handedness are taken into account, with a corresponding reduction in the characteristic ratio towards the experimental values. The same result is obtained by Boyd and Breitling within the ris scheme by (i) minimizing the energy of the local conformations by allowing several parameters to participate, and (ii) assuming a relative large number (*i.e.*, 7) of rotational isomers per each skeletal bond.[3] Since our treatment does not involve energy minimization, the energies corresponding to the different conformations are larger in our case than in Boyd and Breitling's. Had the minimization process been carried out by us as well, it seems plausible that both the calculated characteristic ratio and the absolute value of its temperature coefficient would have even lower values.

We believe that both Boyd and Breitling's results and ours make any hypothesis about the presence of significant amounts of steric inversion in IPP[6] unnecessary.

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Form Factor of an Infinite Kratky-Porod Chain

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ABSTRACT: The form factor of an infinite Kratky-Porod chain of persistence length b can be defined by $bS(bq) \equiv \int_{-\infty}^{+\infty}\langle\exp[i\mathbf{q}\cdot\mathbf{r}(L)]\rangle \mathrm{d}L$; ($\mathbf{r}(L)$ represents the position of a point of the chain), where $S(p)$ is a universal function which is studied here. Analytic properties and precise values of this function are given.

The intensity of radiation scattered by an isolated chain molecule (for instance a dilute solution) is proportional to the form factor

$$\mathcal{S}(\mathbf{q}) = \langle\sum_{ij}\exp[i\mathbf{q}(\mathbf{r}_i - \mathbf{r}_j)]\rangle \qquad (1.1)$$

Here the angular brackets indicate that $\mathcal{S}(\mathbf{q})$ is obtained by averaging over all chain configurations and $\mathbf{q}$ is the momentum transfer.

For small-angle X-ray scattering of long molecules, it is tempting to use for comparison with experiments, a simplified model, the well-known Kratky-Porod chain.[1-7]

For an infinite Kratky-Porod chain of persistence length b, the form factor can be defined by

$$\mathcal{S}_\infty(\mathbf{q}) = \int_{-\infty}^{+\infty}\mathrm{d}L\langle\exp\{i\mathbf{q}[\mathbf{r}(L) - \mathbf{r}(0)]\}\rangle \qquad (1.2)$$

Here $\mathbf{r}(L)$ indicates the position of a point on the chain and L the length measured along the chain (see Figure 1). The derivative of $\mathbf{r}(L)$ with respect to L is a unit vector $\dot{\mathbf{r}}(L)$ ($|\dot{\mathbf{r}}(L)| = 1$) which is tangent to the curve and we recall that b is defined by

$$\cos\alpha_{12} \equiv \langle\dot{\mathbf{r}}(L_1)\dot{\mathbf{r}}(L_2)\rangle = \exp[-|L_1 - L_2|/b] \qquad (1.3)$$

where α_{12} is the angle between the chain directions in positions L_1 and L_2. For $L \gg b$, we have also

$$\langle[\mathbf{r}(L) - \mathbf{r}(0)]^2\rangle \simeq 2Lb$$

which is a consequence of eq 1.3.

Introducing dimensionless quantities, we see immediately that

$$\mathcal{S}_\infty(\mathbf{q}) = bS(bq) \qquad (1.4)$$

where $S(p)$ is a universal function which we plan to study here. Actually, it is the form factor of a Kratky-Porod chain of unit persistence length. Therefore, in the following, we shall consider only such chains.

Basic Equations

It is convenient to introduce the auxiliary function $F(\mathbf{p},\mathbf{t};L)$ which is the expectation value of $\exp\{i\mathbf{p}[\mathbf{r}(L) - \mathbf{r}(0)]\}$ for chains of length L, starting in a given direction $\mathbf{t}$, *i.e.*, such that $\dot{\mathbf{r}}(0) = \mathbf{t}$ (with $|\mathbf{t}| = 1$ for any L). More explicitly

$$F(\mathbf{p},\mathbf{t};L) = \langle\delta_s[\dot{\mathbf{r}}(0) - \mathbf{t}]\exp\{i\mathbf{p}[\mathbf{r}(L) - \mathbf{r}(0)]\}\rangle \qquad (2.1)$$

where δ_s is a surface Dirac function.

