of gyration as those of code 1 and the KP chain, respectively.

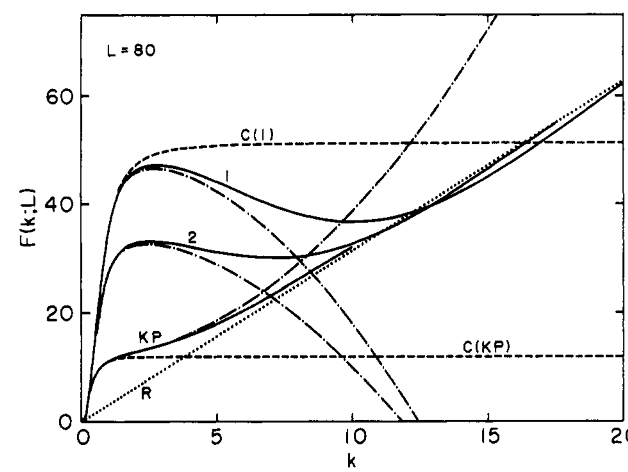

Figure 3. Scattering functions F for reduced contour length L = 80. See legend to Figure 2.

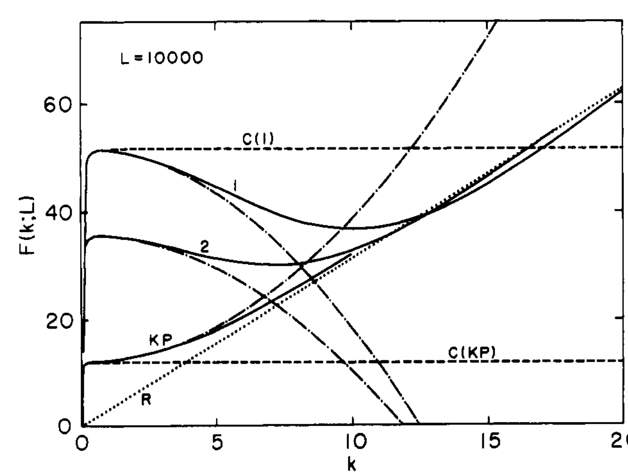

Figure 4. Scattering functions F for reduced contour length L = 10000. See legend to Figure 2.

k, the first Daniels approximation is quite successful for $L \gtrsim 10$ but breaks down for smaller L.[15] This approximation is bad also for the HW chain at $L = 5$, as seen from Figure 2. We note that for the KP chain with $L = 5$ in the range of $k \leq 3$, the approximation seems to be good, but

Table I
Values of the Coefficients $a_{k,ij}$ and $b_{k,ij}$ as Functions of μ and ν in Eq 22 and 23

