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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(3) J. J. Hermans and R. Ullman, *Physica*, **18,** 951 (1952).

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(6) (a) W. Gobush, H. Yamakawa, W. H. Stockmayer, and W. S. Magee, *J. Chem. Phys.*, **57,** 2839 (1972); (b) H. Yamakawa and W. H. Stockmayer, *ibid.*, **57,** 2843 (1972).

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(8) J. E. Hearst and W. H. Stockmayer, *J. Chem. Phys.*, **37,** 1425 (1962).

(9) O. B. Ptitsyn and Yu. E. Eizner, *Vysokomol. Soedin.*, **3,** 1863 (1961); *Dokl. Acad. Nauk SSSR*, **142,** 134 (1962).

(10) J. G. Kirkwood, *Recl. Trav. Chim.*, **68,** 649 (1949); *J. Polym. Sci.*, **12,** 1 (1954).

(11) See, for example, H. Yamakawa, "Modern Theory of Polymer Solutions," Harper & Row, New York, N. Y., 1971, Chapter VI.

(12) R. Ullman, *J. Chem. Phys.*, **49,** 5486 (1968).

(13) R. Ullman, *J. Chem. Phys.*, **53,** 1734 (1970).

(14) J. G. Kirkwood and J. Riseman, *J. Chem. Phys.*, **16,** 565 (1948).

seems to us that his criticism is not correct for at least two reasons. First, the Kirkwood procedure[10,14] gives correctly Stokes' law for a single bead in a uniform and constant unperturbed solvent flow field provided that the bead possesses a Stokes diameter. Second, from the point of view of classical hydrodynamics, all final results should rather be written in terms of the dimensions of a given system, *i.e.*, the diameter of each bead and the spacing, or the spatial distribution of beads, for the present case. Thus, the Kirkwood procedure for bead models is not unphysical except that the Zwanzig singularities[15] occur. However, it is known that fortunately these singularities disappear apparently because of the mathematical approximations, *e.g.*, the preaveraging of the Oseen tensor. Rather, a defect of the Hearst-Stockmayer theory[8] for bead models is concerned with its practical application to experimental data; it does not give correct numerical results, particularly in the limit of rods, for the sums in the Kirkwood formula are inappropriately replaced by integrals. In the previous paper,[16] we have shown that when treated carefully, touched-bead models for rods give numerical results which do not appreciably differ from those obtained by an application of the Oseen-Burgers procedure[17,18] to continuous cylinder models.[19,20] By the term "Oseen-Burgers procedure," we mean a convenient method in classical hydrodynamics for calculating frictional forces from the requirement, or the boundary condition, that the mean relative velocity of a fluid be zero over any cross section of a body.

Although Ullman[12,13] adopted continuous cylinder models, the method he used is not the Oseen-Burgers procedure as defined above and his formulation is not correct, as shown in section I. In fact, his final results are written in terms of not only molecular dimensions but also a phenomenological friction constant per unit length along the cylinder axis. This is absurd, as is evident from the above discussion.

In section I, a correct application of the Oseen-Burgers procedure is made to wormlike cylinder models. Edwards and Oliver[21] have recently solved Stokes' equation of hydrodynamics for flexible Gaussian cylinders to calculate the translational friction coefficient. Although both methods require introduction of several mathematical approximations, the convenient procedure of Oseen and Burgers is amenable to subsequent rigorous mathematical treatments except the use of the well-known Kirkwood-Riseman approximations at least in the Gaussian coil limit. For this reason, we adopt the Oseen-Burgers procedure. The mean reciprocal distance is needed also in the present case. As is well known, its exact evaluation is impossible, and in section II, we carry out both approximate analytical and computer calculations. The final results are summarized in section III, and in section IV applied to a determination of molecular dimensions of DNA.

I. Formulation

Consider a wormlike cylinder of contour length L and radius a, and suppose that the center of mass possesses the translational velocity $\mathbf{U}$ in a solvent with viscosity coefficient η_0, whose unperturbed flow field is nonexistent. For convenience, all lengths appearing in all molecular properties are measured in units of the Kuhn statistical segment length λ^{-1}, the persistence length being $(2\lambda)^{-1}$. Following the Oseen-Burgers procedure, we replace the cylinder by a frictional force distribution $\mathbf{f}(x)$ per unit length along the cylinder axis as a function of the contour distance x from one end. As depicted in Figure 1, let $\mathbf{r}$ be the normal radius vector from the contour point x on the axis to an arbitrary point P which would be just located on the cylinder surface if the cylinder were present, so that

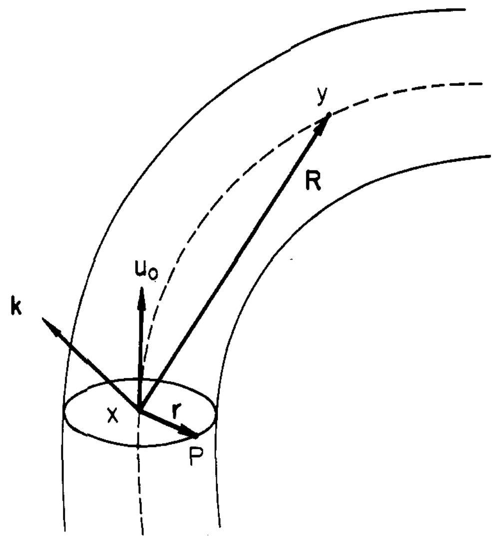

Figure 1. Wormlike cylinder model used for the hydrodynamic calculation on the basis of the Oseen-Burgers procedure.

$$|\mathbf{r}| = a \qquad \mathbf{r}\cdot\mathbf{u}_0 = 0 \tag{1}$$

with $\mathbf{u}_0$ the unit vector tangential to the axis at the point x, and let $\mathbf{R}$ be the distance between the contour points x and y. For an instantaneous configuration, the velocity $\mathbf{v}(P)$ of solvent at the point P relative to the velocity $\mathbf{U}$ of P may then be expressed as

$$\mathbf{v}(P) = -\mathbf{U} + \int_0^L \mathbf{T}(-\mathbf{R} + \mathbf{r})\cdot\mathbf{f}(y)\mathrm{d}y \tag{2}$$

where $\mathbf{T}$ is the Oseen tensor

$$\mathbf{T}(\mathbf{R}) = \frac{1}{8\pi\eta_0 R}\left(\mathbf{I} + \frac{\mathbf{RR}}{R^2}\right) \tag{3}$$

with $\mathbf{I}$ the unit tensor.

Now, the Oseen-Burgers procedure requires that values of $\mathbf{v}(P)$ averaged over a normal cross section of the cylinder vanish for all values of x ranging from 0 to L; that is

$$\langle\mathbf{v}(P)\rangle_{(\mathbf{r})} = 0 \quad \text{for } 0 \leq x \leq L \tag{4}$$

where $\langle\rangle_{(\mathbf{r})}$ designates the average over $\mathbf{r}$, assuming its uniform distribution subject to the conditions given by eq 1. In eq 4, we have ignored end effects, as was done by Burgers[18] and Edwards and Oliver.[21] For an instantaneous configuration, we then have, from eq 2 and 4

$$\int_0^L \langle\mathbf{T}(-\mathbf{R} + \mathbf{r})\rangle_{(\mathbf{r})}\cdot\mathbf{f}(y)\mathrm{d}y = \mathbf{U} \tag{5}$$

Next, we must take the configurational average. In doing this, we preaverage the Oseen tensor, for simplicity

$$\langle\mathbf{T}(-\mathbf{R} + \mathbf{r})\rangle = \frac{1}{6\pi\eta_0}\langle|\mathbf{R} - \mathbf{r}|^{-1}\rangle\mathbf{I} \tag{6}$$

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(15) R. Zwanzig, J. Kiefer, and G. H. Weiss, *Proc. Nat. Acad. Sci. U. S.*, **60**, 381 (1968).