Thus

$$S(p) = \int_{-\infty}^{+\infty}\mathrm{d}L\int\mathrm{d}\Omega(\mathbf{t})F(\mathbf{p},\mathbf{t};L) \qquad (2.2)$$

It is also convenient to set

$$\mathbf{p}\cdot\mathbf{t} = p\cos\theta \qquad (2.3)$$

and with this notation

$$\mathrm{d}\Omega(\mathbf{t}) = 2\pi\sin\theta\,\mathrm{d}\theta \qquad (2.4)$$

For obvious symmetry reasons

$$F(-\mathbf{p},-\mathbf{t};L) = F(-\mathbf{p},\mathbf{t};-L) = F(\mathbf{p},\mathbf{t};L) \qquad (2.5)$$

and therefore, we may write as well

$$F(\mathbf{p},\mathbf{t};L) = \langle\delta_s(\dot{\mathbf{r}}(L) - \mathbf{t})\exp\{i\mathbf{p}[\mathbf{r}(L) - \mathbf{r}(0)]\}\rangle \qquad (2.6)$$

From this definition, we deduce an equation[8] which determines $F(\mathbf{q},\mathbf{t};L)$ for $L > 0$

$$\frac{\partial}{\partial L}F(\mathbf{p},\mathbf{t};L) = \left[i\mathbf{p}\cdot\mathbf{t} + \frac{1}{2}\Delta_s\right]F(\mathbf{p},\mathbf{t};L) \qquad (2.7)$$

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(1) G. Porod, *J. Polym. Sci.*, **10**, 157 (1953).

(2) A. Peterlin, *J. Polym. Sci.*, **47**, 403 (1960).

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(4) N. Saito, K. Takahashi, and Y. Yunoki, *J. Phys. Soc. Jap.*, **22**, 219 (1967); W. Gobush, H. Yamakawa, W. Stockmayer and W. S. Magee, *J. Chem. Phys.* **57**, 2839 (1972).

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(7) J. J. Hermans and R. Ullman, *Physica*, 18 (1952). The author is indebted to Dr. Ullman for bringing this and the previous article to his attention.

(8) This equation is derived by using the fact that the motion of the extremity of $\mathbf{t}(L) \equiv \dot{\mathbf{r}}(L)$ on the unit sphere is Brownian. For chains defined by functional integrals, equations which resembles eq 2.7 have been derived by S. F. Edwards [*Disc. Faraday Soc.*, 49 (1970)] and K. S. Freed [*Advan. Chem. Phys.*, **22**, 1 (1970)]. The difference comes from the fact that the Kratky-Porod chain is not Gaussian (with correlations) as those chains.

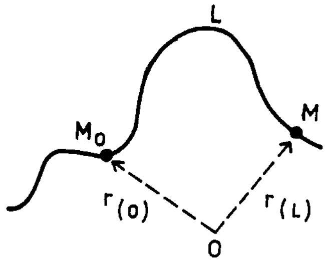

Figure 1. A random chain. L is the distance M_0M measured along the chain.

where Δ_s is a Laplacian defined on the sphere $|\mathbf{t}| = 1$.

Thus

$$\Delta_s = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\right] \tag{2.8}$$

Now, we introduce the functions

$$G^+(p,\cos\theta) = \int_0^{+\infty} F(\mathbf{p},\mathbf{t};L)\mathrm{d}L$$

$$G^-(p,\cos\theta) = \int_{-\infty}^{0} F(\mathbf{p},\mathbf{t};L)\mathrm{d}L = [G^+(p,\cos\theta)]^* \tag{2.9}$$

and

$$G(p,\cos\theta) = G^+(p,\cos\theta) + G^-(p,\cos\theta) \tag{2.10}$$

We note that

$$\begin{aligned} F(\mathbf{p},\mathbf{t};0) &= \frac{1}{4\pi} \\ F(\mathbf{p},\mathbf{t};+\infty) &= 0 \end{aligned} \tag{2.11}$$

and therefore by integrating eq 10 from 0 to $+\infty$ (and from $-\infty$ to 0), we obtain

$$\begin{aligned} [2ip\cos\theta + \Delta_s]G^+(p,\cos\theta) &= -1/2\pi \\ [-2ip\cos\theta + \Delta_s]G^-(p,\cos\theta) &= -1/2\pi \end{aligned} \tag{2.12}$$

