$$\cdot \begin{pmatrix} l_1 & l_2 & l \\ m & 0 & -m \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{pmatrix} \left[\frac{(2l_1 + 1)(2l_2 + 1)(2l + 1)}{4\pi} \right]^{1/2}$$

$$\equiv \sum_{l_1} M_{ll_1}{}^m(|\kappa|\cdot|r_0|)A_{l_1m}(|\kappa|) \quad \text{(A7)}$$

If we approximate the structure by its first L spherical components, we obtain for $L < l < 2L$ and $L < |m| < l$:

$$H_{lm}(|\kappa|) = 0 \quad \text{(A8)}$$

The quantities S_{lm}' solved via eq 25–27 are related to the "true" S_{lm} of eq 13 by unknown rotations. So do the $S_{lm}{}^{\mathrm{H}\prime}$ which are obtained from the SSL. If we assign $R = \mathbf{R}(\omega_l)$ as the angles of rotation for S_{lm}' and $R^{\mathrm{H}}\cdot R = \mathbf{R}(\omega_l{}^{\mathrm{H}})$ for $S_{lm}{}^{\mathrm{H}\prime}$ we can write:

$$[(S^{\mathrm{H}}R^{\mathrm{H}} - S)R]_{lm} = \sum_{l_1} M_{ll_1}{}^m A_{l_1m} \quad (m \leq L) \quad \text{(A9)}$$

and

$$(S^{\mathrm{H}}R^{\mathrm{H}} - S)_{lm} = 0 \quad (m > L) \quad \text{(A10)}$$

These relations used for different values of κ can be used to derive $A_{lm}(\kappa)$ as well as ω_l, $\omega_l{}^{\mathrm{H}}$, and $|r_0|$.

References and Notes

(1) Coherent scattering from different particles can usually be decreased in x-ray and neutron scattering at high enough dilutions. This is obviously not the case in scattering of laser light. The application of spatial correlation for this case will be treated separately.
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(5) A. Guinier, *Ann. Phys.* (*N.Y.*), **12**, 161–237 (1939).
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(7) As $S_{lm} = (-1)^m S_{l-m}{}^*$ one can use a representation for which S_{lm} is real.
(8) In preparation.

Transport Coefficients of Helical Wormlike Chains. 1. Characteristic Helices†

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ABSTRACT: The translational diffusion coefficient and intrinsic viscosity of the characteristic regular helix corresponding to the minimum configurational energy of the helical wormlike chain are evaluated by an application of the Oseen–Burgers procedure of hydrodynamics to the cylinder model. The model is discussed in relation to the transport length scales to be adopted, and the possible effect of the coupling between translational and rotational motions is examined. Evaluation is carried out with the use of the Oseen hydrodynamic interaction tensor nonpreaveraged or preaveraged. The results may be written in terms of four model parameters: the total contour length L, the diameter d of the cylinder, and the radius ρ and pitch h of the helix. In all cases, the asymptotic solutions are found. In the case of the preaveraged Oseen tensor, the numerical solutions are also obtained.

Recently, we proposed a very general continuous model, called the helical wormlike chain,[1,2] for stiff or flexible chain macromolecules of all types, and already developed the statistical mechanical theory for some of its equilibrium properties.[2–6] In the present series of papers, we study its steady-state transport properties. The model may be regarded as a hybrid of the three extreme forms of rod, random coil, and regular helix. Thus, first in this paper, we evaluate the translational diffusion coefficient, which is related to the sedimentation coefficient, and the intrinsic viscosity of the characteristic regular helix,[1] i.e., one of these extreme forms corresponding to the minimum configurational energy of the model chain.

As in the case of the Kratky–Porod (KP) wormlike chain,[7–9] evaluation is carried out by an application of the Oseen–Burgers procedure of hydrodynamics to cylinder models, the cylinder axis or chain contour being a regular helix for the present case. The procedure is rather well established for the KP wormlike cylinder, but two new fundamental problems to be considered arise for the present model and therefore also for the helical wormlike cylinder. One is in the hydrodynamic molecular model itself and the other in the hydrodynamic analysis of the frictional force. As previously discussed,[1] the shift factor M_{L}, as defined as the molecular weight per unit contour length of the helical wormlike model, is closely related to the length scales to be adopted for a given real chain which is replaced by the former, and such length scales depend, to some extent, on the latter and also on the property or behavior to be considered. Thus, the values of M_{L} and also of the radius and pitch of the characteristic helix determined for various real chains from their characteristic ratios and persistence vectors do not necessarily apply to the transport properties. This is the first problem. The second fundamental problem is to examine the effect of the coupling between translational and rotational motions such that cross terms occur in the generalized 6×6 diffusion tensor of skew bodies like the regular helix.[10,11] Note that the coupling of this kind does not occur for nonskew bodies like rigid rods and rings.

Thus, in section I, the hydrodynamic molecular model is discussed in relation to the length scales to be adopted. In section II, a formal solution for the instantaneous frictional force of the helical cylinder is obtained in the Oseen–Burgers approximation without preaveraging the Oseen hydrodynamic interaction tensor. In sections III and IV, the translational diffusion coefficient and intrinsic viscosity are evaluated, respectively, each with the Oseen tensor nonpreaveraged or preaveraged. In particular, a large part of section III is devoted to a rather detailed discussion of the coupling effect. In all cases, the asymptotic solutions are found. For the case of the preaveraged Oseen tensor, the numerical solutions are also obtained.

(I) Hydrodynamic Molecular Model

As stated in our hypothesis on polymer chain configurations,[1] the length scales to be adopted in the replacement of

† This paper is contributed to the celebration of the 80th birthday of Dr. Maurice L. Huggins, in recognition of his lasting contributions to polymer science.

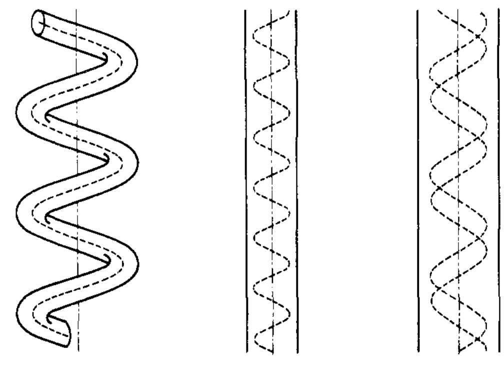

Figure 1. Hydrodynamic molecular models. (a) Helical wormlike cylinder with the transport length scales nearly equal to the equilibrium configurational ones. (b) Wormlike cylinder with the transport length scales larger than the equilibrium ones (α helices, polyoxymethylene and polystyrene chains, etc.). (c) Wormlike cylinder with the transport length scales equal to the equilibrium ones (DNA, etc.).

a given real chain by the continuous helical wormlike model depend on the property of the former to be considered but are of the same order as or somewhat larger than the real bond length. In general, the length scales are closely related to the time scales when the nonequilibrium properties are considered.[12] The steady-state transport process is one of the slowest processes, and its length scales must be of the same order as or larger than those associated with the equilibrium chain configurations. In other words, it is difficult to dissolve the more precise microscopic structure of the chain from the steady-state transport properties. Furthermore, the transport length scales for the cylinder model are also affected by geometrical restrictions on the model, as discussed later.

Now, the shape of the regular helix as a space curve may be determined by the curvature κ_0 and torsion τ_0, or by the radius ρ and pitch h,[1,13]

$$\begin{aligned}\rho &= \kappa_0/(\kappa_0^2 + \tau_0^2)\\ h &= 2\pi\tau_0/(\kappa_0^2 + \tau_0^2)\end{aligned} \qquad (1)$$

In order to determine the size of the helical cylinder model, we must further introduce two parameters, the total contour length L and the diameter d of the cylinder. Among these, the three parameters ρ, h, and d (or κ_0, τ_0, and d) are related to the transport length scales.

If both ρ and h determined from the equilibrium chain configurations, i.e., characteristic ratios or persistence vectors, are much larger than the bond length, as in the case of tactic and atactic poly(methyl methacrylate) chains (see Table I of ref 1), then they may be adopted as the ρ and h of the hydrodynamic cylinder model. This case is illustrated in Figure 1a. On the other hand, if both of the equilibrium configurational ρ and h, or one of them, are much smaller than the bond length, as in the case of polymethylene, polyoxymethylene, and polystyrene chains, then the helix axis should rather be chosen as the chain contour of the hydrodynamic model. Thus, it reduces to the KP wormlike cylinder whose characteristic contour corresponding to minimum configurational energy is a straight line (with $\kappa_0 = \rho = 0$), as illustrated in Figure 1b. Complete α helices or polypeptide chains in the helical state may also be regarded as belonging to this class, as usual. In this case, it is clear that the transport length scales are larger than the equilibrium length scales. Indeed, when the equilibrium configurational ρ and h are small, d cannot be given independently of them because of the volume exclusion in one turn of the helix. In other words, there are upper bounds of d for given ρ and h. Such bounds of d are determined in the next section. For chains of high axial symmetry like DNA, which may be represented by the KP chain, the helix axis should also be taken as the chain contour. For this class of chains, as illustrated in Figure 1c, the KP wormlike cylinder model is hydrodynamically valid as in class b, but the equilibrium configurational and transport length scales are of the same order.

The definition of class c is obvious. In most cases of classes a and b, however, it is in general difficult to determine a priori which class a given real chain belongs to. The hydrodynamic model parameters ρ, h, and d should rather be determined from experiment with the use of theoretical expressions for the transport coefficients. In the following sections, we develop the hydrodynamics of the helical cylinder specified by L, d, ρ, and h, apart from the consideration above.