(16) H. Yamakawa and G. Tanaka, *J. Chem. Phys.*, **57**, 1537 (1972).

(17) C. W. Oseen, "Hydrodynamik," Akademische Verlagsgesellschaft, Leipzig, 1927.

(18) J. M. Burgers, "Second Report on Viscosity and Plasticity of the Amsterdam Academy of Sciences," Nordemann, New York, N. Y., 1938, Chapter 3.

(19) C. M. Tchen, *J. Appl. Phys.*, **25**, 463 (1954).

(20) S. Broersma, *J. Chem. Phys.*, **32**, 1632 (1960).

(21) S. F. Edwards and M. A. Oliver, *J. Phys. A, Gen. Phys.*, **4**, 1 (1971).

where we have simply designated the two averaging processes by the symbol ⟨⟩. Equation 5 then becomes

$$\int_0^L \langle|\mathbf{R} - \mathbf{r}|^{-1}\rangle\langle\mathbf{f}(y)\rangle \mathrm{d}y = 6\pi\eta_0\mathbf{U} \qquad (7)$$

If we define a function $\psi(y)$ by

$$\langle\mathbf{f}(y)\rangle = 6\pi\eta_0\psi(y)\mathbf{U} \qquad (8)$$

then from eq 7 and 8, there is obtained an integral equation satisfied by ψ

$$\int_0^L K(|x - y|)\psi(y)\mathrm{d}y = 1 \qquad (9)$$

with

$$K(|x - y|) \equiv \langle|\mathbf{R} - \mathbf{r}|^{-1}\rangle \qquad (10)$$

Now, the mean total frictional force ⟨**F**⟩ is given by

$$\langle\mathbf{F}\rangle = \int_0^L \langle\mathbf{f}(x)\rangle\mathrm{d}x = 6\pi\eta_0\mathbf{U}\int_0^L \psi(x)\mathrm{d}x \qquad (11)$$

and the translational friction coefficient Ξ is defined by

$$\langle\mathbf{F}\rangle = \Xi\mathbf{U} \qquad (12)$$

so that

$$\Xi = 6\pi\eta_0\int_0^L \psi(x)\mathrm{d}x \qquad (13)$$

If we use the Kirkwood–Riseman approximation[14] to solve the integral equation 9, we obtain

$$\Xi = 6\pi\eta_0 L^2\left[\int_0^L\int_0^L K(|x - y|)\mathrm{d}x\mathrm{d}y\right]^{-1} \qquad (14)$$

$$\frac{3\pi\eta_0 L}{\Xi} = L^{-1}\int_0^L (L - t)K(t)\mathrm{d}t \qquad (15)$$

with $|x - y| = t$. In the later sections, we evaluate Ξ on the basis of eq 15.

It is seen that the integral eq 9 does not contain the exceptional part $\psi(x)$ leading to the so-called draining term. On the other hand, it appears in the Kirkwood–Riseman integral equation for bead models and also in the Ullman integral equation for wormlike cylinder models. In fact, our eq 15 formally corresponds to the nondraining limit in the formulation of Ullman, and therefore does not contain the phenomenological friction constant ζ. Furthermore, Ullman has not explicitly stated the physical meaning of the kernel. As seen from eq 10, our kernel has the meaning of the mean reciprocal distance between a point on the cylinder surface and a point on the cylinder axis.

Very recently, Fujita[22] has applied the Oseen–Burgers procedure to flexible bead models. In this case, it is supposed that discrete point forces are distributed at the centers of beads, or small spheres, and average velocities at the surface of each bead are required to vanish. His integral equation contains an exceptional part $\psi(x)$ as in the Kirkwood–Riseman integral equation, though the kernels are somewhat different from each other. His final result in a first approximation is equivalent to that obtained previously by Yamakawa.[23] Therefore, we may draw the following conclusions:[24] (1) The occurrence of the draining term is peculiar to discrete bead models and it never appears for continuous cylinder models; (2) both the Kirkwood procedure and the Oseen–Burgers procedure give equivalent answers for bead models; and (3) the former procedure is therefore not unphysical except the occurrence of the Zwanzig singularities. Thus, both touched-bead models treated by the Kirkwood procedure and continuous cylinder models treated by the Oseen–Burgers procedure may be regarded as valid for wormlike chains, though somewhat different numerical results will be obtained from the two approaches.

II. Mean Reciprocal Distance

The problem is to evaluate the kernel, or the mean reciprocal distance, $K(t)$. However, it is impossible to do this exactly, and we therefore adopt the second Daniels approximation[6] to the distribution function together with the cubic approximation of Hearst and Stockmayer.[8] This approximation is tested with the use of computer values.

Theoretical Evaluation. It is evident that in the limit $t \to 0$ (rods)

$$\lim_{t\to 0} K(t) \equiv K_0(t) = (t^2 + a^2)^{-1/2} \qquad (16)$$

In the case of $t \gg 1$, it is usual to expand $|\mathbf{R} - \mathbf{r}|^{-1}$ in terms of spherical harmonics in order to take the average over **r**. However, this expansion is not convenient in finding the subsequent average over **R**, and we must resort to a different method. Now, we recall the relation[21]

$$\mathbf{T}(-\mathbf{R} + \mathbf{r}) = \frac{1}{8\pi^3\eta_0}\int\left(\frac{k^2\mathbf{I} - \mathbf{kk}}{k^4}\right)\exp[i\mathbf{k}\cdot(\mathbf{R} - \mathbf{r})]\mathrm{d}\mathbf{k} \qquad (17)$$

From eq 6, 10, and 17, we have

$$K(t)\mathbf{I} = \frac{3}{4\pi^2}\int\left(\frac{k^2\mathbf{I} - \mathbf{kk}}{k^4}\right)\langle\exp[i\mathbf{k}\cdot(\mathbf{R} - \mathbf{r})]\rangle\mathrm{d}\mathbf{k} \qquad (18)$$

Clearly the average in the integrand must be a function of $|\mathbf{k}|$, and therefore eq 18 reduces to

$$K(t) = \frac{2}{\pi}\int_0^\infty \langle\exp[i\mathbf{k}\cdot(\mathbf{R} - \mathbf{r})]\rangle\mathrm{d}k \qquad (19)$$