From eq 2.2, 2.9, and 2.10, we deduce

$$S(p) = 2\pi\int_0^{\pi} G(p,\cos\theta)\sin\theta\mathrm{d}\theta \tag{2.13}$$

and finally by setting

$$u = \cos\theta$$

we obtain the following set of equations, which form the basis of our study of $S(p)$

$$G(p,u) = G^+(p,u) + G^-(p,u) \tag{2.14}$$

$$[2ipu + \Delta_s]G^+(p,u) = -1/2\pi \tag{2.15}$$

$$[-2ipu + \Delta_s]G^-(p,u) = -1/2\pi \tag{2.16}$$

with

$$\Delta_s = (1-u^2)\frac{\partial^2}{\partial u^2} - 2u\frac{\partial}{\partial u}$$

and

$$S(p) = 2\pi\int_{-1}^{1} G(p,u)\mathrm{d}u \tag{2.17}$$

Asymptotic Behavior of $S(p)$ for Large Values of p

In this section, we want to show that, when $p \to \infty$

$$p^2S(p) \simeq \pi p + \frac{2}{3} \tag{3.1}$$

The first term can be easily obtained by remarking that, when $p \to \infty$, the parts of the chain which are important are those for which L is small. But, for such values of L, the chain may be considered as a straight line and for a rigid rod, it is easy to show that

$$S(p) = \pi/p \tag{3.2}$$

More elaborate considerations are necessary for obtaining the second term which can be found as follows.

When p is large, two regions in u space have to be considered; either $up^{1/3} = 0(1)$ or $|up^{1/3}| \gg 1$. In the first region, we may set

$$\begin{aligned} u &= p^{-1/3}v \\ G(p,u) &= p^{-2/3}H(p,v) \end{aligned} \tag{3.3}$$

Thus eq 2.15 becomes

$$\left(2iv + \frac{\partial^2}{\partial v^2}\right)H^+ + \frac{1}{2\pi} = p^{-2/3}\left(v^2\frac{\partial^2}{\partial v^2} + 2v\frac{\partial}{\partial v}\right)H^+ \tag{3.4}$$

If v remains of order one, the member on the right-hand side may be dropped; then, the solution $H(v)$ becomes independent of p. The corresponding equation can be solved by introducing the Fourier transform

$$h(k) = \int_{-\infty}^{+\infty} \mathrm{d}v e^{-ikv}H(v) \tag{3.5}$$

We obtain the equation

$$\left[2\frac{\partial}{\partial k} + k^2\right]h^+(k) = \delta(k) \tag{3.6}$$

and its solution is

$$h^+(k) = \frac{1}{2}\Theta(k)e^{-k^3/6} \tag{3.7}$$

(where $\Theta(k)$ is the step function).

In the same way, we have

$$h^-(k) = \frac{1}{2}\Theta(-k)e^{k^3/6} \tag{3.8}$$

Adding these results, we find

$$h(k) = \frac{1}{2}e^{-|k|^3/6} \tag{3.9}$$

Thus, for $up^{1/3} = 0(1)$

$$G(p,u) \simeq G_0(p,u) \equiv p^{-2/3}H(p^{1/3}u) \tag{3.10}$$

where $H(v)$ is the Fourier transform of $h(k)$ and we have also

$$\int_{-\infty}^{+\infty} G_0(p,u)\mathrm{d}u = p^{-1}\int_{-\infty}^{+\infty} H(v)\mathrm{d}v = p^{-1}h(0) = 1/2p \tag{3.11}$$

In the second region ($|up^{1/3}| \gg 1$), the terms which have been dropped in eq 3.4 are not negligible.

There, $G^+(p,u)$ and $G_0{}^+(p,u)$ satisfy different equations (the second equation coincides with the equation obtained by dropping the right-hand side of eq 3.4)

$$\begin{aligned} \left[2ipu + (1-u^2)\frac{\partial^2}{\partial u^2} - 2u\frac{\partial}{\partial u}\right]G^+(p,u) &= -1/2\pi \\ \left[2ipu + \frac{\partial^2}{\partial u^2}\right]G_0{}^+(p,u) &= -1/2\pi \end{aligned} \tag{3.12}$$

However, in this region, both solutions can be expanded with respect to $1/p$. Accordingly, we find

$$G^{+}(p,u) \simeq G_0^{+}(p,u) \simeq \frac{i}{4\pi pu} - \frac{1}{4\pi p^2u^4} \qquad (3.13)$$

and it turns out, by chance, that the first two terms of each expansion are the same (but it would not be true for the next terms). Consequently

$$G(p,u) \simeq G_0(p,u) \simeq -\frac{1}{2\pi p^2u^4} \qquad (3.14)$$

Thus, to this order of approximation

$$G(p,u) \simeq G_0(p,u) \qquad (3.15)$$

for any value of u.