(II) Frictional Force

Let $\mathbf{v}^0$ be the unperturbed flow field of a solvent with viscosity coefficient η_0, which is assumed to be linear in space (or nonexistent), and let $\mathbf{U}$ be the velocity of the helical cylinder moving in the solvent. In the Oseen–Burgers approximation, a frictional force distribution $\mathbf{f}(x)$ per unit length along the cylinder axis as a function of the contour distance x ($-L/2 \leq x \leq L/2$) satisfies the integral equation, eq 6 of ref 9,

$$(8\pi\eta_0)^{-1} \int_{-L/2}^{L/2} \mathbf{K}(x,y) \cdot \mathbf{f}(y)\,dy = \mathbf{U}(x) - \mathbf{v}^0(x) \qquad (2)$$

with $\mathbf{K}$ the tensor defined by

$$\mathbf{K}(x,y) = 8\pi\eta_0\langle \mathbf{T}(\mathbf{R} - \mathbf{r})\rangle_{\mathbf{r}} \qquad (3)$$

where $\mathbf{R}$ is the vector distance from the contour point x to the contour point y, $\mathbf{r}$ is the normal radius vector from x to an arbitrary point on the cylinder surface so that $|\mathbf{r}| = d/2$, $\langle\,\rangle_{\mathbf{r}}$ designates the average over $\mathbf{r}$, i.e., over the normal cross section of the cylinder at x, and $\mathbf{T}$ is the Oseen tensor,

$$\mathbf{T}(\mathbf{R}) = (8\pi\eta_0 R)^{-1}(\mathbf{I} + \mathbf{RR}/R^2) \qquad (4)$$

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

We define the inverse $\mathbf{K}^{-1}(x,y)$ of $\mathbf{K}(x,y)$ as

$$\delta(x-y)\mathbf{I} = \int_{-L/2}^{L/2} \mathbf{K}^{-1}(x,x') \cdot \mathbf{K}(x',y)dx' = \int_{-L/2}^{L/2} \mathbf{K}(x,x') \cdot \mathbf{K}^{-1}(x',y)\,dx' \qquad (5)$$

with $\delta(x)$ the Dirac delta function. [This inverse is not to be confused with the inverse $\mathbf{K}(x,y)^{-1}$ of the 3×3 matrix $\mathbf{K}(x,y)$.] By the use of the first part of eq 5, the formal solution of eq 2 is obtained as

$$\mathbf{f}(x) = 8\pi\eta_0 \int_{-L/2}^{L/2} dy\mathbf{K}^{-1}(x,y) \cdot [\mathbf{U}(y) - \mathbf{v}^0(y)] \qquad (6)$$

Now, we derive expressions for various vector distances and the tensor $\mathbf{K}(x,y)$ required to complete eq 6. It is then convenient to introduce instead of ρ and h the parameters μ and ν defined by

$$\begin{aligned}\mu &= \tau_0(\kappa_0^2 + \tau_0^2)^{-1/2} = \pm(1 + 4\pi^2\rho^2/h^2)^{-1/2}\\ \nu &= (\kappa_0^2 + \tau_0^2)^{1/2} = 2\pi/l_0\end{aligned} \qquad (7)$$

with $l_0 = 2\pi(\rho^2 + h^2/4\pi^2)^{1/2}$ the contour length of one turn of the helix. Note that μ determines h/ρ, i.e., the form of the helix apart from its size, the helix being right handed for $\mu > 0$ and left handed for $\mu < 0$, so that the rod and ring correspond to the limits $|\mu| = 1$ and $\mu = 0$, respectively ($0 \leq |\mu| \leq 1$).

Further, it is convenient to introduce localized and molecular Cartesian coordinate systems besides the external Cartesian system ($\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z$) used above. The axes of the localized system ($\mathbf{e}_\xi, \mathbf{e}_\eta, \mathbf{e}_\zeta$) defined at the contour point x are taken in the directions of the unit vectors forming the moving trihedron ($\mathbf{a}, \mathbf{b}, \mathbf{u}$),[2] where $\mathbf{u}$ is the unit tangent vector of the helix at x,

a is the unit curvature vector at x, and $\mathbf{b} = \mathbf{u} \times \mathbf{a}$ is the unit binormal vector. The superscript (l) is used to indicate vectors and tensors expressed in this system. The molecular coordinate system $(\mathbf{e}_1,\mathbf{e}_2,\mathbf{e}_3)$ is defined as follows: the 3 axis is taken along the helix axis, the 1 axis is taken to pass through the contour point $x = 0$, and the 2 axis completes the right-handed system. The superscript (m) is used to indicate vectors and tensors expressed in this system. No superscript is used for vectors and tensors in the external system.

Let $\mathbf{R}(x)$ be the vector distance from the origin of the molecular coordinate system to the contour point x, and let $\mathbf{S}(x)$ be the vector distance from the center of mass of the helical cylinder to the contour point x. We then have, from differential geometry,

$$\mathbf{R}^{(\mathrm{m})}(x) = (1-\mu^2)^{1/2}\nu^{-1}\cos(\nu x)\mathbf{e}_1 + (1-\mu^2)^{1/2}\nu^{-1}\sin(\nu x)\mathbf{e}_2 + \mu x\mathbf{e}_3 \quad (8)$$

$$\mathbf{R}^{(\mathrm{m})}(x,y) \equiv \mathbf{R}^{(\mathrm{m})}(y) - \mathbf{R}^{(\mathrm{m})}(x) = (1-\mu^2)^{1/2}\nu^{-1}[\cos(\nu y) - \cos(\nu x)]\mathbf{e}_1 + (1-\mu^2)^{1/2}\nu^{-1} \times [\sin(\nu y) - \sin(\nu x)]\mathbf{e}_2 + \mu(y-x)\mathbf{e}_3 \quad (9)$$

$$[R^{(\mathrm{m})}(x,y)]^2 = [R(x,y)]^2 = \mu^2(y-x)^2 + 2(1-\mu^2)\nu^{-2}\{1 - \cos[\nu(y-x)]\} \quad (10)$$

$$\mathbf{S}^{(\mathrm{m})}(x) = (1-\mu^2)^{1/2}\nu^{-1}[\cos(\nu x) - (\nu L/2)^{-1}\sin(\nu L/2)]\mathbf{e}_1 + (1-\mu^2)^{1/2}\nu^{-1}\sin(\nu x)\mathbf{e}_2 + \mu x\mathbf{e}_3 \quad (11)$$

Useful transformation formulas are

$$\mathbf{S}(x) = \mathbf{A}(\alpha,\beta,\gamma)\cdot\mathbf{S}^{(\mathrm{m})}(x)$$
$$\mathbf{K}(x,y) = \mathbf{A}(\alpha,\beta,\gamma)\cdot\mathbf{K}^{(\mathrm{m})}(x,y)\cdot\mathbf{A}(\alpha,\beta,\gamma)^{\mathrm{T}}$$
$$\mathbf{R}^{(\mathrm{l})}(x,y) = \mathbf{N}(x)^{\mathrm{T}}\cdot\mathbf{R}^{(\mathrm{m})}(x,y)$$
$$\mathbf{K}^{(\mathrm{m})}(x,y) = \mathbf{N}(x)\cdot\mathbf{K}^{(\mathrm{l})}(x,y)\cdot\mathbf{N}(x)^{\mathrm{T}} \quad (12)$$

where the superscript T indicates the transpose, **A** is the matrix transforming the $(\mathbf{e}_1,\mathbf{e}_2,\mathbf{e}_3)$ system to the $(\mathbf{e}_x,\mathbf{e}_y,\mathbf{e}_z)$ system with α, β, and γ the Euler angles for the latter in the former such that $\mathbf{e}_3\cdot\mathbf{e}_z = \cos\alpha$, and **N** is the matrix transforming the $(\mathbf{e}_\xi,\mathbf{e}_\eta,\mathbf{e}_\zeta)$ system to the $(\mathbf{e}_1,\mathbf{e}_2,\mathbf{e}_3)$ system, eq 13 and 14.

$$\mathbf{A} = \begin{bmatrix} \cos\alpha\cos\beta\cos\gamma - \sin\beta\sin\gamma & \cos\alpha\sin\beta\cos\gamma + \cos\beta\sin\gamma & -\sin\alpha\cos\gamma \\ -\cos\alpha\cos\beta\sin\gamma - \sin\beta\cos\gamma & -\cos\alpha\sin\beta\sin\gamma + \cos\beta\cos\gamma & \sin\alpha\sin\gamma \\ \sin\alpha\cos\beta & \sin\alpha\sin\beta & \cos\alpha \end{bmatrix} \quad (13)$$

$$\mathbf{N} = \begin{bmatrix} -\cos(\nu x) & \mu\sin(\nu x) & -(1-\mu^2)^{1/2}\sin(\nu x) \\ -\sin(\nu x) & -\mu\cos(\nu x) & (1-\mu^2)^{1/2}\cos(\nu x) \\ 0 & (1-\mu^2)^{1/2} & \mu \end{bmatrix} \quad (14)$$

The evaluation of $\mathbf{K}^{(\mathrm{l})}(x,y)$ is rather easy, and $\mathbf{K}^{(\mathrm{m})}(x,y)$ and $\mathbf{K}(x,y)$ are obtained by the use of eq 12–14. If we use the Fourier representation of the Oseen tensor[7,14] in eq 3, we have

$$\mathbf{K}^{(\mathrm{l})}(x,y) = \pi^{-2}\int q^{-4}(q^2\mathbf{I} - \mathbf{qq})\exp[i\mathbf{q}\cdot\mathbf{R}^{(\mathrm{l})}(x,y)] \times \langle\exp[-i\mathbf{q}\cdot\mathbf{r}^{(\mathrm{l})}(x)]\rangle_{\mathbf{r}}\,d\mathbf{q} \quad (15)$$