Now, the average in eq 19, which we designate by $G(k;t)$, may be written in the form

$$G(k;t) \equiv \langle\exp[i\mathbf{k}\cdot(\mathbf{R} - \mathbf{r})]\rangle = \frac{1}{2\pi}\int \mathrm{d}\mathbf{R}\mathrm{d}\mathbf{u}_0 P(\mathbf{R},\mathbf{u}_0;t)\exp(i\mathbf{k}\cdot\mathbf{R})\int' \mathrm{d}\mathbf{r}\ \exp(-i\mathbf{k}\cdot\mathbf{r}) \qquad (20)$$

where $P(\mathbf{R},\mathbf{u}_0;t)$ is the distribution of the end-to-end vector **R** and the initial unit tangent vector $\mathbf{u}_0$ for the chain of contour length t, and the prime on the integration sign indicates that the integration is carried out under the conditions given by eq 1. In this paper, we do not consider the excluded-volume effect, and therefore P is the unperturbed distribution. If we introduce the Fourier transform, or the characteristic function, I of the conditional distribution function $P(\mathbf{R}|\mathbf{u}_0;t)$

$$I(\mathbf{k}|\mathbf{u}_0;t) = \int P(\mathbf{R}|\mathbf{u}_0;t)\exp(i\mathbf{k}\cdot\mathbf{R})\mathrm{d}\mathbf{R} \qquad (21)$$

with

$$P(\mathbf{R}|\mathbf{u}_0;t) = 4\pi P(\mathbf{R},\mathbf{u}_0;t) \qquad (22)$$

then eq 20 may be rewritten in the form

$$G(k;t) = \frac{1}{8\pi^2}\int \mathrm{d}\mathbf{u}_0 I(\mathbf{k}|\mathbf{u}_0;t)\int' \mathrm{d}\mathbf{r}\ \exp(-i\mathbf{k}\cdot\mathbf{r}) \qquad (23)$$

When we perform the integration over **r** and **R**, we choose $\mathbf{u}_0$ in the direction of the z axis of the Cartesian coordinate system, and use spherical polar coordinates

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(22) H. Fujita, private communication.

(23) H. Yamakawa, *J. Chem. Phys.*, **53**, 436 (1970).

(24) We have arrived at these conclusions through discussions with H. Fujita.

$$\mathbf{u}_0 = \mathbf{e}_z$$
$$\mathbf{k} = (k,\theta_0,\varphi_0) \quad \varphi_0 = 0$$
$$\mathbf{r} = (a,\theta,\varphi) \quad \theta = \frac{\pi}{2}$$
$$\mathbf{R} = (R,\Theta,\Phi) \tag{24}$$

The integral over $\mathbf{r}$ in eq 23 may then be evaluated as

$$\int' \exp(-i\mathbf{k}\cdot\mathbf{r})\mathrm{d}\mathbf{r} = \int_0^{2\pi} \exp(-iak \sin\theta_0 \cos\varphi)\mathrm{d}\varphi = 2\pi J_0(ak \sin\theta_0) \tag{25}$$

where J_0 is the Bessel function of the zeroth order

$$J_0(x) = \frac{2}{\pi}\int_0^1 \frac{\cos xt}{(1-t^2)^{1/2}}\mathrm{d}t \tag{26}$$

Note that we have put $\varphi_0 = 0$ since the characteristic function I is independent of φ_0, as shown below.

Further, the conditional distribution P, which was previously obtained in the second Daniels approximation,[6] reads in the present notation

$$P(\mathbf{R}|\mathbf{u}_0;t) = \left(\frac{1}{2\pi t}\right)^{3/2} \exp\left(-\frac{3R^2}{2t}\right)\Bigg[1 - \frac{5}{8t} + \frac{2R^2}{t^2} - \frac{33R^4}{40t^3} - \frac{79}{640t^2} - \frac{329R^2}{240t^3} + \frac{6799R^4}{1600t^4} - \frac{3441R^6}{1400t^5} + \frac{1089R^8}{3200t^6} + \left(\frac{3R}{2t} - \frac{25R}{16t^2} + \frac{153R^3}{40t^3} - \frac{99R^5}{80t^4}\right)P_1(\cos\Theta) + \left(\frac{R^2}{2t^2} - \frac{67R^2}{60t^3} + \frac{961R^4}{560t^4} - \frac{33R^6}{80t^5}\right)P_2(\cos\Theta) + \frac{3R^3}{40t^3}P_3(\cos\Theta) + \frac{9R^4}{1400t^4}P_4(\cos\Theta) + \cdots\Bigg] \quad \text{for } t \gg 1 \tag{27}$$

The characteristic function I has also been obtained previously, though not given explicitly, in the course of the derivation of P; it reads in the second Daniels approximation

$$I(\mathbf{k}|\mathbf{u}_0;t) = \exp\left(-\frac{1}{6}tk^2\right)\Bigg(1 + \frac{1}{9}k^2 - \frac{11}{1080}tk^4 + \frac{917}{43{,}200}k^4 - \frac{19}{7560}tk^6 + \frac{121}{2{,}332{,}800}t^2k^8 - \frac{1}{12}k^2\cos^2\theta_0 - \frac{31}{2160}k^4\sin^2\theta_0\cos^2\theta_0 - \frac{121}{8640}k^4\cos^4\theta_0 + \frac{11}{12{,}960}tk^6\cos^2\theta_0 + \frac{1}{2}ik\cos\theta_0 + \frac{11}{144}ik^3\sin^2\theta_0\cos\theta_0 + \frac{5}{72}ik^3\cos^3\theta_0 - \frac{11}{2160}itk^5\cos\theta_0 + \ldots\Bigg) \quad \text{for } t \gg 1 \tag{28}$$

where we have retained terms of $0(t^{-2})$. Note that $k^2 = 0(t^{-1})$. Since I is independent of φ_0, it is convenient to change the direction of the z axis from $\mathbf{u}_0$ to $\mathbf{k}$ in order to perform the integration over $\mathbf{u}_0$ in eq 23. Thus, from eq 19, 20, 23, and 25, $K(t)$ may be written in the form

$$K(t) = \frac{1}{\pi}\int_0^\infty\int_0^\pi \sin\theta_0 J_0(ak\sin\theta_0)I(\mathbf{k}|\mathbf{u}_0;t)\mathrm{d}k\mathrm{d}\theta_0 \tag{29}$$

We first consider the limit $t \to \infty$ (coil limit), for convenience. From eq 28, we have

$$\lim_{t\to\infty} I(\mathbf{k}|\mathbf{u}_0;t) = \exp\left(-\frac{1}{6}tk^2\right) \tag{30}$$

Substitution of eq 30 into eq 29 and integration leads to

$$\lim_{t\to\infty} K(t) \equiv K_\infty(t) = \left(\frac{6}{\pi t}\right)^{1/2} {}_1F_1\left(\frac{1}{2},\frac{3}{2};-\frac{3a^2}{2t}\right) \tag{31}$$

Table I
Computer Values of $tK(t)$ of the Discrete Chain with $d = 0.005$ for Various Sets of Parameter Values

n	l	t	$\cos\theta$	m	$tK(t)$
500	0.0002	0.1	0.9996	788	1.0345
200	0.0005	0.1	0.999	469	1.0328
50	0.002	0.1	0.996	1000	1.0336
10	0.01	0.1	0.980	2000	1.0330
80	0.01	0.8	0.980	2000	1.3142
40	0.02	0.8	0.960	4000	1.3196
20	0.04	0.8	0.920	2000	1.3148
20	0.04	0.8	0.920	3000	1.3195
20	0.04	0.8	0.920	4000	1.3203

where ${}_1F_1$ is a hypergeometric function defined by

$${}_1F_1(\alpha;\gamma;z) = \frac{\Gamma(\gamma)}{\Gamma(\alpha)}\sum_{n=0}^{\infty}\frac{\Gamma(\alpha+n)z^n}{\Gamma(\gamma+n)n!} \tag{32}$$

with $\Gamma(\alpha)$ the gamma function. It can be shown that the expansion of $K_\infty(t)$ given by eq 31 and 32 is identical with that of the error function; and we find