Therefore, using eq 2.13, 3.15, 3.11, and 3.14 we find for $p \gg 1$

$$\begin{aligned} S(p) &= 2\pi\int_{-1}^{1} G_0(p,u)\mathrm{d}u \\ &= \pi p^{-1} - 4\pi\int_{1}^{\infty} G_0(p,u)\mathrm{d}u \qquad (3.16) \\ &= \frac{\pi}{p} + \frac{2}{3p^2} \end{aligned}$$

as announced, and this result is in perfect agreement with the machine calculations described in the next sections.

Representation of $S(p)$ by a Continued Fraction. Expansion of $S(p)$ for Small Values of p

The solutions of eq 2.15 and 2.16 can be expressed in terms of spherical harmonics, *i.e.*, we may set

$$G^{+}(p,u) = \frac{1}{4\pi}\sum_{n=0}^{\infty} A_n(p)P_n(u) \qquad (4.1)$$

Bringing this expansion in eq 2.15 and using well-known properties of the Legendre Polynomials,[9] namely

$$\Delta_s P_n(u) = -n(n+1)P_n(u) \qquad (4.2)$$

$$(2n+1)uP_n(u) = (n+1)P_{n+1}(u) + nP_{n-1}(u) \qquad (4.3)$$

we obtain the equation

$$ip\left[\left(\frac{n+1}{2n+3}\right)A_{n+1}(p) + \left(\frac{n}{2n-1}\right)A_{n-1}(p)\right] - \frac{n(n+1)}{2}A_n(p) = -\delta_{n0} \qquad (4.4)$$

In particular, we find (for $n = 0$)

$$A_1(p) = 3i/p \qquad (4.5)$$

on the other hand, from eq 2.17, we deduce

$$S(p) = A_0(p) + A_0^{*}(p) \qquad (4.6)$$

$$\left(\text{since} \int_{-1}^{1}\mathrm{d}uP_n(u) = 2\delta_{n0}\right)$$

Now, it appears convenient to set

$$c_n(p) = \frac{ip}{(n+1/2)(n+2)}\frac{A_n(p)}{A_{n+1}(p)} \qquad (4.7)$$

These quantities obey the recurrence relation

$$c_n(p) = 1 + \frac{p^2}{(n+1)(n+3)(n+3/2)(n+5/2)}\frac{1}{c_{n+1}(p)} \qquad (4.8)$$

which has the advantage of being real.

Using eq 4.5, 4.6, and 4.7, we find also

$$S(p) = 6p^{-2}c_0(p) \qquad (4.9)$$

Thus, we can use eq 4.8 for obtaining an expansion of $S(p)$ for small p. The first two terms are

$$S(p) = \frac{6}{p^2} + \frac{8}{15} + 0(p^2) \qquad (4.10)$$

The first term is trivial and may be obtained directly by remarking that, for small values of p, very large values of L are important, thus for small p, the chain can be considered as Brownian (with $[r(L) - r(0)]^2 = 2Lb$), and the first term of $S(p^2)$ corresponds to this Brownian case.

As we see, it is not difficult to write more terms; however, it is better to represent $S(p)$ by the continued fraction defined by eq 4.9 and 4.8.

Iteration of the Continued Fraction

Approximate values of $c_0(p)$ can be obtained by choosing for $c_N(p)$ an arbitrary positive value $c'_N(p)$ and by using the recurrence relation (4.8) for calculating, step by step, the N functions $c'_{N-1}(p), \ldots, c'_0(p)$. In particular, we may immediately choose a value $c'_N(p) \geq 1$, since, in any case, $c'_n(p) \geq 1$ for any n ($n > N$). In any finite domain, $p < p_0$ and for any value of $c'_n(p)$, $c'_0(p)$ converges uniformly to $c_0(p)$, the sum of the continued fraction. This result can be established by using general theorems[10] and may also be derived as follows.