We express $\mathbf{q}$, $\mathbf{R}^{(\mathrm{l})}$, and $\mathbf{r}^{(\mathrm{l})}$ in a cylindrical coordinate system associated with the $(\mathbf{e}_\xi,\mathbf{e}_\eta,\mathbf{e}_\zeta)$ system; $\mathbf{q} = (\rho_q,\chi_q,z_q)$, and so on. By the use of the Fourier–Bessel expansion of the exponential in $\langle\,\rangle_{\mathbf{r}}$,

$$\exp(-i\mathbf{q}\cdot\mathbf{r}^{(\mathrm{l})}) = \exp(-iz_qz_r)\sum_{n=-\infty}^{\infty}(-i)^nJ_n(\rho_q\rho_r)\exp[in(\chi_r - \chi_q)] \quad (16)$$

with J_n the Bessel function of the first kind, we find

$$\langle\exp(-i\mathbf{q}\cdot\mathbf{r}^{(\mathrm{l})})\rangle_{\mathbf{r}} = J_0(\tfrac{1}{2}d\rho_q) \quad (17)$$

Substitution of eq 17 into eq 15 and integration over **q** leads to

$$\mathbf{K}^{(\mathrm{l})}(x,y) = (R^2 + \tfrac{1}{4}d^2)^{-1/2}[f_1(X)\mathbf{I} + (R^2 + \tfrac{1}{4}d^2)^{-1}\mathbf{\Lambda}^{(\mathrm{l})}] \quad (18)$$

where

$$\Lambda^{(\mathrm{l})} = \begin{bmatrix} \tfrac{1}{2}[C_1 + (R_\xi^2 - R_\eta^2)C_2] & R_\xi R_\eta C_2 & R_\xi R_\zeta C_3 \\ R_\xi R_\eta C_2 & \tfrac{1}{2}[C_1 - (R_\xi^2 - R_\eta^2)C_2] & R_\eta R_\zeta C_3 \\ R_\xi R_\zeta C_3 & R_\eta R_\zeta C_3 & R_\zeta^2 f_2(X) \end{bmatrix} \quad (19)$$

$$C_1 = (R_\xi^2 + R_\eta^2 + \tfrac{1}{4}d^2)f_2(X) - \frac{3d^2(R_\xi^2 + R_\eta^2)}{4(R^2 + \tfrac{1}{4}d^2)}f_3(X)$$

$$C_2 = f_1(X) - \frac{3d^2R_\zeta^2}{4(R^2 + \tfrac{1}{4}d^2)^2}f_3(X) - \frac{9d^4}{128(R^2 + \tfrac{1}{4}d^2)^2}f_4(X)$$

$$C_3 = f_2(X) - \frac{3d^2}{8(R^2 + \tfrac{1}{4}d^2)}f_3(X) \quad (20)$$

$$X = d^2(R_\xi^2 + R_\eta^2)/(R^2 + \tfrac{1}{4}d^2)^2 \quad (21)$$

with $R \equiv R(x,y)$; R_ξ, R_η, and R_ζ are the components of $\mathbf{R}^{(\mathrm{l})}(x,y)$,

$$\mathbf{R}^{(\mathrm{l})}(x,y) = (1-\mu^2)^{1/2}\nu^{-1}\{1 - \cos[\nu(y-x)]\}\mathbf{e}_\xi + \mu(1-\mu^2)^{1/2}\nu^{-1}\{\nu(y-x) - \sin[\nu(y-x)]\}\mathbf{e}_\eta + \{\mu^2(y-x) + (1-\mu^2)\nu^{-1}\sin[\nu(y-x)]\}\mathbf{e}_\zeta \quad (22)$$

and $f_i(x)$ (i = 1–4) are the Gauss hypergeometric functions F,

$$f_1(x) = F(\tfrac{1}{4},\tfrac{3}{4},1;x)$$
$$f_2(x) = F(\tfrac{5}{4},\tfrac{3}{4},1;x)$$
$$f_3(x) = F(\tfrac{5}{4},\tfrac{7}{4},2;x)$$
$$f_4(x) = F(\tfrac{5}{4},\tfrac{7}{4},3;x) \quad (23)$$

Note that F is defined by

$$F(\lambda_1,\lambda_2,\lambda_3;x) = \frac{\Gamma(\lambda_3)}{\Gamma(\lambda_1)\Gamma(\lambda_2)} \times \sum_{n=0}^{\infty}\frac{\Gamma(\lambda_1+n)\Gamma(\lambda_2+n)}{\Gamma(\lambda_3+n)}\frac{x^n}{n!} \quad (24)$$

with Γ the gamma function. Equation 18 gives the kernel with the nonpreaveraged Oseen tensor.

In the case of the preaveraged Oseen tensor, we may replace $\mathbf{K}(x,y)$ by its configurational average $\langle\mathbf{K}\rangle$, i.e., the value averaged over the orientation (α,β,γ) of the helical cylinder. Since the 3 × 3 tensor $\mathbf{K}^{(\mathrm{l})}$ is symmetric, and **A** and **N** are orthogonal, $\langle\mathbf{K}\rangle$ becomes equal to the unit tensor multiplied by one-third of the trace of $\mathbf{K}^{(\mathrm{l})}$. After some algebraic manipulation with the hypergeometric functions, we obtain

$$\langle\mathbf{K}(x,y)\rangle = \tfrac{4}{3}K(x,y)\mathbf{I} \quad (25)$$

with

$$K(x,y) = (R^2 + \tfrac{1}{4}d^2)^{-1/2}f_1(X) \quad (26)$$

Note that in general $K(x,y) = \langle\langle|\mathbf{R} - \mathbf{r}|^{-1}\rangle_{\mathbf{r}}\rangle$ and that in the present case without internal degrees of freedom $K(x,y) = \langle|\mathbf{R} - \mathbf{r}|^{-1}\rangle_{\mathbf{r}}$. Since $K(x,y)$ depends only on $|x - y| \equiv t$, we may put

$$K(x,y) = K(t) \quad (27)$$

Finally, we give geometrical restrictions on d which arise from the volume exclusion in one turn of the helix. Let $\bar{d}_0$ be

Table I
Values of the Upper Bound $\bar{d}_0$ of νd as a Function of $|\mu|$

$\|\mu\|$	$\bar{d}_0$	$\|\mu\|$	$\bar{d}_0$
0.025	0.1570	0.175	1.083
0.050	0.3138	0.200	1.231
0.075	0.4699	0.250	1.520
0.100	0.6252	0.300	1.796
0.125	0.7792	0.350	2.053
0.150	0.9318	0.3712[a]	2.154

[a] For $0.3712 \le |\mu| \le 1$, $\bar{d}_0 = 2(1-\mu^2)^{-1/2}$.

the upper bound of νd. For $0.3712 \le |\mu| \le 1$, we have $\bar{d}_0 = 2\nu/\kappa_0 = 2(1-\mu^2)^{-1/2}$, where we note that the radius of curvature of the helix is equal to κ_0^{-1}. For $0 \le |\mu| \le 0.3712$, $\bar{d}_0$ is equal to the smallest minimum (>0) of the function $\bar{d}(x)$,

$$\bar{d}(x) = [\mu^2 x^2 + 2(1-\mu^2)(1-\cos x)]^{1/2} \tag{28}$$

The values of $\bar{d}_0$ as a function of $|\mu|$ (≤ 0.3712) are given in Table I. It must however be noted that $\bar{d}_0$ is not an actual hydrodynamic bound, which is somewhat smaller than $\bar{d}_0$ since the solvent molecules have finite size and cannot pass through the helical cylinder if νd exceeds some value smaller than $\bar{d}_0$.

(III) Translational Diffusion Coefficient

For the evaluation of the translational diffusion and friction coefficients, we may consider the unperturbed flow field to be nonexistent,

$$\mathbf{v}^0(x) = 0 \tag{29}$$

In this case, the translational and rotational motions of the helical cylinder in general are coupled since it is a skew body. Let $\mathbf{U}_0$ be the instantaneous translational velocity of an arbitrary point O rigidly affixed to the cylinder, and let Ω be the instantaneous angular velocity of the cylinder. The velocity $\mathbf{U}(x)$ of the contour point x is then given by

$$\begin{aligned}\mathbf{U}(x) &= \mathbf{U}_0 + \Omega \times \mathbf{R}_0(x) \\ &= \mathbf{U}_0 + \mathbf{B}_0(x)\cdot\Omega\end{aligned} \tag{30}$$

where $\mathbf{R}_0(x)$ is the vector distance from the point O to the contour point x, and $\mathbf{B}_0(x)$ is the tensor defined by

$$\mathbf{B}_0 = \begin{bmatrix} 0 & R_{0,z} & -R_{0,y} \\ -R_{0,z} & 0 & R_{0,x} \\ R_{0,y} & -R_{0,x} & 0 \end{bmatrix} \tag{31}$$

with $\mathbf{R}_0 = R_{0,x}\mathbf{e}_x + R_{0,y}\mathbf{e}_y + R_{0,z}\mathbf{e}_z$. Note that the quantities with the subscript 0 in eq 30 depend on the location of the point O but $\mathbf{U}(x)$ does not, Ω being a free vector.