	ij	(μ, ν): (1, -)	(0, 1)	(0.2, 1)	(0.4, 1)	(0, 2)	(0.1, 2)	(0.2, 2)	(0.3, 2)	(0.4, 2)	(0.5, 2)
$a_{1,ij}$	20	1.7207(−1)[a]	4.7392(−2)	1.9066(−1)	2.0609(−1)	−1.9655(−1)	−1.7793(−1)	−1.0917(−1)	−1.7999(−2)	6.5493(−2)	1.6002(−1)
	21	−7.0881	−7.0529	−6.3341	−6.8174	1.3053	8.6779(−1)	−2.7813(−1)	−1.8833	−3.6679	−5.1872
	22	1.9577(1)	4.3385	5.8745	6.6534	5.0068	4.2437	5.5551	7.3069	9.0316	1.1126(1)
	30	7.7459(−2)	5.4594(−1)	−5.3822(−1)	−4.9949(−1)	−7.8912(−1)	−7.8764(−1)	−7.9714(−1)	−7.9020(−1)	−6.9465(−1)	−7.5531(−1)
	31	4.8101	1.6937(1)	1.1993(1)	1.3140(1)	−9.6479	−8.2652	−4.5678	4.7218(−1)	6.0023	9.9450
	32	−2.0099(2)	−7.4620(1)	−7.8628(1)	−7.9956(1)	−6.1045(1)	−5.8466(1)	−6.2194(1)	−6.6726(1)	−7.0176(1)	−7.5903(1)
	40	9.6330(−1)	−3.0523(−1)	1.8184	1.6721	2.7418	2.7343	2.6338	2.4820	2.1647	2.2364
	41	2.6450(1)	−6.8223	2.8410	1.7499	1.8874(1)	1.7639(1)	1.4032(1)	9.2581	3.8941	1.2986
	42	4.0647(2)	1.4867(2)	1.5606(2)	1.5603(2)	1.1363(2)	1.1079(2)	1.1340(2)	1.1589(2)	1.1588(2)	1.2073(2)
	50	−1.1307	−1.5538(−1)	−1.3896	−1.2686	−1.8744	−1.8896	−1.8403	−1.7691	−1.5893	−1.6757
	51	−2.3971(1)	−2.3020	−8.0954	−7.5590	−1.0812(1)	−1.0536(1)	−9.4465	−8.0412	−6.2627	−6.0415
	52	−2.2471(2)	−7.2024(1)	−7.8784(1)	−7.8074(1)	−5.4580(1)	−5.3642(1)	−5.3799(1)	−5.3471(1)	−5.1536(1)	−5.2567(1)
$a_{2,ij}$	21	3.3157(−1)	2.2912(−2)	1.6317(−1)	1.6881(−1)	−5.5218(−1)	−3.2418(−1)	−3.2328(−1)	−3.2595(−1)	−3.4346(−1)	−3.5700(−1)
	22	−1.0692	−7.5504(−2)	−2.6037(−1)	−2.9517(−1)	1.1535	5.1067(−1)	5.1121(−1)	5.1174(−1)	5.2151(−1)	4.8829(−1)
	31	−3.9383	−1.7084	−2.9109	−2.9282	3.0848	1.7465	1.6864	1.6374	1.7119	1.8356
	32	1.1279(1)	3.7409	5.2494	5.4927	−5.9332	−2.1835	−2.1014	−1.9856	−1.9370	−1.6707
	41	1.2608(1)	6.4579	9.7258	9.6700	−5.2143	−2.6369	−2.4243	−2.2274	−2.3724	−2.8327
	42	−3.8021(1)	−1.8440(1)	−2.2442(1)	−2.2885(1)	4.2218	2.8843	−3.1726	−3.5594	−3.7333	−4.1226
	51	−9.7252	−4.8687	−7.5959	−7.4798	3.4072	1.7723	1.5850	1.4150	1.5458	2.0538
	52	3.3515(1)	1.7775(1)	2.1055(1)	2.1288(1)	1.5820	5.9961	6.2537	6.5816	6.6961	6.7583
$b_{1,ij}$	00	1.3489	4.2589(−1)	1.5805	1.4434	2.1783	2.1958	2.1446	2.0670	1.8732	1.9435
	01	1.6527(1)	5.1081	9.9127(−1)	1.5071	−1.6443	−1.7823	−1.8036	−1.8065	−1.5454	−1.7346
	02	−6.5909(1)	−1.1212(1)	−8.0198	−8.8044	−7.5999(−1)	−6.6497(−1)	−5.8647(−1)	−5.2926(−1)	−6.6955(−1)	−7.7474(−1)
	10	−2.0350	−8.9035(−1)	−2.7284	−2.5258	−3.9621	−3.9674	−3.8577	−3.6876	−3.3354	−3.3761
	11	−3.0016(1)	−9.8079	−2.7112	−3.4143	1.4762	1.7054	1.7597	1.7644	1.3635	1.5580
	12	1.1290(2)	2.0371(1)	1.4584(1)	1.5897(1)	2.0122	1.8392	1.6843	1.5794	1.8286	2.1631
	20	1.3744	9.1216(−1)	1.7004	1.6119	2.2581	2.2615	2.2210	2.1505	1.9918	2.0142
	21	1.2268(1)	3.7987	6.2818(−1)	8.5906(−1)	−6.3093(−1)	−7.5603(−1)	−8.5510(−1)	−9.4409(−1)	−8.5889(−1)	−1.0651
	22	−4.6316(1)	−8.7187	−6.0846	−6.6263	−9.5902(−1)	−8.6857(−1)	−7.6718(−1)	−6.8518(−1)	−7.6669(−1)	−9.1627(−1)
$b_{2,ij}$	01	1.3544(1)	6.6501(1)	6.0008(1)	6.3306(1)	4.8886	6.1661	5.6035	5.1074	4.8707	6.5767
	02	6.0772(1)	−4.4812(1)	−4.1853(1)	−4.3045(1)	−1.1418(1)	−1.5124(1)	−1.4628(1)	−1.4033(1)	−1.3368(1)	−1.3627(1)
	11	3.2504(1)	−1.0588(2)	−9.1385(1)	−9.7249(1)	−3.4173	4.9959	−3.6024	−2.2508	−1.7862	−5.5881
	12	−1.3836(2)	6.4802(1)	5.7291(1)	5.8731(1)	1.6904(1)	2.2082(1)	2.0586(1)	1.8719(1)	1.6780(1)	1.6996(1)
	21	−5.1258(1)	3.9133(1)	3.2621(1)	3.4913(1)	1.4300	−8.0880(−1)	−1.5067	−2.2437	−2.5974	−5.7566(−1)
	22	7.2212(1)	−2.2793(1)	−1.9544(1)	−1.9654(1)	−6.6623	−8.8304	−7.8149	−6.4737	−4.9244	−4.3796

[a] $a(n)$ means $a \times 10^n$.