$$K_\infty(t) = \frac{1}{a}\,\mathrm{erf}\left(\frac{3a^2}{2t}\right)^{1/2} \tag{33}$$

where erf (x) is defined by

$$\mathrm{erf}(x) = \frac{2}{\pi^{1/2}}\int_0^x \exp(-t^2)\mathrm{d}t \tag{34}$$

Next, in order to find the second Daniels approximation to $K(t)$, we expand the Bessel function in eq 29 as

$$J_0(ak\sin\theta_0) = 1 - \frac{1}{4}a^2k^2\sin^2\theta_0 + \frac{1}{64}a^4k^4\sin^4\theta_0 - \cdots \tag{35}$$

up to terms of $0(t^{-2})$. Substitution of eq 35 into eq 29 and integration leads to

$$K(t) = \left(\frac{6}{\pi t}\right)^{1/2}\left[1 - \frac{1}{40t}(1 + 20a^2) - \frac{73}{4480t^2}\left(1 - \frac{1176a^2}{73} - \frac{1008a^4}{73}\right) + \cdots\right] \quad \text{for } t \gg 1 \tag{36}$$

We note that the expansion given by eq 36 becomes identical with that of $K_\infty(t)$ given by eq 33 if we retain only terms $(a^2/t)^m$ in eq 36 for a and $t \to \infty$.

Now, we join the $K(t)$ given by eq 36 and the $K_0(t)$ given by eq 16 to complete an approximate expression for $K(t)$ valid for all values of $t(\geq 0)$, following the procedure of Hearst and Stockmayer.[8] That is

$$\begin{aligned} K(t) &= \left(\frac{6}{\pi t}\right)^{1/2}\left[1 - \frac{1}{40t}(1 + 5d^2) - \frac{73}{4480t^2}\left(1 - \frac{294d^2}{73} - \frac{63d^4}{73}\right)\right] \quad \text{for } t > \sigma \\ &= \left(t^2 + \frac{1}{4}d^2\right)^{-1/2}(1 + f_1t + f_2t^2 + f_3t^3) \quad \text{for } t \leq \sigma \end{aligned} \tag{37}$$

where we have used the diameter $d = 2a$ instead of a, for convenience. We determine the constants σ and f_i in such a way that the two $K(t)$'s have the same first and second derivatives at their intersection $t = \sigma$. Then, σ and f_i become functions of d. For simplicity, however, we adopt the value of σ at $d = 0$ for all values of d. Further, we expand f_i in terms of d and retain terms up to d^4 since $d < 1$ for real stiff and flexible chains (with finite stiffness). Indeed, the $K(t)$ given by eq 37 becomes invalid for large d except in the range of $t \gg 1$. With the use of the known relation $f_1 = 1/3$ at $d = 0$,[8] we can then obtain the results

$$\begin{aligned} \sigma &= 2.278 \\ f_1 &= 0.3333 + 0.04080d^2 + 0.004898d^4 + 0(d^6) \\ f_2 &= 0.1130 - 0.04736d^2 - 0.002270d^4 + 0(d^6) \\ f_3 &= -0.02447 + 0.009666d^2 + 0.0002060d^4 + 0(d^6) \end{aligned} \tag{38}$$

Computer Calculations. Consider a freely rotating chain composed of n bonds of length l joined with complementary bond angle θ. It is well known that the wormlike chain composed of n bonds of length l joined with comple- from this discrete chain by letting

$$\begin{aligned} n &\longrightarrow \infty \\ l &\longrightarrow 0 \\ \theta &\longrightarrow 0 \end{aligned} \tag{39}$$

subject to the conditions

$$\begin{aligned} nl &= t \\ 1 - \cos\theta &= 2l \end{aligned} \tag{40}$$

Therefore, we may replace wormlike chains approximately by discrete chains having very small but finite θ and satisfying the conditions given by eq 40, and calculate numerically the mean reciprocal distance and also various moments.

Now, consider a Cartesian coordinate system ($\mathbf{e}_{xj}$, $\mathbf{e}_{yj}$,$\mathbf{e}_{zj}$) associated with the jth bond of the discrete chain, and assume that the j+1th bond vector is given by $\mathbf{r}_{j+1} = (l,0,0) \equiv \mathbf{l}$ (column vector) in its own coordinate system. The j+1th coordinate system may be transformed to the jth one by the transformation matrix $\mathbf{T}_j(\theta,\phi_j)$,[25] where ϕ_j designates the rotational states of the jth bond. When we calculate the moments, the first bond vector $\mathbf{r}_1$ may be fixed. The distribution of the end of the nth bond will then be cylindrically symmetric about $\mathbf{r}_1$. It is therefore convenient to make the first coordinate system ($\mathbf{e}_{x1}$, $\mathbf{e}_{y1}$,$\mathbf{e}_{z1}$) coincide with an external coordinate system ($\mathbf{e}_x$, $\mathbf{e}_y$,$\mathbf{e}_z$). Further, the normal radius vector $\mathbf{r}$ may be fixed so as to satisfy the condition, $\mathbf{r}\cdot\mathbf{u}_0 = \mathbf{r}\cdot\mathbf{e}_x = 0$. Thus we choose $\mathbf{r}$ in the direction of $\mathbf{e}_y$, for convenience. In matrix notation, we then have

$$\mathbf{R} - \mathbf{r} = \sum_{i=2}^{n} \prod_{j=1}^{i-1} \mathbf{T}_j(\theta,\phi_j)\mathbf{l} + \begin{pmatrix} l \\ -d/2 \\ 0 \end{pmatrix} \tag{41}$$

We can calculate $|\mathbf{R} - \mathbf{r}|^{-1}$, $\mathbf{R}\cdot\mathbf{u}_0$, and R^{2k} from eq 41, and then their statistical averages, generating random numbers in the ranges $0 \leq \phi_j \leq 2\pi$ ($j = 1, \cdots, n$) on a computer. Practically we generate random numbers with sine and cosine distributions by the rejection method,[26] since ϕ_j appear as $\sin\phi_j$ and $\cos\phi_j$. All numerical computations have been carried out using a FACOM 230-60 digital computer at this University.

Our first problem is to test the wormlike nature of these discrete chains. For this purpose, we have calculated the product $tK(t)$ for various assigned values of the parameters satisfying the conditions given by eq 40, taking d as 0.005. (Note that the wormlike nature is independent of d.) The results are summarized in Table I, where m designates the number of generated chains. Clearly, the smaller $1 - \cos\theta$ is, the more wormlike the discrete chain is. However, it is seen that $tK(t)$ is rather insensitive to the model, or the value of θ, and also the value of m over the range examined. Thus, for convenience, we have chosen the two sets of parameter values: $l = 0.01$, $\cos\theta = 0.980$, $m = 2000$ for $0 < t < 0.8$ and $l = 0.04$, $\cos\theta = 0.920$, $m = 2000$ for $t \geq 0.8$. Further, we have tested the wormlike nature with respect to the moments $\langle\mathbf{R}\cdot\mathbf{u}_0\rangle$, $\langle R^2\rangle$, $\langle R^4\rangle$, and $\langle R^6\rangle$ whose exact values are known.[1,3,27] For example, the first two of them are given by

$$\langle\mathbf{R}\cdot\mathbf{u}_0\rangle = \frac{1}{2}(1 - e^{-2t}) \tag{42}$$

$$\langle R^2\rangle = t - \frac{1}{2}(1 - e^{-2t}) \tag{43}$$

The results are shown in Figure 2 for $\langle\mathbf{R}\cdot\mathbf{u}_0\rangle$ and in Figure 3 for $\langle R^{2k}\rangle/\langle R^{2k}\rangle_\infty$, where $\langle R^{2k}\rangle_\infty$ is the coil limit of $\langle R^{2k}\rangle$ for $t \rightarrow \infty$. The full curves and small circles represent the exact and computer values, respectively. The statistical fluctuations (relative errors) in these computer calculations are indicated by the vertical line segments in the figures; for example, ±2.4% for $\langle R^2\rangle$, ±3.9% for $\langle R^4\rangle$, ±5.3% for $\langle R^6\rangle$, and ±5.2% for $\langle\mathbf{R}\cdot\mathbf{u}_0\rangle$ at $t = 1.2$. The errors are seen to increase with increasing t. However, our discrete models are seen to represent wormlike chains very well within statistical fluctuations over the range studied.