With the Nonpreaveraged Oseen Tensor. The frictional force distribution for this case is given by eq 6 with eq 29 and 30,

$$\mathbf{f}(x) = 8\pi\eta_0 \int_{-L/2}^{L/2} \mathrm{d}y \mathbf{K}^{-1}(x,y)\cdot[\mathbf{U}_0 + \mathbf{B}_0(y)\cdot\Omega] \tag{32}$$

The total frictional force $\mathbf{F}$ and torque $\mathbf{T}_0$ (not to be confused with the Oseen tensor) are given by

$$\mathbf{F} = \int_{-L/2}^{L/2} \mathbf{f}(x)\,\mathrm{d}x \tag{33}$$

$$\begin{aligned}\mathbf{T}_0 &= \int_{-L/2}^{L/2} [\mathbf{R}_0(x) \times \mathbf{f}(x)]\,\mathrm{d}x \\ &= \int_{-L/2}^{L/2} \mathbf{B}_0(x)^{\mathrm{T}}\cdot\mathbf{f}(x)\,\mathrm{d}x\end{aligned} \tag{34}$$

and may therefore be written in the form,

$$\mathbf{F} = \Xi_{\mathrm{t}}\cdot\mathbf{U}_0 + \Xi_{0,\mathrm{c}}'\cdot\Omega \tag{35}$$

$$\mathbf{T}_0 = \Xi_{0,\mathrm{c}}\cdot\mathbf{U}_0 + \Xi_{0,\mathrm{r}}\cdot\Omega \tag{36}$$

where we note that the torque $\mathbf{T}_0$ and the tensors with the subscript 0 depend on the location of the point O.

Now, we introduce the reduced variables $x' = 2x/L$ and $y' = 2y/L$ and drop the prime in the remainder of this subsection, for simplicity. Then, the tensors in eq 35 and 36 are given by

$$\begin{aligned}\Xi_{\mathrm{t}} &= 8\pi\eta_0 \int_{-1}^{1} \Psi_1(x)\,\mathrm{d}x \\ \Xi_{0,\mathrm{r}} &= 2\pi\eta_0 L^2 \int_{-1}^{1} \mathbf{H}_0(x)^{\mathrm{T}}\cdot\Psi_2(x)\,\mathrm{d}x \\ \Xi'_{0,\mathrm{c}} &= 4\pi\eta_0 L \int_{-1}^{1} \Psi_2(x)\,\mathrm{d}x \\ \Xi_{0,\mathrm{c}} &= 4\pi\eta_0 L \int_{-1}^{1} \mathbf{H}_0(x)^{\mathrm{T}}\cdot\Psi_1(x)\,\mathrm{d}x\end{aligned} \tag{37}$$

with

$$\mathbf{H}_0(x) = (2/L)\mathbf{B}_0(x) \tag{38}$$

From the second of eq 5 and eq 32–37, the tensors Ψ_1 and Ψ_2 are seen to be the solutions of the integral equations,

$$\int_{-1}^{1} \mathbf{K}(x,y)\cdot\Psi_1(y)\,\mathrm{d}y = \mathbf{I} \tag{39}$$

$$\int_{-1}^{1} \mathbf{K}(x,y)\cdot\Psi_2(y)\,\mathrm{d}y = \mathbf{H}_0(x) \tag{40}$$

Equations 35 and 36 are general formulas for the frictional force and torque in the translational and rotational motions of a body in a viscous fluid at rest, and Ξ_{t}, $\Xi_{0,\mathrm{r}}$, and $\Xi_{0,\mathrm{c}}$ are the translational, rotatory, and coupling friction tensors, respectively.[11] In the Stokes flow with exact no-slip boundary conditions, there holds the relation,[11]

$$\Xi_{0,\mathrm{c}}' = \Xi_{0,\mathrm{c}}^{\mathrm{T}} \tag{41}$$

In the present case, however, this relation does not hold strictly but only asymptotically for $L \gg d$, since $\mathbf{K}(x,y)$ is asymmetric with respect to x and y and becomes symmetric asymptotically. It is clear that this breakdown of the self-consistency arises from the Oseen–Burgers approximation. Therefore, we should rather replace *approximately* the $\Xi_{0,\mathrm{c}}'$ in eq 35 by $\Xi_{0,\mathrm{c}}^{\mathrm{T}}$ in order to preserve the self-consistency, so that this replacement may partly compensate the Oseen–Burgers approximation. However, it is the advantage of the Oseen–Burgers procedure that eq 35 and 36 can be derived with explicit expressions for the friction tensors even for complicated bodies like the helical cylinder.

It is instructive to refer to some further general properties of these friction tensors.[11] The translational and rotatory friction tensors are always positive definite and symmetric independently of the location of the point O, while the coupling friction tensor in general is not symmetric. However, there is always a unique point for all bodies at which the coupling tensor is symmetric, and this point O_{R} is called the center of reaction; that is, $\Xi_{0,\mathrm{c}} = \Xi_{0,\mathrm{c}}^{\mathrm{t}}$ at $O = O_{\mathrm{R}}$. For highly symmetric, nonskew bodies such as rods and rings, the translational and rotational motions are decoupled in the sense that $\Xi_{0,\mathrm{c}} = 0$ if the center of reaction is taken as the point O. Then, this point, called the center of hydrodynamic stress, is identical with Zimm's center of resistance.[15] In the particular case of a long helix with $O = O_{\mathrm{R}}$, all the friction tensors are symmetric, and can be diagonalized at the same time for its proper orientation, so that then the force and torque vectors are in the direction of one of the external coordinate axes if the translational and angular velocity vectors are parallel to that axis. In other words, if an external force is applied on

Table II
Values of the Integrals c_i (i = 1–5) as Functions of $|\mu|$ and νd

$\|\mu\|$	νd	c_1	c_2	c_3	c_4	c_5
0.1	0.1	2.0964	408.458	403.078	1.2452	0.0138
	0.3	1.5253	52.489	47.001	1.1844	0.1184
	0.5	1.2388	23.494	19.038	1.0850	0.3150
0.1572	0.1	1.7126	403.584	399.768	0.6399	0.0067
	0.3	1.1482	47.843	44.595	0.6087	0.0559
	0.5	0.8851	19.239	16.280	0.5701	0.1480
	0.7	0.7120	11.230	8.486	0.5227	0.2786
0.3	0.1	1.5967	401.191	398.538	0.2241	0.0029
	0.3	0.9971	45.504	43.407	0.1692	0.0221
	0.5	0.7249	16.991	15.161	0.1431	0.0561
	0.7	0.5529	9.100	7.454	0.1254	0.1029
	1.0	0.3836	4.866	3.426	0.1059	0.1943
0.6227	0.1	2.2876	400.387	398.325	0.7190	0.0012
	0.3	1.3983	44.747	43.234	0.3754	0.0082
	0.5	0.9973	16.262	15.007	0.2234	0.0192
	0.7	0.7464	8.399	7.313	0.1319	0.0332
	1.0	0.5030	4.206	3.300	0.0498	0.0580

it in the direction of, for instance, its helix axis, it translates in this direction and rotates about its axis.

The solutions of eq 35 and 36 with 41 for $\mathbf{U}_0$ and Ω are

$$kT\mathbf{U}_0 = \mathbf{D}_{0,t}\cdot\mathbf{F} + \mathbf{D}_{0,c}^{T}\cdot\mathbf{T}_0 \quad (42)$$

$$kT\Omega = \mathbf{D}_{0,c}\cdot\mathbf{F} + \mathbf{D}_r\cdot\mathbf{T}_0 \quad (43)$$

where k is the Boltzmann constant, T is the absolute temperature, and $\mathbf{D}_{0,t}$, $\mathbf{D}_r$, and $\mathbf{D}_{0,c}$ are the translational, rotatory, and coupling diffusion tensors. We note that the center of diffusion at which $\mathbf{D}_{0,c}$ is symmetric is identical with the center of reaction.[10] The translational and rotatory diffusion tensors are explicitly given by

$$\mathbf{D}_{0,t} = kT(\Xi_t - \Xi_{0,c}^{T}\cdot\Xi_{0,r}^{-1}\cdot\Xi_{0,c})^{-1} \quad (44)$$

$$\mathbf{D}_r = kT(\Xi_{0,r} - \Xi_{0,c}\cdot\Xi_t^{-1}\cdot\Xi_{0,c}^{T})^{-1} \quad (45)$$

If there is no coupling effect ($\Xi_{0,c} = 0$), eq 44 and 45 reduce to the well-known relations.