Table II
Values of the Coefficients $a_{k,ij}$ and $b_{k,ij}$ as Functions of μ and ν in Eq 22 and 23

		(μ, ν)									
	ij	(0, 3)	(0.1, 3)	(0.2, 3)	(0.3, 3)	(0.4, 3)	(0.5, 3)	(0, 4)	(0.1, 4)	(0.2, 4)	(0.3, 4)
$a_{1,ij}$	20	1.1977	−1.0593	−7.3167(−1)	−3.8174(−1)	−1.1049(−1)	8.7982(−2)	−3.1306	−2.5836	−1.4516	−5.5214(−1)
	21	1.4150(1)[a]	1.2278(1)	7.5974	2.1286	−2.4762	−5.5261	3.6314(1)	2.9867(1)	1.6278(1)	3.7998
	22	9.9371(−1)	2.6470	6.6247	1.0686(1)	1.3137(1)	1.4067(1)	−1.5959(1)	−8.1032	5.4942	1.5143(1)
	30	−1.4694	−1.4833	−1.3750	−9.9829(−1)	−5.2028(−1)	−3.4244(−1)	−6.2627(−1)	−1.4803	−2.4598	−1.7796
	31	−6.4443(1)	−5.6653(1)	−3.7505(1)	−1.5839(1)	1.5190	1.1819(1)	−1.8328(2)	−1.5068(2)	−8.5039(1)	−2.8403(1)
	32	−4.2049(1)	−4.7608(1)	−6.0420(1)	−7.1760(1)	−7.5820(1)	−7.4686(1)	3.4322(1)	−1.4149	−5.6389(1)	−8.7854(1)
	40	6.9239	6.4168	4.9818	3.0770	1.4959	1.0491	1.2869(1)	1.2254(1)	9.3531	4.2781
	41	8.6080(1)	7.5915(1)	5.1363(1)	2.4549(1)	4.4280	5.3832	2.6846(2)	2.1787(2)	1.2033(2)	4.1293(1)
	42	9.2900(1)	9.7490(1)	1.0713(2)	1.1255(2)	1.0898(2)	1.0216(2)	2.0843	4.7019(1)	1.0568(2)	1.2886(2)
	50	−4.6018	−4.1868	−3.1119	−1.8498	−9.4390(−1)	−8.3438(−1)	−9.8930	−8.8096	−5.7519	−2.0416
	51	−3.7083(1)	−3.2702(1)	−2.2294(1)	−1.1312(1)	−3.6589	−1.0093	−1.2451(2)	−9.9337(1)	−5.2648(1)	−1.6985(1)
	52	−5.1698(1)	−5.2120(1)	−5.2228(1)	−4.9524(1)	−4.3747(1)	−3.8952(1)	−3.0587(1)	−4.5060(1)	−5.7741(1)	−5.5966(1)
$a_{2,ij}$	21	6.2028(−1)	5.6955(−1)	4.3333(−1)	2.4784(−1)	6.4305(−2)	−4.5098(−2)	1.4733	1.3027	9.8326(−1)	5.6494(−1)
	22	−1.0859	−9.8363(−1)	−7.0959(−1)	3.3169(−1)	5.0991(−2)	2.8987(−1)	−3.1151	−2.8470	−2.1802	−1.2599
	31	−4.1363	−3.8059	−2.9353	−1.8042	−7.9238(−1)	−3.6069(−1)	−1.0749(1)	−9.0141	−6.2047	−3.1715
	32	7.1870	6.4971	4.6837	2.2946	8.1090(−2)	−9.9329(−1)	2.3434(1)	2.0446(1)	1.4244(1)	7.2208
	41	8.1366	7.5210	5.9189	3.9090	2.2840	1.9287	2.2031(1)	1.7387(1)	1.0822(1)	4.7400
	42	−1.9384(1)	1.8027(1)	−1.4495(1)	−9.9642	−6.0369	−4.6036	−5.6038(1)	−4.7729(1)	−3.2572(1)	−1.7640(1)
	51	−4.4614	−4.1232	−3.2489	−2.1819	−1.4174	−1.4825	−1.2992(1)	−9.3926	−4.9473	−1.3532
	52	1.4735(1)	1.3938(1)	1.1877(1)	9.2757	7.1595	6.6841	3.8927(1)	3.2376(1)	2.1671(1)	1.2255(1)
$b_{1,ij}$	00	4.5975	4.2026	3.2089	2.0729	1.2648	1.1895	1.1304(1)	8.7584	4.8456	1.7297
	01	3.6832	−3.2638	−2.1532	−8.2814(−1)	−6.1389(−3)	−4.2118(−1)	−7.9191	−3.3755	2.5815(−1)	1.9750
	02	2.1370	1.9655	1.5002	9.4503(−1)	5.9442(−1)	7.0703(−1)	1.1215	−9.8563(−2)	−4.7795(−1)	−7.1600(−1)
	10	−7.5820	−7.0395	−5.6375	−3.9459	−2.6337	−2.3746	1.7525(1)	−1.3450(1)	−7.7819	−3.5319
	11	2.9130	2.5950	1.6429	2.5329(−1)	−7.5694(−1)	−1.3755(−1)	1.1967(1)	3.4137	−2.5282	−3.6509
	12	−2.5934	2.4484	−2.0000	−1.3700	−9.1768(−1)	−1.0711	−1.2402	1.1086	1.5627	1.3301
	20	3.5312	3.3345	2.8234	2.1901	1.6791	1.5968	7.5023	5.6776	3.3535	1.8473
	21	−1.8595(−1)	−1.8535(−1)	−1.4997(−1)	1.5894(−2)	1.4296(−1)	−3.2962(−1)	−5.2765	−1.1110	1.7337	1.5955
	22	7.7337(−1)	7.6658(−1)	7.2023(−1)	6.1323(−1)	5.3308(−1)	6.6040(−1)	4.8053(−1)	−6.7992(−1)	−9.0353(−1)	−5.7252(−1)
$b_{2,ij}$	01	−2.8556	−4.2142	−7.3682	−1.0548(1)	−1.2079(1)	−1.0419(1)	2.4024(1)	1.0447(1)	−6.2150	−1.4021(1)
	02	−3.0421(1)	−2.7654(1)	−2.1048(1)	−1.3928(1)	−8.7574	−7.0224	−7.4369(1)	−6.4530(1)	−3.9501(1)	−1.6221(1)
	11	1.3848(1)	1.5956(1)	2.0837(1)	2.6012(1)	2.9013(1)	2.6819(1)	−3.7192(1)	−1.3057(1)	1.6480(1)	2.8215(1)
	12	5.2989(1)	4.7685(1)	3.4846(1)	2.0819(1)	1.0323(1)	5.9748	1.0648(2)	9.5451(1)	6.0216(1)	2.2369(1)
	21	−9.3093	−1.0223(1)	−1.2237(1)	−1.4326(1)	−1.5574(1)	−1.4355(1)	1.4238(1)	2.9816	−1.0622(1)	−1.4929(1)
	22	−2.4918(1)	−2.2333(1)	−1.5937(1)	−8.7537	−3.1949	−6.3596(−1)	−3.9363(1)	−3.5726(1)	−2.2716(1)	−6.8613