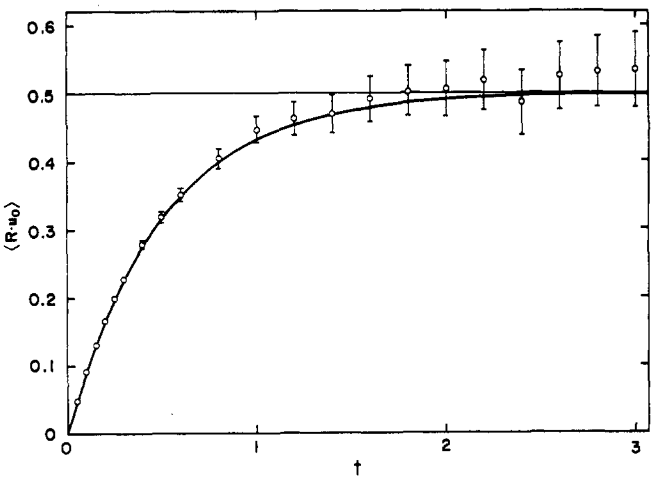

Figure 2. Computer values of the moment $\langle\mathbf{R}\cdot\mathbf{u}_0\rangle$ plotted against the contour length t. The full curve represents the exact values.

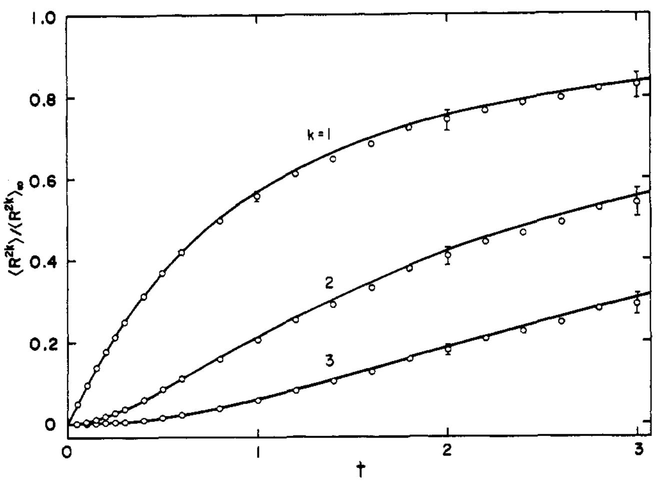

Figure 3. Computer values of the ratios of the moments $\langle R^{2k}\rangle/\langle R^{2k}\rangle_\infty$ plotted against the contour length t. The full curves represent the exact values.

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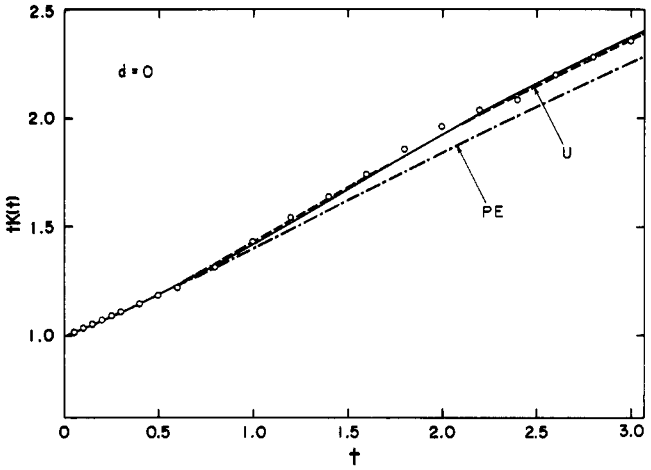

Figure 4. Computer values of $tK(t) = t\langle R^{-1}\rangle$ plotted against the contour length t. The curves represent the approximate theoretical values; full curve, present theory (eq 37); chain curve PE, the Ptitsyn-Eizner theory (eq 44);[9] broken curve U, the Ullman theory (eq 45).[12]

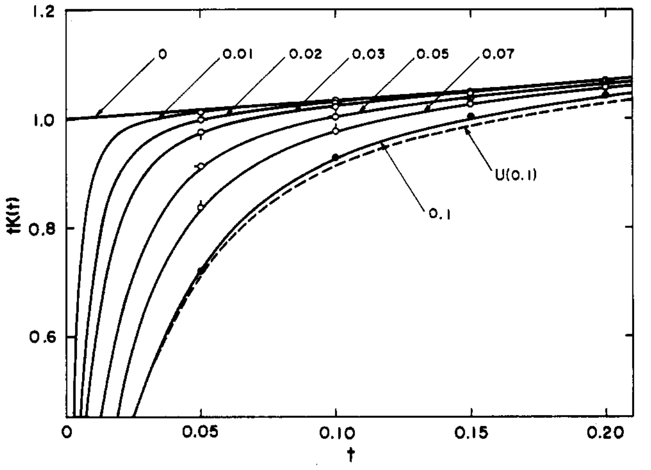

Figure 5. Computer values of $tK(t) = t\langle|\mathbf{R} - \mathbf{r}|^{-1}\rangle$ plotted against the contour length t for d = 0.01 (○), 0.02 (○-), 0.03 (○̩), 0.05 (-○), 0.07 (○̍), and 0.1 (•). The curves represent the approximate theoretical values as in Figure 4, and the numbers attached to them indicate the values of d.

Thus, the numerical results obtained for $tK(t) = t\langle|\mathbf{R} - \mathbf{r}|^{-1}\rangle$ are shown in Figure 4 for $d = 0$ and in Figures 5 and 6 for various finite values of d. The errors at $t = 1.2$ are ±2.5% almost independently of d for $d \leq 0.1$ and ±3.8% for $d = 1.0$, and these errors increase with increasing t as before. The accuracy of $K(t)$ is of the same order as that of $\langle R^2\rangle$ and is fairly high compared with those of the other moments. In these figures, the full curves represent the theoretical values calculated from eq 37 and 38, and the numbers attached to them indicate the values of d. It is seen that our approximate expression for $K(t)$ is fairly satisfactory, especially for typical stiff chains with $d < 0.1$. We note that the second Daniels approximation to $K(t)$ is quite accurate for $t > \sigma$, and that the values predicted by the Hearst-Stockmayer approximation based on the first Daniels approximation are very close to ours. In the figures are also shown the values predicted by the Ptitsyn-Eizner approximation to $K(t)$ for $d = 0$ (chain curve)[9]

$$K(t) = [t - \frac{1}{2}(1 - e^{-2t})]^{-1/2}\{0.427 + 0.573[180t^2 - 312t + 214 - 108(t + 2)e^{-2t} + 2e^{-6t}]/27 \times (2t - 1 + e^{-2t})^2\} \quad \text{(PE)} \quad (44)$$