Now, we are interested in the sedimentation coefficient s, which is related to the mean translational diffusion coefficient D, averaged over the molecular orientation. The latter may be calculated from

$$D = \tfrac{1}{3}\mathrm{Tr}\mathbf{D}_{0,t} = \tfrac{1}{3}\mathrm{Tr}\mathbf{D}_{0,t}^{(m)} \quad (46)$$

where Tr indicates the trace. Note that the mean translational velocity $\langle\mathbf{U}\rangle$ produced by the centrifugal force $\mathbf{F}$ (in the absence of an external torque) is equal to $(D/kT)\mathbf{F}$ independently of the location of the point O. The evaluation of D is carried out conveniently with the use of the molecular coordinate system. Then, note that eq 37–45 (as well as eq 46) are valid if the vectors and tensors are replaced by the corresponding quantities in the molecular coordinate system. The problem is to solve the integral eq 39 and 40 for Ψ_1 and Ψ_2. As shown in the Appendix, this can be done semianalytically for $|\mu|^{-1}\nu d \ll 1$ and $\nu L \to \infty$, i.e., for the cylinder diameter much smaller than the pitch and for a large number of helix turns. Thus we find the asymptotic solution for D, from eq 37, 44, and 46, as

$$D = \frac{kT}{3\pi\eta_0|\mu|L}\left[\ln\left(\frac{|\mu|L}{d}\right) + 2\ln 2 - \tfrac{5}{4} - c_0 + \tfrac{1}{2}|\mu|(1-\mu^2)(3c_1 + c_2 - c_3 + c_4) + \tfrac{1}{16}|\mu|\nu^2 d^2 c_2 + O(\nu^{-1}L^{-1})\right] \quad (47)$$

with

$$c_0 = \tfrac{1}{2}\ln\left[1 + 8(1-\mu^2)\nu^{-2}d^{-2}\right]$$

$$c_1 = \int_0^\infty \frac{\cos t}{k_1 k_2(k_1 + k_2)}\,dt$$

$$c_2 = \int_0^\infty k_1^{-3}\,dt$$

$$c_3 = \int_0^\infty k_1^{-3}\cos t\,dt$$

$$c_4 = \mu^2\int_0^\infty \frac{t^2(k_1^2 + k_1 k_2 + k_2^2)\cos t}{(k_1 k_2)^3(k_1 + k_2)}\,dt \quad (48)$$

where k_1 and k_2 are functions of t defined by

$$k_1(t) = [\mu^2 t^2 + \tfrac{1}{4}\nu^2 d^2 + 2(1-\mu^2)(1-\cos t)]^{1/2}$$

$$k_2(t) = [\mu^2 t^2 + \tfrac{1}{4}\nu^2 d^2 + 2(1-\mu^2)]^{1/2} \quad (49)$$

The values of c_i (i = 1–4) as functions of $|\mu|$ and νd are given in Table II.

It is important to note that the terms displayed in eq 47 arise only from Ξ_t in eq 44, so that the coupling effect occurs in higher order terms. In this connection, it should be stated that for helical bead models, Hoshikawa and Saito[16] have evaluated the coupling friction coefficient between the translation in the direction of the helix axis and the rotation about it, which becomes negligibly small for $L \to \infty$. When $|\mu| = 1$, the coupling effect vanishes completely, and eq 47 reduces to the corresponding equation for the rod,

$$D(\mathrm{rod}) = \frac{kT}{3\pi\eta_0 L}\left[\ln\left(\frac{L}{d}\right) + 2\ln 2 - 1 + O(L^{-1})\right] \quad (50)$$

so that

$$\lim_{L\to\infty}\frac{D(\mathrm{helix})}{D(\mathrm{rod})} = |\mu|^{-1} \quad (51)$$

We note that the restriction $|\mu|^{-1}\nu d \ll 1$ is not necessary to derive eq 50.

Unfortunately, numerical solutions for this case with arbitrary L and d cannot be obtained with sufficient accuracy at the present time.

With the Preaveraged Oseen Tensor. If the Oseen tensor is preaveraged, $\mathbf{K}(x,y)$ in eq 32 may be replaced by $\tfrac{4}{3}K(x,y)\mathbf{I}$, and the same development as in the preceding subsection except this replacement may be repeated, thereby in principle leading to the mean translational diffusion coefficient with some coupling effect. However, its physical meaning is not clear. In the present case, we should rather take the orientational average of both sides of eq 32 at constant $\mathbf{U}_0$),U) and Ω, so that the coupling term $\langle\mathbf{B}_0(y)\rangle\cdot\Omega$ in eq 32 vanishes. This procedure gives, instead of the mean translational diffusion

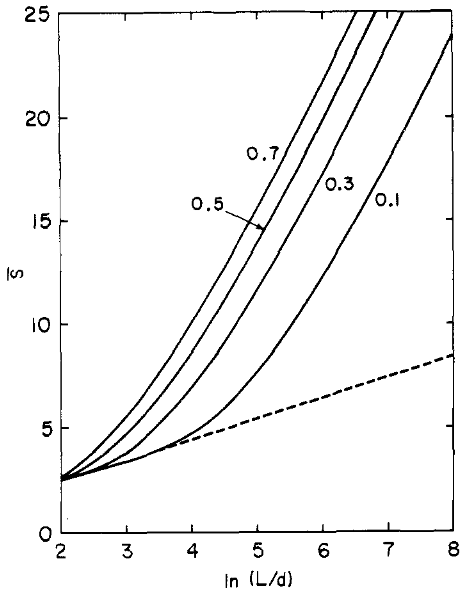

Figure 2. The reduced sedimentation coefficient $\bar{s}$ plotted against ln (L/d) for $|h|/\rho = 1$ ($|\mu| = 0.1572$) and for the indicated values of νd. The broken curve represents the corresponding values for the rod ($|\mu| = 1$).

coefficient D, the mean translational friction coefficient Ξ defined by

$$\langle \mathbf{F} \rangle = \Xi \mathbf{U} \tag{52}$$

D being obtained from Ξ by the use of the Einstein relation, as in the Kirkwood–Riseman procedure.[17] If we adopt the Kirkwood–Riseman approximation[7,17] in which the dependence of $\mathbf{f}(x)$ on x is ignored, D may then be computed from

$$D = \frac{kT}{3\pi\eta_0 L^2}\int_0^L (L-t)K(t)\,\mathrm{d}t \tag{53}$$

where $K(t)$ is given by eq 26 and 27.

The integral in eq 53 may be evaluated semianalytically for $\nu L \to \infty$ (without the restriction $|\mu|^{-1}\nu d \ll 1$), as shown in the Appendix, and we find

$$D = \frac{kT}{3\pi\eta_0|\mu|L}\left[\ln\left(\frac{|\mu|L}{d}\right) + 2\ln 2 - 1 - c_0 + 2|\mu|(1-\mu^2)c_1 + |\mu|c_5 + O(\nu^{-1}L^{-1})\right] \tag{54}$$

where c_0 and c_1 are given by eq 48, and c_5 is defined by

$$c_5 = \int_0^\infty k_1^{-1}[f_1(X) - 1]\,\mathrm{d}t \tag{55}$$

with $t = \nu|x - y|$. The values of c_5 are also given in Table II. If the restriction $|\mu|^{-1}\nu d \ll 1$ is imposed, the c_5 term drops in eq 54. It is important to observe that the leading term of the D given by eq 54 agrees with that given by eq 47 and that when $|\mu| = 1$, eq 54 becomes identical with eq 50 (and also with eq 54 of ref 7) since then $f_1(X) - 1 = c_5 = 0$, so that eq 51 is also valid in this case. This is the advantage of the present procedure using eq 53.

The integral in eq 53 may also be evaluated numerically. It is then convenient to introduce the dimensionless quantity $\bar{s}$ defined by

$$\bar{s} = 3\pi\eta_0 LD/kT \tag{56}$$

which is related to the sedimentation coefficient s by

$$s = M_L(1 - \bar{v}\rho_0)\bar{s}/3\pi\eta_0 N_A \tag{57}$$

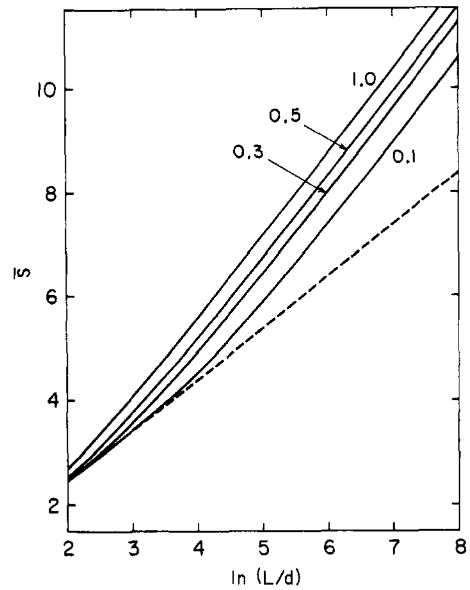

Figure 3. The reduced sedimentation coefficient $\bar{s}$ plotted against ln (L/d) for $|h|/\rho = 5$ ($|\mu| = 0.6227$); see legend to Figure 2.

where N_A is the Avogadro number, M_L is the shift factor, $\bar{v}$ is the partial specific volume of the solute, and ρ_0 is the mass density of the solvent. The values of $\bar{s}$ thus obtained (for $L/d \gtrsim 10$) are plotted against ln (L/d) for various values of νd in Figure 2 for $|h|/\rho = 1$ ($|\mu| = 0.1572$) and in Figure 3 for $|h|/\rho = 5$ ($|\mu| = 0.6227$). The numbers attached to the curves indicate the values of νd. The broken curves represent the corresponding values of $\bar{s}$ for the rod. For large L/d, the slope of $\bar{s}$ for the helix is equal to $|\mu|^{-1}$ and larger than that for the rod, and it appears that $\bar{s}$ for the helix becomes identical with that for the rod at small L/d, as expected.

(IV) Intrinsic Viscosity

Consider the unperturbed shear flow $\mathbf{v}^0$ in the direction of $\mathbf{e}_x$ with the time-independent velocity gradient g. The first problem is to give an explicit expression for the velocity $\mathbf{U}(x)$ of the contour point x. In the case of a highly symmetric, nonskew body, whose center of resistance (approximately the center of mass) is assumed to be located at the origin of the external coordinate system, there is no need of considering any coupling effect, and the body may be regarded as rotating about the z axis with the rotational part of the flow, i.e., with the angular velocity $-g/2$ in the limit $g \to 0$. This is the Kirkwood–Riseman assumption,[17] and indeed, it has already been verified by the Brownian motion theory in the case of, for instance, rods.[18] However, this is not necessarily the case with skew bodies. The coupling effect on the convective part of $\mathbf{U}$ has indeed been formulated,[10] but the diffusive part is also necessary for the present problem.[19] In other words, we must evaluate the coupling effect on $\mathbf{U}$ under the influence of Brownian motion. This problem will be considered elsewhere. In the present paper, we simply adopt the Kirkwood–Riseman assumption, expecting that the coupling effect may be ignored for the intrinsic viscosity as well as the diffusion coefficient of long enough helical cylinders. It will be physically reasonable. We then have[8]

$$\mathbf{v}^0(x) - \mathbf{U}(x) = \tfrac{1}{2}g(\mathbf{e}_x\mathbf{e}_y + \mathbf{e}_y\mathbf{e}_x)\cdot\mathbf{S}(x) \tag{58}$$

where the center of mass is fixed at the origin of the external coordinate system (its x and y axes not to be confused with the contour distances x and y).