[a] $a(n)$ means $a \times 10^n$.

Table III
Values of the Coefficients $a_{k,ij}$ and $b_{k,ij}$ as Functions of μ and ν in Eq 22 and 23

		(μ, ν)									
	ij	(0.4, 4)	(0.5, 4)	(0, 5)	(0.1, 5)	(0.2, 5)	(0.3, 5)	(0.4, 5)	(0.5, 5)	(0.1, 6)	(0.2, 6)
$a_{1,ij}$	20	−1.1219(−1)[a]	1.2076(−1)	−6.0085	−4.5098	−1.9028	−3.9435(−1)	5.3845(−2)	2.1829(−1)	−6.7140	−1.9258
	21	−3.9943	−7.4088	6.9991(1)	5.4729(1)	2.3411(1)	2.3069	−7.1563	−9.8639	8.2155(1)	2.6675(1)
	22	1.8064(1)	1.6533(1)	−6.6629(1)	−4.3875(1)	4.9747(−1)	1.9992(1)	2.2436(1)	1.8040(1)	−1.0711(2)	−3.0703
	30	−3.0313(−1)	2.1768(−1)	2.9393	−1.0896	−5.0029	−3.1904	−9.4200(−2)	7.3089(−1)	−3.3001(−2)	−9.2092
	31	4.6711	1.7405(1)	−4.0329(2)	3.1344(2)	−1.3692(2)	−2.8953(1)	1.4998(1)	2.5683(1)	−5.3242(2)	−1.7660(2)
	32	−8.9503(1)	−7.6577(1)	3.5120(2)	2.1440(2)	−2.7639(1)	−1.0795(2)	−1.0300(2)	−7.5787(1)	7.3394(2)	8.1198
	40	1.0115(−1)	−6.4754(−1)	1.9553(1)	2.1564(1)	1.7152(1)	5.8263	−1.6526	−2.1688	3.3710(1)	2.8005(1)
	41	−1.1278	−1.3572(1)	6.7680(2)	5.1613(2)	2.1323(2)	4.4887(1)	−1.5208(1)	−2.4116(1)	9.9655(2)	3.0183(2)
	42	1.1706(2)	9.6096(1)	−5.7525(2)	−3.3156(2)	5.4756(1)	1.4723(2)	1.2353(2)	8.7072(1)	−1.5629(3)	−3.4655(1)
	50	3.2003(−1)	3.2725(−1)	−1.8548(1)	−1.7573(1)	−1.0795(1)	−2.2112	1.8093	1.2998	−3.0788(1)	−1.7829(1)
	51	4.7744(−1)	3.4866	−3.5772(2)	−2.6689(2)	−1.0193(2)	−1.8061(1)	7.6707	8.1276	−5.8616(2)	−1.5692(2)
	52	4.4057(1)	−3.4493(1)	2.7884(2)	1.4670(2)	−3.4719(1)	−5.8834(1)	−4.1078(1)	−2.8534(1)	1.0242(3)	2.3920(1)
$a_{2,ij}$	21	9.3356(−2)	−2.6189(−1)	2.6863	2.6453	1.7145	7.2405(−1)	4.2873(−2)	−5.4018(−1)	−2.2161(−1)	2.5668
	22	−2.4991(−1)	5.1796(−1)	3.8551	−4.3017	−3.8673	−2.0839	−4.7044(−1)	8.6260(−1)	3.6765	−5.3176
	31	−1.6296(−1)	1.7370	−2.5150(1)	−2.3639(1)	−1.2674(1)	−3.8165	6.6533(−1)	3.7344	−2.3772	−2.0804(1)
	32	5.9540(−1)	−3.5940	3.9820(1)	4.0566(1)	2.9060(1)	1.2005(1)	7.9288(−1)	−6.3439	−1.8726(1)	4.3291(1)