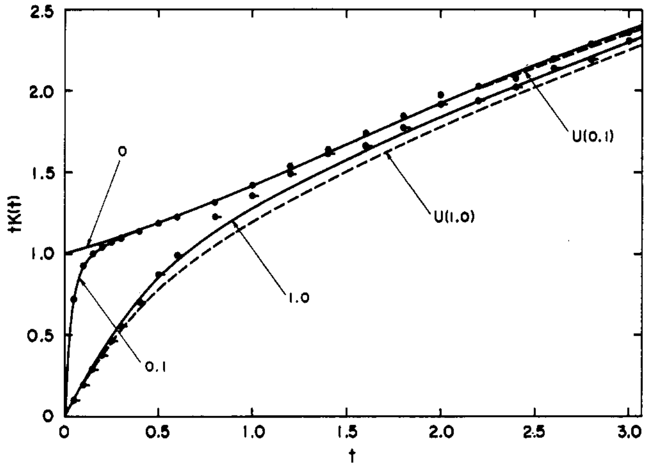

Figure 6. Computer values of $tK(t) = t\langle|\mathbf{R} - \mathbf{r}|^{-1}\rangle$ plotted against the contour length t for d = 0.1 (•) and 1.0 (•-). The curves represent the approximate theoretical values as in Figure 4, and the numbers attached to them indicate the values of d.

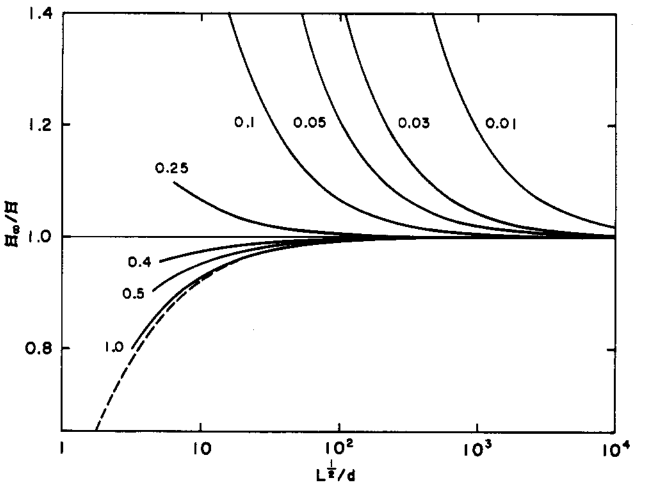

Figure 7. The ratio Ξ_∞/Ξ of the translational friction coefficients plotted against the logarithm of the ratio of the square root of the contour length L to the diameter d. The numbers attached to the curves indicate the values of d. The broken curve represents the coil limiting values calculated from eq 46 and 48.

Table II
Molecular Dimensions of DNA

Theory	λ^{-1} (Å)	d (Å)
Present theory	1250	25-26
	1300	24-26
	1350	24-26
Hearst-Stockmayer	1250	18-20
	1300	17-19
	1350	16-19

and by the Ullman approximation for d = 0, 0.1, and 1.0 (broken curves)[12]

$$K(t) = [t - \frac{1}{2}(1 - e^{-2t}) + \frac{1}{4}d^2]^{-1/2} \times [1 + 0.38(1 - e^{-0.34t}) - 0.2te^{-2t}] \quad \text{(U)} \quad (45)$$

It is seen that the Ullman values are close to ours, while the Ptitsyn-Eizner values are slightly underestimated. However, we note that for large t all the curves coincide with one another irrespective of the values of d.

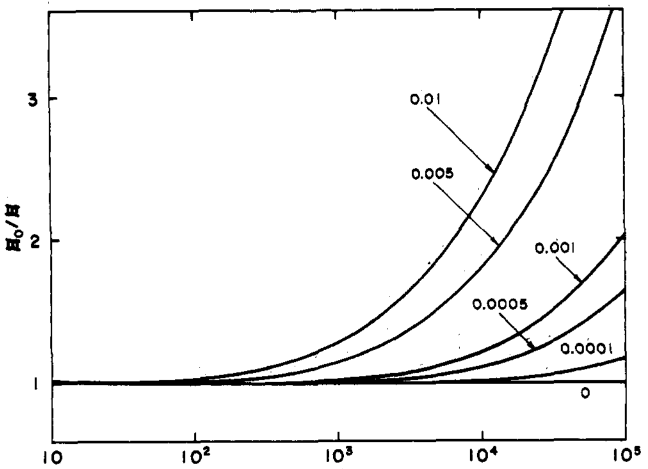

Figure 8. The ratio Ξ_0/Ξ of the translational friction coefficients plotted against the logarithm of the ratio of the contour length L to the diameter d. The numbers attached to the curves indicate the values of d.

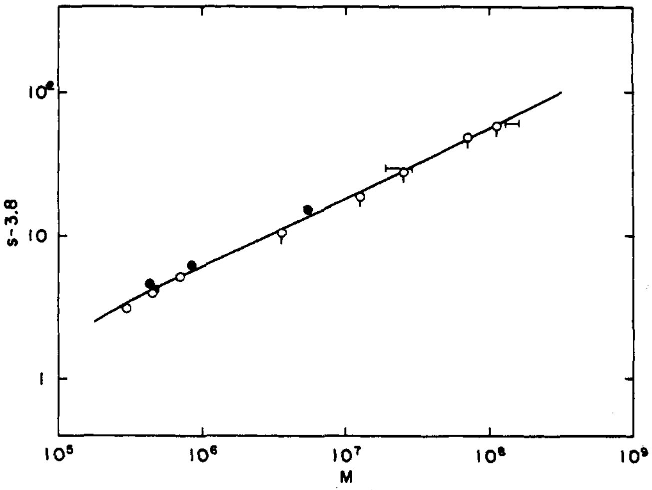

Figure 9. Double-logarithmic plots of s (sedimentation coefficient in svedbergs) − 3.8 against the molecular weight M; ●, data of Kawade and Watanabe[31] and Iso and Watanabe[32]; ○, data of Doty, McGill, and Rice[33]; —, data of Crothers and Zimm[34]; ♀, data summarized in the table of Schmid, Rinehart, and Hearst.[35] The full curve represents the theoretical values calculated from eq 49 to 52, 57, and 58 with λ^{-1} = 1300 Å and d = 25 Å.