If $c'_N(p)$ and $c''_N(p)$ are two different starting values (with $c'_N(p) > 1$, $c''_N(p) > 1$), we see immediately that $1 < c'_{N-1} < 1 + p^2N^4$ and the same is true for c''_{N-1}, so that

$$|c''_{N-1}(p) - c''_{N-1}(p)| < \frac{p^2}{N^4} \qquad (5.1)$$

On the other hand, we have

$$|c'_{n-1}(p) - c''_{n-1}(p)| < \frac{p^2}{n^4}|c'_n(p) - c''_n(p)| \qquad (5.2)$$

These inequalities give

$$|c'_0(p) - c''_0(p)| < \frac{p^2N}{[N!]^4} \qquad (5.3)$$

Thus, the process converges very quickly when $N \to \infty$. In particular, the relation remains true, if $c''_N(p)$ coincides with the exact value $c_N(p)$ and, therefore, we have also

$$|c'_0(p) - c_0(p)| < \frac{p^2N}{[N!]^4} \qquad (5.4)$$

Still, for practical calculations, it is better to use a good starting function $c_N(p)$.

We remark that for $p \gg 1$, according to eq 3.15, 4.9, and 4.8 we have

$$c_0(p) \simeq \pi p/6$$

$$c_n(p)c_{n+1}(p) \simeq \frac{p^2}{(n+1)(n+3)(n+3/2)(n+5/2)} \qquad (5.5)$$

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[9] See, for instance, I. S. Gradshtein and J. M. Ryzhik, "Table of Integrals, Series and Products," Academic Press, New York, N.Y., 1965.

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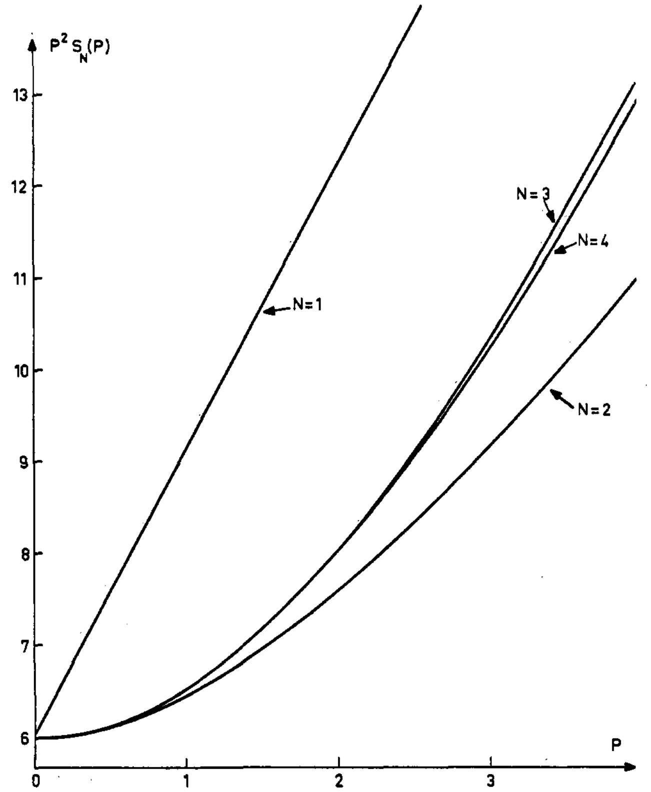

Figure 2. Successive approximations $S_N(p)$ of $S(p)$ obtained by the iteration method. The curve corresponding to N = 5, nearly coincides with the curve N = 4 and, for this reason, has not been drawn.

The solution of this equation is

$$c^{\infty}{}_n(p) \simeq \frac{p}{(n + 2)(n + 3/2)} \frac{(n/2 - 1/2)!(n/2 + 1/2)!}{[(n/2)!]^2} \quad (5.6)$$

Therefore, in order to start from a value $c_N(p)$, nearly exact, both for small and large values of p, we may choose as starting value for $c_N(p)$

$$c_N(p) = 1 + c^{(\infty)}{}_N(p) \quad (5.7)$$

The corresponding approximations $S_N(p)$ of $S(p)$ for N = 1, 2, 3 are given by

$$p^2S_1(p) = 6 + \pi p$$

$$p^2S_2(p) = 6\left[\frac{1 + (8/15\pi)p + (4/45)p^2}{1 + (8/15\pi)p}\right]$$

$$p^2S_3(p) = 6\left[\frac{1 + (3\pi/112)p + (13/126)p^2 + (\pi/420)p^3}{1 + (3\pi/112)p + (1/70)p^2}\right] \quad (5.8)$$

The functions $p^2S_N(p)$ are plotted on Figure 2 and the function $p^2S(p)$ on Figure 3. Exact values of $p^2S(p)$ obtained by machine calculation of $S_N(p)$ for large values of N, are given in Table I.