Now, the intrinsic viscosity $[\eta]$ may be written in the form,

$$[\eta] = -(N_A/M\eta_0 g)\int_{-L/2}^{L/2} \mathbf{e}_x \cdot \langle \mathbf{f}(x)\mathbf{S}(x)\rangle \cdot \mathbf{e}_y \, dx \quad (59)$$

with M the molecular weight of the helical cylinder. If we substitute eq 6 with 58 into eq 59 and reduce x and y by $L/2$ as before, we obtain

$$[\eta] = \frac{N_A L}{M}\int_{-1}^{1} \Psi(x)\, dx \quad (60)$$

with

$$\Psi(x) = \pi L \int_{-1}^{1} dy\, \mathbf{e}_x \cdot \langle \mathbf{A}\cdot \mathbf{K}^{(m)-1}(x,y)\cdot \mathbf{A}^T \cdot (\mathbf{e}_x\mathbf{e}_y + \mathbf{e}_y\mathbf{e}_x)\cdot \mathbf{A}\cdot [\mathbf{S}^{(m)}(y)\mathbf{S}^{(m)}(x)]\cdot \mathbf{A}^T\rangle \cdot \mathbf{e}_y \quad (61)$$

where $\mathbf{K}$ and $\mathbf{S}$ are expressed in the molecular coordinate system, for convenience.

For the evaluation of the orientational average in eq 61, it is convenient to expand the transformation matrix $\mathbf{A}(\alpha,\beta,\gamma)$ and the matrix product $\mathbf{A}^T\cdot(\mathbf{e}_x\mathbf{e}_y + \mathbf{e}_y\mathbf{e}_x)\cdot\mathbf{A}$ in terms of the Wigner functions $\mathcal{D}_l^{kj}(\alpha,\beta,\gamma)$, as defined by eq 15 of ref 3, as follows,

$$\mathbf{A} = (8/3)^{1/2}\pi \sum_{k,j=-1}^{1} \mathbf{M}_1^{kj}\mathcal{D}_1^{kj} \quad (62)$$

$$\mathbf{A}^T\cdot(\mathbf{e}_x\mathbf{e}_y + \mathbf{e}_y\mathbf{e}_x)\cdot\mathbf{A} = (8/5)^{1/2}\pi \sum_{k,j=-2}^{2} (\delta_{j2}+\delta_{j,-2})\mathbf{M}_2^{kj}\mathcal{D}_2^{kj} \quad (63)$$

where

$$\mathbf{M}_1^{00} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\mathbf{M}_1^{01} = -\mathbf{M}_1^{0(-1)*} = 2^{-1/2}\begin{bmatrix} 0 & 0 & -1 \\ 0 & 0 & -i \\ 0 & 0 & 0 \end{bmatrix}$$

$$\mathbf{M}_1^{10} = -\mathbf{M}_1^{(-1)0*} = 2^{-1/2}\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ -1 & i & 0 \end{bmatrix}$$

$$\mathbf{M}_1^{11} = \mathbf{M}_1^{(-1)(-1)*} = \tfrac{1}{2}\begin{bmatrix} 1 & -i & 0 \\ i & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\mathbf{M}_1^{1(-1)} = \mathbf{M}_1^{(-1)1*} = \tfrac{1}{2}\begin{bmatrix} -1 & i & 0 \\ i & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (64)$$

and

$$\mathbf{M}_2^{02} = \mathbf{M}_2^{0(-2)*} \equiv 6^{-1/2} i \mathbf{M}_1$$

$$\mathbf{M}_2^{12} = \mathbf{M}_2^{(-1)2*} = -\mathbf{M}_2^{1(-2)} = -\mathbf{M}_2^{(-1)(-2)*} \equiv -\tfrac{1}{2}(\mathbf{M}_2 + i\mathbf{M}_3)$$

$$\mathbf{M}_2^{22} = \mathbf{M}_2^{(-2)(-2)*} = -\mathbf{M}_2^{2(-2)} = -\mathbf{M}_2^{(-2)2*} \equiv \tfrac{1}{2}(\mathbf{M}_4 + i\mathbf{M}_5) \quad (65)$$

with

$$\mathbf{M}_1 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{bmatrix}$$

$$\mathbf{M}_2 = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}$$

$$\mathbf{M}_3 = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}$$

$$\mathbf{M}_4 = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\mathbf{M}_5 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (66)$$

the asterisk indicating the complex conjugate.

With the Nonpreaveraged Oseen Tensor. In this case, eq 61 may be rewritten as

$$\Psi(x) = [16(10)^{1/2}\pi^3/15] \times \sum_{k_i,j_i=-1}^{1}\sum_{k,j=-2}^{2} (\delta_{j2}+\delta_{j,-2})\mathbf{e}_x\cdot \mathbf{M}_1^{k_1j_1} \times [\boldsymbol{\Psi}_{kj}^{(m)}(x)\mathbf{S}^{(m)}(x)]\cdot(\mathbf{M}_1^{k_2j_2})^T \cdot \mathbf{e}_y \langle \mathcal{D}_1^{k_1j_1}\mathcal{D}_1^{k_2j_2}\mathcal{D}_2^{kj}\rangle \quad (67)$$

with

$$\boldsymbol{\Psi}_{02}^{(m)} = \boldsymbol{\Psi}_{0,-2}^{(m)*} \equiv [5(6)^{1/2}/3] i \boldsymbol{\psi}_1^{(m)}$$

$$\boldsymbol{\Psi}_{12}^{(m)} = \boldsymbol{\Psi}_{-1,2}^{(m)*} = -\boldsymbol{\Psi}_{1,-2}^{(m)} = -\boldsymbol{\Psi}_{-1,-2}^{(m)*} \equiv -5(\boldsymbol{\psi}_2^{(m)} + i\boldsymbol{\psi}_3^{(m)})$$

$$\boldsymbol{\Psi}_{22}^{(m)} = \boldsymbol{\Psi}_{-2,-2}^{(m)*} = -\boldsymbol{\Psi}_{2,-2}^{(m)} = -\boldsymbol{\Psi}_{-2,2}^{(m)*} \equiv 5(\boldsymbol{\psi}_4^{(m)} + i\boldsymbol{\psi}_5^{(m)}) \quad (68)$$

where the vectors $\boldsymbol{\psi}_j^{(m)}$ (j = 1–5) are the solutions of the integral equations,

$$\int_{-1}^{1} \mathbf{K}^{(m)}(x,y)\cdot\boldsymbol{\psi}_j^{(m)}(y)\, dy = (2\pi/5L)\mathbf{M}_j \cdot \mathbf{S}^{(m)}(x) \quad (69)$$

From the property of the Wigner function (eq 33 of ref 3), we have

$$\langle \mathcal{D}_1^{k_1j_1}\mathcal{D}_1^{k_2j_2}\mathcal{D}_2^{kj}\rangle = \frac{15}{16(10)^{1/2}\pi^3}\begin{pmatrix} 1 & 1 & 2 \\ k_1 & k_2 & k \end{pmatrix}\begin{pmatrix} 1 & 1 & 2 \\ j_1 & j_2 & j \end{pmatrix} \quad (70)$$

where $(\because)$ is the Wigner $3-j$ symbol.[20] Thus, if $\boldsymbol{\psi}_j^{(m)} = (\psi_{j1},\psi_{j2},\psi_{j3})$ and $\mathbf{S}^{(m)} = (S_1,S_2,S_3)$, we obtain

$$\Psi(x) = \tfrac{1}{3}(-\psi_{11}S_1 - \psi_{12}S_2 + 2\psi_{13}S_3) + (\psi_{22}S_3 + \psi_{23}S_2) + (\psi_{31}S_3 + \psi_{33}S_1) + (\psi_{41}S_2 + \psi_{42}S_1) + (\psi_{51}S_1 - \psi_{52}S_2) \quad (71)$$

As in the preceding section, the integral eq 69 may be solved semianalytically for $|\mu|^{-1}\nu d \ll 1$ and $\nu L \rightarrow \infty$ (see the Appendix), and we find the asymptotic solution for $[\eta]$, from eq 60 and 71, as

$$[\eta] = \frac{2\pi N_A|\mu|^3L^3}{45M}\left[\ln\left(\frac{|\mu|L}{d}\right) + 2\ln 2 - \frac{59}{24} - c_0 + \frac{1}{32}|\mu|(2+\mu^2)\nu^2 d^2 c_2 + \tfrac{1}{4}|\mu|(1-\mu^2)(7c_1 + 3c_2 - 3c_3 + c_4) + O(\nu^{-1}L^{-1})\right]^{-1} \quad (72)$$

where c_i (i = 0–4) are given by eq 48. When $|\mu| = 1$, eq 72 reduces to the corresponding equation for the rod previously derived,[9]

$$[\eta](\text{rod}) = \frac{2\pi N_A L^3}{45M}\left[\ln\left(\frac{L}{d}\right) + 2\ln 2 - \frac{25}{12} + O(L^{-1})\right]^{-1} \quad (73)$$

so that

$$\lim_{L\to\infty} \frac{[\eta](\text{helix})}{[\eta](\text{rod})} = |\mu|^3 \quad (74)$$

Note that the restriction $|\mu|^{-1}\nu d \ll 1$ is not necessary to derive eq 73. Numerical solutions of eq 69 cannot be obtained with sufficient accuracy at the present time.