	41	−8.8002(−1)	−4.0072	6.4880(1)	5.9001(1)	2.6567(1)	5.0139	−3.2270	−8.1419	1.1879(1)	4.8123(1)
	42	−4.8045	2.3968	−1.1404(2)	−1.1044(2)	−6.9013(1)	−2.6423(1)	−4.5719	7.0573	2.1019(1)	−1.0739(2)
	51	1.9124	3.6162	4.9849(1)	−4.4093(1)	−1.6544(1)	−9.0996(−1)	3.6781	6.3532	−1.2570(1)	−3.3941(1)
	52	4.5985	6.1246(−1)	9.2385(1)	8.6473(1)	4.8156(1)	1.6974(1)	4.1206	−2.0159	−2.9320	7.8674(1)
$b_{1,ij}$	00	−7.3418(−2)	1.1767(−1)	4.9783(1)	3.5931(1)	9.4294	8.9772(−1)	−1.6289	−7.2728(−1)	9.1778(1)	1.8217(1)
	01	3.2855	2.1657	−7.7070(1)	−5.3870(1)	−8.6286	2.6248	4.4894	2.9398	−1.8283(2)	−2.3752(1)
	02	−1.2242	−9.1477(−1)	2.2854(1)	1.6415(1)	2.6233	−9.2166(−1)	−1.5518	−1.1641	4.5267(1)	8.0539
	10	−7.7566(−1)	−8.3918(−1)	−7.9614(1)	−5.7230(1)	−1.4453(1)	−2.2638	1.4609	3.5991(−1)	−1.6404(2)	−2.7490(1)
	11	−5.1684	−3.6416	1.2444(2)	8.8152(1)	1.5446(1)	−3.4537	−6.1245	−3.9974	3.4222(2)	3.9376(1)
	12	2.0088	1.6907	−3.8135(1)	−2.7814(1)	−4.9339	1.2784	2.2321	1.8481	−8.5581(1)	−1.4209(1)
	20	8.3805(−1)	9.3756(−1)	3.4191(1)	2.4460(1)	5.8942	1.1189	−1.4671(−1)	4.5557(−1)	7.8919(1)	1.1037(1)
	21	1.7898	9.3202(−1)	−5.0409(1)	−3.6047(1)	−7.2084	9.8643(−1)	1.7899	6.8620(−1)	−1.6734(2)	−1.6322(1)
	22	−7.4140(−1)	−6.0359(−1)	1.5955(1)	1.1793(1)	2.4073	−3.7799(−1)	−7.0383(−1)	−5.6949(−1)	4.1742(1)	6.2921
$b_{2,ij}$	01	−1.6273(1)	−1.3050(1)	2.1876(2)	1.4017(2)	−1.9127	2.0920(1)	−2.0797(1)	−1.6405(1)	7.7638(2)	2.8234(1)
	02	−3.6429	−3.0811(−1)	−2.2620(2)	−1.6437(2)	−4.3120(1)	−9.1062	4.7924	5.5067	−4.9031(2)	−7.6891(1)
	11	3.0917(1)	2.4476(1)	−3.2135(2)	−2.0527(2)	1.0757(1)	3.7864(1)	3.7392(1)	2.7216(1)	−1.4206(3)	−2.4505(1)
	12	9.3723(−1)	−4.3776	3.2822(2)	2.3088(2)	4.0861(1)	5.1085	−1.5984(1)	−1.5765(1)	8.1146(2)	8.0074(1)
	21	−1.5318(1)	−1.1282(1)	1.1732(2)	7.3773(1)	−8.0792	−1.7862(1)	−1.7321(1)	−1.1211(1)	6.9967(2)	1.3091
	22	2.8350	5.0360	1.3912(2)	−9.5292(1)	−7.0124	3.3506	1.1619(1)	1.0907(1)	−3.8811(2)	−2.3914(1)