Thus the function $S(p)$ is completely and precisely known for all values of p and can be conveniently used for testing scattering experiments by polymer chains.

Discussion

Our results are in good agreement with the calculations made by Peterlin[2] and by Heine, Kratky, Porod, and Schmitz.[3]

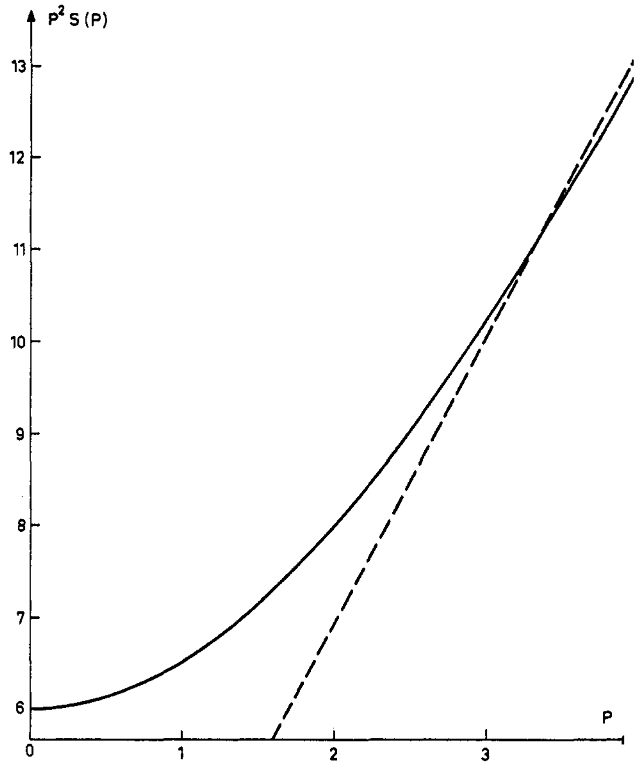

Figure 3. The exact function $S(p)$ with its asymptote (dotted line) of equation $S = \pi p + 2/3$.

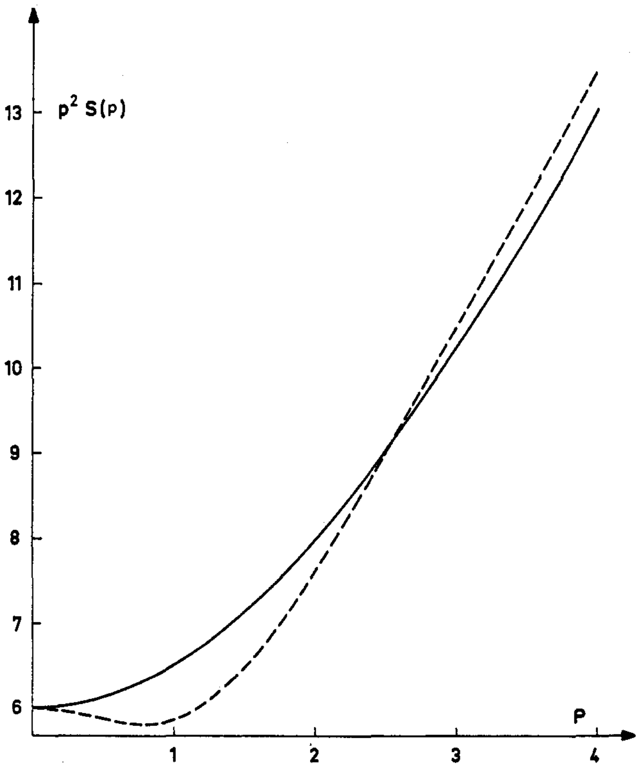

Figure 4. The exact function $S(p)$ (solid line) and the values obtained by using the approximation of Heine, Kratky, Porod, and Schmitz for $L \to \infty$ (dotted line).