III. Results

Having established the expression for the kernel $K(t)$, we now proceed to a calculation of the friction coefficient Ξ. We first calculate the coil limit of Ξ, which we designate by Ξ^*. Substitution of eq 33 into eq 15 and integration leads to

$$\frac{3\pi\eta_0 L}{\Xi^*} = (6L)^{1/2}\left[\left(\frac{1}{4x} + x + \frac{1}{3}x^3\right)\operatorname{erf}(x) + \frac{1}{6\pi^{1/2}}(5 + 2x^2)\exp(-x^2) - x - \frac{1}{3}x^3\right] = \frac{4}{3}\left(\frac{6}{\pi}\right)^{1/2} L^{1/2}\left[1 - \frac{9}{8}\left(\frac{\pi}{6}\right)^{1/2}\left(\frac{d}{L^{1/2}}\right) + \frac{3}{8}\left(\frac{d}{L^{1/2}}\right)^2 - \frac{9}{64}\left(\frac{\pi}{6}\right)^{1/2}\left(\frac{d}{L^{1/2}}\right)^3 + \cdots\right] \quad (46)$$

with

$$x^2 = \frac{3d^2}{8L} \quad (47)$$

and we therefore have

$$\lim_{L\to\infty} \Xi^* \equiv \Xi_\infty = \frac{9}{4}\left(\frac{\pi}{6}\right)^{1/2}\pi\eta_0 L^{1/2} \quad (48)$$

The Ξ_∞ given by eq 48 is equal to the Kirkwood-Riseman value for flexible chains (with $\langle R^2\rangle^{1/2} = L^{1/2}$) in the nondraining limit.[14] In the present theory, Ξ_∞ is the friction coefficient of infinitely long and infinitely flexible chains. Although Edwards and Oliver[21] have derived an expansion similar to eq 46, their numerical coefficients involve several mathematical errors.

For wormlike chains, substitution of eq 37 and 38 into eq 15 and integration leads to

$$\frac{3\pi\eta_0 L}{\Xi} = A_1 L^{-1/2} + A_2 + A_3 L^{-1/2} + A_4 L^{-1} + A_5 L^{-3/2} \quad \text{for } L > \sigma \quad (49)$$

with

$$A_1 = \frac{4}{3}\left(\frac{6}{\pi}\right)^{1/2} = 1.843$$

$$A_2 = -[1 - 0.01412d^2 + 0.00592d^4 + 0(d^6)]\ln d - 1.0561 - 0.1667d - 0.1900d^2 - 0.0224d^3 + 0.0190d^4 + 0(d^5)$$

$$A_3 = 0.1382 + 0.6910d^2 \quad (50)$$

$$A_4 = -[0.04167d^2 + 0.00567d^4 + 0(d^6)]\ln d - 0.3301 + 0.5d - 0.5854d^2 - 0.0094d^3 - 0.0421d^4 + 0(d^5)$$

$$A_5 = -0.0300 + 0.1209d^2 + 0.0259d^4$$

and

$$\frac{3\pi\eta_0 L}{\Xi} = C_1 \ln\left(\frac{L}{d}\right) + C_2 + C_3 L + C_4 L^2 + C_5 L^3 + C_6\left(\frac{d}{L}\right)\ln\left(\frac{L}{d}\right. + C_7\left(\frac{d}{L}\right) + C_8\left(\frac{d}{L}\right)^2 + C_9\left(\frac{d}{L}\right)^3 + C_{10}\left(\frac{d}{L}\right)^4 + 0\left[\left(\frac{d}{L}\right)^5\right] \quad \text{for } L \leq \sigma \quad (51)$$

with

$$C_1 = 1 - 0.01412d^2 + 0.00592d^4 + 0(d^6)$$

$$C_2 = 0.3863 - 0.1667d + 0.0016d^2 - 0.0224d^3 - 0.0007d^4 + 0(d^5)$$

$$C_3 = 0.1667 + 0.0222d^2 + 0.0017d^4 + 0(d^6)$$

$$C_4 = 0.01883 - 0.00789d^2 - 0.00038d^4 + 0(d^6)$$

$$C_5 = -0.002039 + 0.000805\mathrm{d}^2 + 0.000017\mathrm{d}^4 + 0(d^6)$$

$$C_6 = 0.04167\mathrm{d} + 0.00567d^3 + 0(d^5) \quad (52)$$

$$C_7 = 0.5 + 0.0786d - 0.0094d^2 + 0.0107d^3 + 0.0039d^4 + 0(d^5)$$

$$C_8 = -0.06250 + 0.00132d^2 - 0.00055d^4 + 0(d^6)$$

$$C_9 = 0.001302d + 0.000181d^3 + 0(d^5)$$

$$C_{10} = 0.001953 - 0.000064d^2 + 0.000027d^4 + 0(d^6)$$

As seen from eq 48 and 49, in the limit $L \to \infty$, Ξ becomes Ξ_∞ irrespective of the values of d. On the other hand, the long-rod limit of Ξ, which we designate by Ξ_0, may be obtained from eq 51 by letting d and L approach zero at constant L/d ($\gg$1); that is

$$\lim_{\substack{d,L\to 0\\ L/d\to\infty}} \Xi \equiv \Xi_0 \tag{53}$$

$$\frac{3\pi\eta_0 L}{\Xi_0} = \ln\left(\frac{L}{d}\right) + 0.3863 \tag{54}$$

Broersma has applied the modified Oseen–Burgers procedure to rigid straight cylinders, and obtained the value of 0.38 for the corresponding constant on the right of eq 54.[20,28]

The results obtained by Hearst and Stockmayer (HS)[8] for wormlike touched-bead models are similar to our eq 49–52. Their first two coefficients in eq 49 and 51 are given by

$$\begin{aligned} A_1(\mathrm{HS}) &= 1.843 \\ A_2(\mathrm{HS}) &= -\ln d - 1.431 \\ C_1(\mathrm{HS}) &= 1 \\ C_2(\mathrm{HS}) &= 0 (d \longrightarrow 0) \end{aligned} \tag{55}$$

Their A_1 is exactly the same as ours, and our A_2 becomes equal to $-\ln d - 1.0561$ for small d. Therefore, application of the Hearst–Stockmayer equation to experimental data for typical stiff chains leads to smaller estimates of d. Further, their C_1 is equal to ours for small d. However, it is important to observe that their C_2 differs from ours for small d. If the sums appearing in the Kirkwood formula are treated correctly, the Hearst–Stockmayer procedure gives the Euler constant 0.5772 instead of 0 for C_2 at $d = 0$. As stated in the Introduction, this is a defect of the Hearst–Stockmayer theory.

As shown in section II, Ullman's kernel is numerically close to our kernel, and the important difference between his and our theories consists in the existence of the draining term in the former. Therefore, Ullman's theory will predict approximately the same values for Ξ as our theory when we let his parameter α (friction constant per unit length) approach infinity.

The values of Ξ_∞/Ξ calculated from eq 48 to 52 as a function of $L^{1/2}/d$ for various values of d and for $L/d \geq 10$ are plotted against the logarithm of $L^{1/2}/d$ in Figure 7. The numbers attached to the curves indicate the values of d, and the broken curve represents the coil limiting values calculated from eq 46 and 48. This figure is useful for typical flexible and wormlike chains. It is interesting to observe that the curve for $d = 1.0$ is already very close to the broken curve for the coil limit. Now, the ratio Ξ_∞/Ξ is equal to the ratio s/s_∞ of the sedimentation coefficients. From Figure 7, it is seen that the ratio s/s_∞ is almost independent of L and hence of the molecular weight M for $d = 0.3 - 0.5$ and $L/d \gtrsim 10^2$. This may well explain the well-known experimental results for flexible chains at theta temperatures that indicate the nonexistence of the draining effect in Kirkwood's language. A similar explanation may also be given by the use of wormlike bead models.[8,29] Another explanation has already been given for flexible bead models;[23] the ratio s/s_∞ has been shown to be nearly independent of M when the ratio of the diameter of the bead to the bond length has appropriate values. There will probably be no possibility of any other explanation of the constancy of the ratio s/s_∞. The values of Ξ_0/Ξ calculated from eq 49 to 54 as a function of L/d for various values of d are plotted against the logarithm of L/d in Figure 8. The numbers attached to the curves indicate the values of d; the case of $d = 0$ corresponds to rigid straight rods. Thus, this figure is useful for rigid rods and weakly bending (wormlike) rods.