With the Preaveraged Oseen Tensor. In this case, $\mathbf{K}(x,y)$ and hence $\mathbf{K}^{(m)}(x,y)$ may be replaced by $\frac{4}{3}K(x,y)\mathbf{I}$, so that eq 61 reduces to

$$\Psi(x) = 8\pi^2 \sum_{k_i,j_i=-1}^{1} \mathbf{e}_y \cdot \mathbf{M}_1^{k_1j_1} \cdot [\boldsymbol{\psi}^{(m)}(x)\mathbf{S}^{(m)}(x)] \cdot (\mathbf{M}_1^{k_2j_2})^{\mathrm{T}} \cdot \mathbf{e}_y \,\langle \mathcal{D}_1^{k_1j_1}\mathcal{D}_1^{k_2j_2}\rangle \quad (75)$$

where the vector $\boldsymbol{\psi}^{(m)}(x)$ is the solution of the integral equation,

$$\int_{-1}^{1} K(x,y)\boldsymbol{\psi}^{(m)}(y)\mathrm{d}y = (\pi/L)\mathbf{S}^{(m)}(x) \quad (76)$$

From the orthogonality property of the Wigner functions (eq 18 with 32 of ref 3), we have

$$\langle \mathcal{D}_1^{k_1j_1}\mathcal{D}_1^{k_2j_2}\rangle = (8\pi^2)^{-1}(-1)^{k_1-j_1}\delta_{-k_1,k_2}\delta_{-j_1,j_2} \quad (77)$$

Then eq 75 becomes

$$\Psi(x) = \boldsymbol{\psi}^{(m)}(x) \cdot \mathbf{S}^{(m)}(x) \quad (78)$$

The integral eq 76 may be solved semianalytically for $\nu L \to \infty$ (without the restriction $|\mu|^{-1}\nu d \ll 1$), and we find

$$[\eta] = \frac{\pi N_A|\mu|^3L^3}{24M}\left[\ln\left(\frac{|\mu|L}{d}\right) + 2\ln 2 - \frac{7}{3} - c_0 + 2|\mu|(1-\mu^2)c_1 + |\mu|c_5 + O(\nu^{-1}L^{-1})\right]^{-1} \quad (79)$$

When $|\mu| = 1$, eq 79 reduces to the corresponding equation for the rod previously derived,[8]

$$[\eta](\text{rod}) = \frac{\pi N_A L^3}{24M}\left[\ln\left(\frac{L}{d}\right) + 2\ln 2 - \frac{7}{3} + O(L^{-1})\right]^{-1} \quad (80)$$

so that eq 74 is still valid in this case.

The integral eq 76 may also be solved numerically. In this connection, we note that it is not of the Kirkwood–Riseman type but of the Zimm–Stockmayer type[21,22] in the sense that it is an integral equation for the instantaneous force $\mathbf{f}$ instead of for the average $\langle \mathbf{e}_x \cdot \mathbf{f}(x)\mathbf{S}(x') \cdot \mathbf{e}_y\rangle$ as in the Kirkwood–Riseman procedure. However, integral equations of the latter type had already been used necessarily in the evaluation of $[\eta]$ for rods[9,18] and rings[23] with the nonpreaveraged Oseen tensor, as in the preceding subsection, before Zimm[21] recommended them from the point of view of the efficiency in numerical solution. Now, for a computer job, both types of integral equations with the preaveraged Oseen tensor may in general be replaced by m sets of n simultaneous linear equations, which read in matrix notation

$$\mathbf{K} \cdot \mathbf{X} = \mathbf{Y} \quad (81)$$

where $\mathbf{K}$ is the $n \times n$ matrix whose xy element is $K(x,y)$, and $\mathbf{X}$ (unknown) and $\mathbf{Y}$ are $n \times m$ matrices. Note that $\mathbf{Y}$ depends

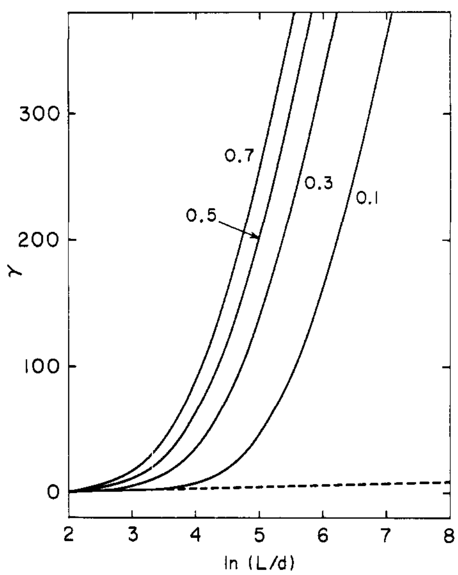

Figure 4. The function γ (proportional to $M^2/[\eta]$) plotted against ln (L/d) for $|h|/\rho = 1$ ($|\mu| = 0.1572$) and for the indicated values of νd. The broken curve represents the corresponding values for the rod ($|\mu| = 1$).

on the type of integral equation, and that in the case of rigid molecules, $m \leq 3$ for the Zimm–Stockmayer type and $m = n$ for the Kirkwood–Riseman type, while in the case of flexible chains, $m = n$ for both types. (In the latter case, the xy element of $\mathbf{Y}$ is δ_{xy} for the ZS type.) We have found that the computation time depends mainly on the value of m. Indeed, in the case of rigid molecules, the total time of the KR-type computation of $[\eta]$ is two or three times as long as that of the ZS type, while in the case of flexible chains, both are about the same, despite the recommendation of Zimm. However, the ZS-type formulation is of course more elegant.

In practice, the method of Schlitt[24] has been applied to solve the integral equations, and integrations have been carried out by the use of Gaussian quadratures with n = 40, 64, 80, and 96, followed by extrapolation to $n = \infty$. All numerical work has been done by the use of a FACOM M-190 digital computer at this University. For the present case (eq 76), the error in $[\eta]$ does not exceed 1% for $L/d \geq 40$ and 5% for $10 \lesssim L/d < 40$, sufficient accuracy being unattainable for $L/d \lesssim 10$. For the presentation of the results, it is convenient to introduce the dimensionless quantity γ defined by

$$[\eta] = \pi N_A M^2/24M_L{}^3\gamma \quad (82)$$

The values of γ thus obtained are plotted against ln (L/d) for various values of νd in Figure 4 for $|h|/\rho = 1$ ($|\mu| = 0.1572$) and in Figure 5 for $|h|/\rho = 5$ ($|\mu| = 0.6227$). The numbers attached to the curves indicate the values of νd, and the broken curves represent the corresponding values of γ for the rod. The slope of γ for the helix is equal to $|\mu|^{-3}$ for large L/d, and therefore the effect of the helix formation is much more remarkable on the intrinsic viscosity than on the sedimentation coefficient.

(V) Conclusion

We have evaluated the translational diffusion coefficient and intrinsic viscosity of helical cylinders by the Oseen–Burgers procedure, as in the case of wormlike cylinders. Actually, very few real chains, or none of them, may probably be represented by the regular helix as far as the transport properties are concerned. It has the significance only as the characteristic helix, i.e., one of the three extreme forms of the helical wormlike chain corresponding to minimum configurational energy. The end-to-end distance of the helix is smaller

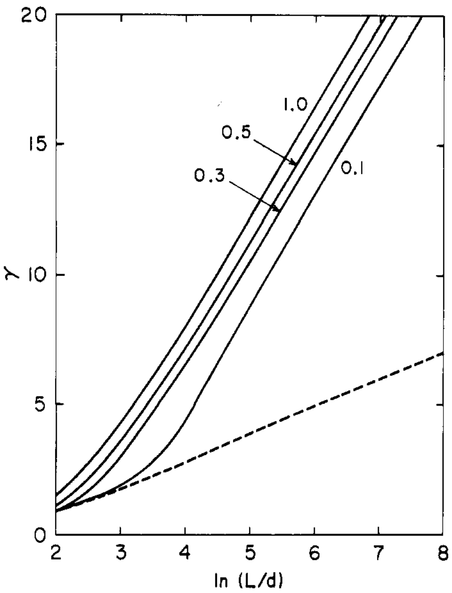

Figure 5. The function γ plotted against $\ln(L/d)$ for $|h|/\rho = 5$ ($|\mu| = 0.6227$); see legend to Figure 4.

than that of the rod of the same contour length, and the helix formation from the rod increases the translational diffusion and sedimentation coefficients and decreases the intrinsic viscosity, the effect on the latter being larger, as seen from the present results. Such helical behavior or trend will remain in the transport coefficients of the helical wormlike chain. These problems will be studied in later papers. As for the coupling, it may be concluded that if the Oseen tensor is preaveraged in the Kirkwood–Riseman scheme, it does not affect the translational diffusion and sedimentation coefficients at all, while even then there is a possibility of its influence on the intrinsic viscosity of short helices, though it has not been explicitly shown.

Appendix. Asymptotic Solutions.