Our function $p^2S(P)$ is to be compared with the function $2Zt^2P(t)$ of Peterlin where, in our notation, $t = p$ and $Z = L/2a$. For finite chains as those studied by Peterlin, the form factor is finite for $p = 0$ and therefore its product by p^2 vanishes quadratically at the origin. Thus, for small

Table I

p	$p^2S(p)$	p	$p^2S(p)$	p	$p^2S(p)$	p	$p^2S(p)$
0.2	6.021	1.2	6.752	2.2	8.417	3.2	10.789
0.4	6.085	1.4	7.017	2.4	8.843	3.4	11.326
0.6	6.191	1.6	7.317	2.6	9.295	3.6	11.879
0.8	6.338	1.8	7.652	2.8	9.772	3.8	12.446
1	6.525	2	8.019	3	10.270	4	13.026

p, no comparison is possible, but for $p > 2$ and $Z > 10$, the values obtained by Peterlin coincide with ours to a few per cent. Peterlin remarked that for large values of q, the curve becomes nearly a straight line pointing through the origin. We note that, in the limit $L \rightarrow \infty$, this statement is only approximate; the asymptote of the curve representing $q^2S(q)$ does not pass through the origin but only in the vicinity (actually $\frac{2}{3}$ is rather small compared with 6, the lower bound of $p^2S(p)$).

On the other hand, in the limit $L \rightarrow \infty$, the approximation of Heine, Kratky, Porod, and Schmitz leads to values of $p^2S(p)$ which are not very different from ours (see Figure 4) and in the range $0 < p < 4$, the error is only of the order of five per cent.

The method used here gives exact results and therefore is more powerful in this limit but it is not so easy to extend it to the case of finite chains.

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Translational Friction Coefficient of Wormlike Chains

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ABSTRACT: The translational friction coefficient of stiff chains without excluded volume is evaluated by an application of the Oseen–Burgers procedure of hydrodynamics to wormlike cylinder models. Some comments on polymer hydrodynamics are given in connection with Ullman's criticism on the Hearst–Stockmayer theory for wormlike bead models. The mean reciprocal distance between a point on the cylinder surface and a point on the cylinder axis is required for the present calculation, and is evaluated using the second Daniels approximation to the distribution function together with the cubic approximation. In order to test this approximation, numerical results obtained for the mean reciprocal distance by the use of a computer are also presented. The final results may be written in terms of only the chain contour length, the Kuhn statistical segment length λ^{-1}, and the molecular diameter d. Estimates of $\lambda^{-1} = 1300 \pm 50$ Å and $d = 25 \pm 1$ Å are obtained for DNA by an analysis of its sedimentation coefficients on the basis of the present theory.

The wormlike chain model of Kratky and Porod[1] has very often been adopted as a useful approximation to the equilibrium and nonequilibrium behavior of stiff chain macromolecules such as DNA and cellulose derivatives in solution. The study of the distribution functions for wormlike chains was made first by Daniels,[2] and subsequently by Hermans and Ullman[3] and others.[4,5] In particular, the Daniels distribution function has provided a basis for many investigations of the physical properties, for instance, the hydrodynamic properties of stiff chains. Recently, Gobush and his collaborators[6a] have derived the asymptotic solution for the bivariate distribution function of the position and tangent vectors at the end point of the chain in an approximation higher than the Daniels approximation, and Yamakawa and Stockmayer[6b] have applied it to a calculation of the expansion factor and second virial coefficient for wormlike chains with small excluded volume. The object of the present paper is to apply the same distribution function further to a calculation of the translational friction coefficient, which is related to the sedimentation and diffusion coefficients. The intrinsic viscosity will be studied in the next paper, for convenience.

The first hydrodynamic theories for wormlike chains were developed independently by Peterlin,[7] by Hearst and Stockmayer,[8] and by Ptitsyn and Eizner.[9] These investigators calculated the sedimentation coefficient for wormlike bead models on the basis of the Kirkwood general theory[10] of transport in polymer solutions but with the use of somewhat different approximations to the mean reciprocal distance between two points on the chain contour. Further investigations along this line were later made by many workers.[11] However, such bead models were criticized by Ullman[12,13] from the point of view of classical hydrodynamics. For the reason stated below, he adopted wormlike cylinder models, instead of bead models, to calculate the intrinsic viscosity[12] and translational friction coefficient[13] on the basis of the Kirkwood–Riseman theory.[14]

Now, Ullman's criticism on the Kirkwood procedure for bead models is the following. The Kirkwood procedure assumes that hydrodynamic interaction exists between any two beads but does not within a given bead, and this assumption leads to the manifestly absurd result that all final equations are written in terms of an arbitrarily chosen bond length between contiguous beads. However, it

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