[a] $a(n)$ means $a \times 10^n$.

Table IV
Values of the Coefficients $a_{k,ij}$ and $b_{k,ij}$ as Functions of μ and ν in Eq 22 and 23

		(μ, ν)									
	ij	(0.3, 6)	(0.4, 6)	(0.5, 6)	(0.2, 7)	(0.3, 7)	(0.4, 7)	(0.5, 7)	(0.2, 8)	(0.3, 8)	(0.4, 8)
$a_{1,ij}$	20	−2.8923(−2)[a]	2.3926(−1)	3.0190(−1)	−1.4959	4.1128(−1)	3.9882(−1)	3.5589(−1)	−6.6896(−1)	8.1451(−1)	5.3262(−1)
	21	−1.5280	−1.0458(1)	−1.1890(1)	2.3784(1)	−6.4446	−1.3241(1)	−1.3157(1)	1.7206(1)	−1.0836(1)	−1.5539(1)
	22	2.5436(1)	2.4884(1)	1.8654(1)	4.9745	3.0873(1)	2.4544(1)	1.8602(1)	2.1623(1)	3.4309(1)	2.2857(1)
	30	−4.4827	4.6556(−1)	1.2355	−1.4865(1)	−5.2246	1.1930	1.6413	−2.1599(1)	−5.1852	1.8359
	31	−1.8138(1)	2.7032(1)	3.2708(1)	−1.8238(2)	5.5024(−2)	3.8041(1)	3.6593(1)	−1.6390(2)	1.7744(1)	4.7916(1)
	32	−1.3248(2)	−1.0952(2)	−7.3530(1)	−2.1536(1)	−1.6001(2)	−1.0351(2)	−6.9813(1)	−1.1404(2)	−1.8003(2)	−9.0862(1)
	40	6.2964	−3.9843	−3.3471	4.0831(1)	5.2174	−6.2504	−3.9557	5.4667(1)	2.5894	−7.8909
	41	3.2596(1)	−3.1730(1)	−3.2188(1)	3.3752(2)	7.5172	−4.7208(1)	−3.5211(1)	3.2943(2)	−1.8556(1)	−6.1156(1)
	42	1.7586(2)	1.2483(2)	8.0909(1)	−1.9465(1)	2.1672(2)	1.1159(2)	7.6446(1)	1.2709(2)	2.5318(2)	8.9589(1)
	50	−1.5452	3.5073	1.9338	−2.5918(1)	9.1610(−2)	4.9646	2.0771	−3.4367(1)	2.5306	5.8622
	51	−1.2095(1)	1.5611(1)	1.0940(1)	−1.8712(2)	4.4206(−1)	2.2777(1)	1.0947(1)	−1.9371(2)	1.3907(1)	2.8856(1)
	52	−6.7303(1)	−3.7814(1)	−2.6316(1)	3.7549(1)	−8.4714(1)	−2.9869(1)	−2.6502(1)	−2.8325(1)	−1.0403(2)	−1.8676(1)
$a_{2,ij}$	21	9.8125(−1)	−6.1525(−2)	−7.0002(−1)	3.1307	1.0968	−5.1620(−1)	−1.2433	4.0576	1.0173	−1.0061
	22	−3.0478	−4.8768(−1)	1.1962	−7.1974	−3.9849	1.7229(−1)	1.9255	−1.1067(1)	−4.4555	1.3179
	31	−5.6448	1.4263	4.3459	−2.5207(1)	−6.5475	4.2536	7.8475	−3.1567(1)	−6.4758	6.6760
	32	1.8060(1)	2.3450(−1)	−8.4680	5.7496(1)	2.3952(1)	−5.2466	−1.3675(1)	8.4425(1)	2.7089(1)	−1.2833(1)