IV. Application to DNA

The translational friction coefficient Ξ is related to the sedimentation coefficient s, which is experimentally observable, by

$$s = \frac{\lambda M(1 - \bar{v}\rho)}{N_A \Xi} \tag{56}$$

where N_A is the Avogadro number, $\bar{v}$ the partial specific volume of the polymer, and ρ the density of the solvent, and Ξ is measured in units of λ^{-1} as before. If M_L is the molecular weight per unit length of the cylinder axis, we have

$$L = \lambda M/M_L \tag{57}$$

so that s becomes a function of M, λ, and d when M_L is given.

It is known that $M_L = 195$ daltons/Å for DNA, and the published data for DNA solutions have been obtained under the conditions that $\bar{v}\rho = 0.556$ and $\eta_0 = 0.01$ P. We therefore have

$$s = 1.525\left(\frac{3\pi\eta_0 L}{\Xi}\right) \quad \text{(for DNA)} \tag{58}$$

where s is expressed in Svedbergs. We apply eq 58 to the published data, assuming that the excluded-volume effect is small for most of the studied samples.[30] Figure 9 shows double-logarithmic plots of $s - 3.8$ (in Svedbergs) against M, following Hays, Magar, and Zimm.[30] It includes not only the data[31-34] displayed in the figure of ref 30 but also the data summarized in the table of Schmid, Rinehart, and Hearst.[35] If we assume a linear relationship between log ($s - 3.8$) and log M over the range displayed in Figure 9, the method of least squares gives the experimental equation

$$\log (s - 3.8) = 0.476 \log M - 2.066 \tag{59}$$

Now, we can obtain theoretical values of s as a function of M for given values of λ and d from eq 49–52, 57, and 58. Then, we can choose the best values of λ and d to make the theoretical values of s come as close as possible to the values given by eq 59. Three possible pairs of values of λ^{-1} and d thus determined are given in Table II, where we have used the symbol d in place of $\lambda^{-1}d$. Thus we may conclude that $\lambda^{-1} = 1300 \pm 50$ Å and $d = 25 \pm 1$ Å. The full curve of Figure 9 represents the theoretical values for $\lambda^{-1} = 1300$ Å and $d = 25$ Å. A similar analysis has been made by the use of the Hearst–Stockmayer equation, and the results are given in Table II, the best values being $\lambda^{-1} = 1300 \pm 50$ Å and $d = 18 \pm 2$ Å. Thus, both theories give the same value of λ^{-1}, though the Hearst–Stockmayer theory gives a smaller value of d than does our theory. This value of λ^{-1} is in agreement with its well-established value,[30,35] and our value of 25 Å seems more reasonable as the hydrated helix diameter of DNA.[36]

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(28) See also Table I of ref 16.

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V. Conclusions

We have evaluated the translational friction coefficient of wormlike cylinders by the Oseen-Burgers procedure. The final results may be written in terms of only the molecular dimensions. From the point of view of classical hydrodynamics, the Ullman theory is not correct; it is correct only when his parameter α (friction constant per unit length) is taken as infinity. The Hearst-Stockmayer theory is not unphysical, though its application leads to smaller estimates of the diameter of the cylinder than does the present theory in the case of typical stiff chains. An analysis of the intrinsic viscosity of wormlike cylinders will be given in the next paper.

Acknowledgment. The authors benefited from numerous discussions with Professor H. Fujita in the course of the present work and from his similar calculation for flexible bead models, for which the authors thank him.

Thermodynamic and Structural Properties of Polystyrene–Polybutadiene–Polystyrene Block Copolymers

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ABSTRACT: Four polystyrene-polybutadiene-polystyrene (SBS) triblock polymers were anionically polymerized under controlled conditions so that (1) the polystyrene composition remained constant (~27%), (2) the diblock and homopolymer impurities were low (<1%), (3) the heterogeneity of molecular weight was low ($M_w/M_n < 1.1$), and (4) the overall molecular weight (M_n) varied over a large range; 4.9×10^4, 9.0×10^4, 1.4×10^5, and 9×10^5. The polymer films were cast from tetrahydrofuran-methyl ethyl ketone (90:10), dried under vacuum, and then examined by low-angle X-ray scattering. The placement of the spherical polystyrene domains was found to be a face-centered cubic array. From the cell dimensions and the sphere size, the end-to end distance of chains, the interfacial region, and the molecular weight dependence of domain size and spacing were deduced. The data are found to be in good agreement with the theory of Meier if the interfacial tension is assumed to be 1 dyn cm^{-1}; a value that is in good agreement with estimates made independently.

For some time the existence of phase separated domains in carefully prepared triblock (ABA) copolymers has been accepted. The most detailed theoretical description of thermodynamic and conformational features leading to microphase separations of pure A domains and pure B domains from an AB chain has been given by Meier.[2a] In all cases the sizes of the domains are related to the molecular sizes of the A or B part of the triblock copolymer as well as the ratio of A:B. Of course the compatibility of A and B with each other and the flexibility of the individual chains has a considerable influence on whether or not phase separation will indeed take place and what type of microphases can be expected to grow. For example, two segments, A and B, that are scarcely different chemically, are not likely to phase separate into pure A and pure B domains, if indeed at all. Similarly any tendency to crystallize will interfere with the separation because crystal growth kinetics will interfere with the separation.

The ideal study of the thermodynamic parameters involved in phase formation naturally would be concerned with polymers that are: (1) not too similar chemically, (2) are not readily crystallizable, (3) mobile throughout the whole phase separation process, and (4) available over a large range of molecular weight as well-prepared triblock copolymers having no homopolymer or diblock copolymer impurities. The polystyrene-polybutadiene-polystyrene (SBS) triblock copolymers have these desirable features and were chosen for this study, since: (1) the homopolymers are known to be incompatible and therefore are enough different chemically for phase separation;[2b] (2) neither polystyrene nor polybutadiene is a crystalline polymer when either is anionically polymerized; (3) the glass temperatures of butadiene (−100°) and polystyrene (~100°) are sufficiently low so that these materials will have considerable mobility during the casting of films from solution; and (4) the synthesis of these materials by anionic polymerization poses no problems in obtaining high molecular weights other than the rigorous exclusion of impurities during the polymerization. Earlier work in these laboratories had shown that this system could easily yield good triblock copolymers,[3,4] and that the morphological features could be studied by low-angle X-ray scattering.[5]

The study of the thermodynamic factors involved in the triblock domain morphology assumes that somehow an equilibrium state is attained. There is no sure way to determine if kinetic processes are so hindered as to prevent such an equilibrium state. However, it seems desirable to avoid the high viscosity of the bulk state for as long as possible. For this reason, this study of triblock copolymers has concentrated on the morphology of solvent-cast films. No attempt has been made to consider molded or extruded specimens. All samples were annealed under high vacuum at high temperatures in order to be certain that there was only a one-component polymer system free of solvent and that the final state of the cast film was as near as possible to an equilibrium state.

The choice of the ratio A/B was made to ensure spherical domains for the microphases. In particular, a 27 vol % of A was chosen. Other studies of the SBS triblocks at higher and lower volume per cents polystyrene will be reported later. The 27% polystyrene samples also had the de-

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