	41	8.9628	−4.2428	−7.8364	5.8154(1)	1.1182(1)	−8.7657	−1.4046(1)	7.1002(1)	1.2626(1)	−1.0669(1)
	42	−3.8923(1)	−3.2301	8.0710	−1.3957(2)	−5.1861(1)	3.8932	1.5074(1)	−1.9593(2)	−6.1459(1)	1.2928(1)
	51	−3.6621	3.7505	5.0723	4.1102(1)	−5.2791	5.7320	8.4920	4.8919(1)	−7.3655	4.6870
	52	2.4751(1)	3.9536	−6.0217(−1)	1.0069(2)	3.2965(1)	1.4252	−2.9982	1.3577(2)	4.0551(1)	1.7146(−1)
$b_{1,ij}$	00	−1.0018	−3.2400	−1.1841	1.3501(1)	−3.7822	−4.4478	−1.1309	−1.0548(1)	−6.8778	−5.0008
	01	2.7071	4.7608	3.3193	5.5382	7.2123(−1)	3.5976	3.8755	2.1109(1)	−2.8058	8.3263(−1)
	02	−7.8159(−1)	−1.4944	−1.1624	4.6479(−1)	2.1971(−1)	−1.0990	−1.5860	−1.7270	2.7208	3.7978(−1)
	10	6.6005(−1)	3.8156	9.5848(−1)	−1.8076(1)	4.9152	5.5648	7.9433(−1)	1.6719(1)	9.5785	6.2983
	11	−1.9303	−5.6292	−3.5923	−1.2455(1)	3.1218	−2.9858	−3.6788	−2.6252(1)	1.0690(1)	2.1977
	12	5.4064(−1)	1.8309	1.4765	−8.3947(−1)	−1.6414	9.6890(−1)	2.0392	2.6567(−1)	−6.5793	−1.8582
	20	−3.0586(−1)	−1.1587	2.8480(−1)	6.9405	−2.2622	1.8783	5.0990(−1)	−5.1316	−4.3233	−2.1215
	21	−2.8803(−1)	1.1992	1.4013(−2)	6.4439	−3.0275	−2.0417(−1)	−5.5140(−1)	7.7136	−6.7425	−2.6842
	22	1.4399(−1)	−3.9708(−1)	−2.3361(−1)	4.2041(−1)	1.2635	6.3733(−2)	−3.4530(−1)	8.8488(−1)	3.6458	1.4393
$b_{2,ij}$	01	−1.9444(1)	−1.8298(1)	−1.5496(1)	−1.0448(2)	−1.9803(1)	−1.3471(1)	−1.7625(1)	−1.6460(2)	−3.7693(1)	−9.0428
	02	−6.3077(−1)	1.0837(1)	4.7954	−8.0609(1)	2.3339(1)	1.7547(1)	4.9931	3.9374(1)	6.9024(1)	2.0677(1)
	11	3.1742(1)	3.2612(1)	2.3751(1)	2.0780(2)	2.9596(1)	2.5605(1)	2.2416(1)	2.3936(2)	6.3309(1)	2.3116(1)
	12	−1.3742(1)	−2.8940(1)	−1.7268(1)	8.0660(1)	−5.8818(1)	−4.4316(1)	−1.8226(1)	−7.9191(1)	−1.4344(2)	−5.5463(1)
	21	−1.2502(1)	−1.4265(1)	−8.2270	−9.8960(1)	−9.5297	−1.1619(1)	−5.4647	−8.7279(1)	−2.4562(1)	−1.1657(1)
	22	1.2925(1)	1.8004(1)	1.1872(1)	−2.7970(1)	3.3516(1)	2.5873(1)	1.2494(1)	1.8666(1)	7.1757(1)	3.1341(1)

[a] $a(n)$ means $a \times 10^n$.

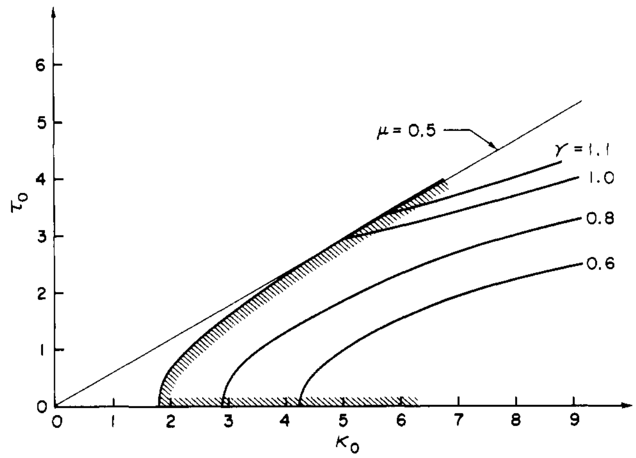

Figure 5. Curves with constant γ in the (κ_0, τ_0) plane. The (first) maximum and minimum of F occur for the values of κ_0 and τ_0 in the shaded domain.

the function $P_{(D1)}$ itself deviates appreciably from the exact P. For large L and small k, however, the first Daniels approximation is very good for the HW chain as well as for the KP chain, as seen from Figures 3 and 4.

The full curves in Figures 2–4 are seen to approach straight lines asymptotically as k is increased. Indeed, we have

$$F(k; L) \rightarrow \pi k + C(L) \qquad (k \rightarrow \infty) \tag{34}$$

with

$$C(L) = -2L^{-1} \qquad \text{(rod)} \tag{35}$$

$$C(\infty) = 2/3 \qquad \text{(KP)} \tag{36}$$

where eq 36 is due to des Cloizeaux.[14] It is impossible to evaluate $C(L)$ analytically for the KP and HW chains with finite L. Therefore, eq 13 has not been constructed so as to give the correct $C(L)$, though it is useful within the range of its application.

des Cloizeaux[14] has evaluated F numerically for the KP chain with $L = \infty$ for $k \leq 8$. His results almost agree with the corresponding values shown in Figure 4 for $L = 10000$ in the range of $k \geq 0.5$. Note that $F(k; \infty) = 12$ at $k = 0$ for $\kappa_0 = 0$ (see below). For the KP chain, therefore, we may conclude that $F(k; L)$ increases monotonically with increasing k for all values of L (see Figures 2–4). In other words, it does not exhibit even a plateau in the transition range of k from random coil to rod, as observed in the small-angle neutron scattering by polystyrene[25,26] and polyethylene[27] chains. Earlier theories[12,13] happen to predict the existence of the plateau region for the KP chain because of the approximations involved. Thus, within the framework of the continuous model, it can be explained by the HW chain but not by the KP chain, as seen from Figures 3 and 4.

Finally, we briefly discuss the dependence of the behavior of $F(k; L)$ on the model parameters κ_0 and τ_0. When F exhibits a (first) maximum with a (first) minimum for certain values of κ_0 and τ_0, the latter value of F, which we designate by $F_{\min}$, has been found to be almost independent of L (and also k). Thus, we define a dimensionless ratio γ by

$$\gamma = F_{\min}/F(0; \infty) \tag{37}$$

where $F(0; \infty)$ is given by eq 20 of ref 3

$$F(0; \infty) \equiv \lim_{k \to 0} [\lim_{L \to \infty} F(k; L)] = 12c_\infty^{-1} \tag{38}$$

and we may take as $F_{\min}$ its value for $L = \infty$, so that γ depends on κ_0 and τ_0 but not on L. The curves with constant γ in the (κ_0, τ_0) plane, which have been determined by interpolation, are shown in Figure 5, where the first maximum and minimum of F occur for the values of κ_0 and τ_0 in the shaded domain. It is seen that the stronger the helical nature of the chain, the smaller the ratio γ, and therefore the sharper the maximum and minimum of F, as expected.

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