We derive the asymptotic forms for D and $[\eta]$ in the limit $\nu L \to \infty$. We first consider the case of the nonpreaveraged Oseen tensor. Then, the kernels of the integral eq 39, 40, and 69 to be solved are $\mathbf{K}^{(m)}(x,y)$ $(-1 \le x, y \le 1)$, evaluation being carried out in the molecular coordinate system. For this purpose, we must further introduce the restriction $|\mu|^{-1}\nu d \ll 1$, so that $\mathbf{K}^{(m)}$ may be written as

$$\mathbf{K}^{(m)}(x,y) = \frac{\nu}{k_1(\frac{1}{2}\nu L|x-y|)}\left\{\mathbf{I} + \left[\frac{\nu}{k_1(\frac{1}{2}\nu L|x-y|)}\right]^2 \times [\mathbf{R}^{(m)}(x,y)\mathbf{R}^{(m)}(x,y) + \tfrac{1}{8}d^2\mathbf{N}(x)\cdot\mathbf{M}\cdot\mathbf{N}(x)^T] + O(|\mu|^{-1}\nu d)\right\} \quad \text{(A1)}$$

where k_1 is given by eq 49, $\mathbf{N}(x)$ is the transformation matrix given by eq 14, and $\mathbf{M}$ is a matrix defined by

$$\mathbf{M} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad \text{(A2)}$$

Although the solutions $\mathbf{\Psi}_1^{(m)}$ and $\mathbf{\Psi}_2^{(m)}$ for eq 39 and 40 are tensors and the solutions $\boldsymbol{\psi}_j^{(m)}$ for eq 69 are vectors, we may apply essentially the same method of solution. We therefore take eq 39 as an example.

Following the procedure of Yamakawa and Fujii,[8] we expand the solution $\mathbf{\Psi}_1^{(m)}(x)$ in terms of the Legendre polynomials $P_l(x)$,

$$\mathbf{\Psi}_1^{(m)}(x) = \sum_{l=0}^{\infty} \mathbf{\Psi}_{1,l}P_l(x) \quad \text{(A3)}$$

Then, the integral eq 39 reduces to a set of linear equations,

$$\sum_{l=0}^{\infty} \mathbf{a}_{kl}\cdot\mathbf{\Psi}_{1,l} = \mathbf{I}_k \quad \text{(A4)}$$

with

$$\mathbf{a}_{kl} = \int_{-1}^{1}\int_{-1}^{1} \mathbf{K}^{(m)}(x,y)P_k(x)P_l(y)\,dx\,dy \quad \text{(A5)}$$

$$\mathbf{I}_k = \int_{-1}^{1} \mathbf{I}P_k(x)\,dx \quad \text{(A6)}$$

Note that in the present case of $\mathbf{\Psi}_1^{(m)}$, $\mathbf{I}$ is the unit tensor, so that $\mathbf{I}_k = 2\delta_{0k}\mathbf{I}$. Let $\mathbf{a}$ be the supermatrix whose kl component is $\mathbf{a}_{kl}$, and let $\mathbf{A}_{kl}$ be the 3×3 component matrix of $\mathbf{A} = \mathbf{a}^{-1}$. Then, the solution of eq A4 is

$$\mathbf{\Psi}_{1,k} = \sum_{l=0}^{\infty} \mathbf{A}_{kl}\cdot\mathbf{I}_l \quad \text{(A7)}$$

The friction tensors and intrinsic viscosity may be expressed in terms of $\mathbf{A}_{kl}$. For example, we have, from eq 37, A3, and A7,

$$\mathbf{\Xi}_t^{(m)} = 8\pi\eta_0\int_{-1}^{1}\mathbf{\Psi}_1^{(m)}(x)\,dx = 32\pi\eta_0\mathbf{A}_{00} \quad \text{(A8)}$$

Now, it can be shown that in the limit $\nu L \to \infty$, $|\mathbf{a}_{kl}|$ $(k \ne l)$ become negligibly small compared to $|\mathbf{a}_{kk}|$, and therefore $\mathbf{A}_{kl}$ may be expanded in the form,

$$\mathbf{A}_{kl} = \mathbf{a}_{kk}^{-1}\cdot\Big[\delta_{kl}\mathbf{I} - (1-\delta_{kl})\mathbf{a}_{kl}\cdot\mathbf{a}_{ll}^{-1} + \sum_{\substack{m=0\\k\ne m\ne l}}^{\infty}\mathbf{a}_{km}\cdot\mathbf{a}_{mm}^{-1}\cdot\mathbf{a}_{ml}\cdot\mathbf{a}_{ll}^{-1} - \ldots\Big] \quad \text{(A9)}$$

Further, it can be shown that the leading term of eq A9 and therefore only $\mathbf{a}_{kk}$ are required for the derivation of the desired asymptotic forms; that is,

$$D = \frac{kT}{96\pi\eta_0}\mathrm{Tr}\mathbf{a}_{00} \quad \text{(A10)}$$

$$[\eta] = \frac{2\pi N_A\mu^2L^2}{45M}[(\mathbf{a}_{11}^{-1})_{11} + (\mathbf{a}_{11}^{-1})_{22} + \tfrac{4}{3}(\mathbf{a}_{11}^{-1})_{33}] \quad \text{(A11)}$$

with $(\mathbf{a}_{11}^{-1})_{ij}$ $(i,j = 1, 2, 3)$ the ij elements of $\mathbf{a}_{11}^{-1}$. Note that no coupling effect occurs in eq A10.

The elements $(\mathbf{a}_{kk})_{ij}$ of $\mathbf{a}_{kk}$ required in eq A10 and A11 are given by

$$(\mathbf{a}_{00})_{11} = (\mathbf{a}_{00})_{22} = \frac{8}{|\mu|L}\times\Big[\ln\left(\frac{|\mu|L}{d}\right) + 2\ln 2 - 1 - c_0 + |\mu|(1-\mu^2)(2c_1 + c_2 - c_3) + \frac{1}{16}|\mu|(1+\mu^2)\nu^2d^2c_2 + O(\nu^{-1}L^{-1})\Big]$$

$$(\mathbf{a}_{00})_{33} = \frac{16}{|\mu|L}\Big[\ln\left(\frac{|\mu|L}{d}\right) + 2\ln 2 - \tfrac{3}{2} - c_0 + |\mu|(1-\mu^2)(c_1 + c_4) + \frac{1}{16}|\mu|(1-\mu^2)\nu^2d^2c_2 + O(\nu^{-1}L^{-1})\Big]$$

$$(\mathbf{a}_{11})_{11} = (\mathbf{a}_{11})_{22} = \frac{8}{3|\mu|L}\times\Big[\ln\left(\frac{|\mu|L}{d}\right) + 2\ln 2 - \tfrac{7}{3} - c_0 + |\mu|(1-\mu^2)(2c_1 + c_2 - c_3) + \frac{1}{16}|\mu|(1+\mu^2)\nu^2d^2c_2 + O(\nu^{-1}L^{-1})\Big]$$

$$(\mathbf{a}_{11})_{33} = \frac{16}{3|\mu|L}\left[\ln\left(\frac{|\mu|L}{d}\right) + 2\ln 2 - \frac{17}{6} - c_0 + |\mu|(1-\mu^2)(c_1+c_4) + \frac{1}{16}|\mu|(1-\mu^2)\nu^2 d^2 c_2 + O(\nu^{-1}L^{-1})\right] \quad \text{(A12)}$$

where c_i (i = 0–4) are given by eq 48. We note that the off-diagonal elements of $\mathbf{a}_{00}$ and $\mathbf{a}_{11}$ are of higher order than the diagonal elements. Substitution of eq A12 into eq A10 and A11 leads to eq 47 for D and eq 72 for $[\eta]$, respectively. The restriction $|\mu|^{-1}\nu d \ll 1$ has some influence on the constant terms independent of L in the square brackets of eq A12 and hence eq 47 and 72 but does not in the case of rods ($|\mu| = 1$).

In the derivation of eq A12, we must find the asymptotic forms of the integral,

$$J = \int_0^{\nu L} [k_1(t)]^{-1}\, dt \quad \text{(A13)}$$

and of similar integrals, where k_1 is given by eq 49. This can be done as follows. We rewrite eq A13 as

$$J = \int_0^{\nu L} k_2^{-1}\, dt + \int_0^{\nu L} (k_1^{-1} - k_2^{-1})\, dt \quad \text{(A14)}$$

where k_2 is also given by eq 49. The first integral of eq A14 can be evaluated analytically, and the integrand of the second integral may be expanded as

$$\frac{1}{k_1(t)} - \frac{1}{k_2(t)} = \sum_{n=1}^{\infty} \frac{2^n \cdot (2n-1)!!(1-\mu^2)^n}{(2n)!!} \frac{\cos^n t}{[k_2(t)]^{2n+1}} \quad \text{(A15)}$$

so that its contribution to J is at most of order $(\nu L)^0$ in the limit $\nu L \to \infty$, and the range of integration may be extended to infinity. Thus we find

$$J = \frac{1}{|\mu|}\left[\ln\left(\frac{|\mu|L}{d}\right) + 2\ln 2 - c_0 + 2|\mu|(1-\mu^2)c_1 + O(\nu^{-1}L^{-1})\right] \quad \text{(A16)}$$

Similarly, asymptotic forms of other similar integrals can be found.

Next, we consider the case of the preaveraged Oseen tensor, for which the restriction $|\mu|^{-1}\nu d \ll 1$ is not necessary. In the case of D, the problem is to find the asymptotic form of the integral in eq 53, but the derivation is similar to that of eq A16 and is omitted. In the case of $[\eta]$, the solution of the integral eq 76 may be again expanded in terms of the Legendre polynomials, and $\mathbf{a}_{kl}$ is given by

$$\mathbf{a}_{kl} = a_{kl}\mathbf{I} \quad \text{(A17)}$$

with

$$a_{kl} = \int_{-1}^{1}\int_{-1}^{1} K(x,y)P_k(x)P_l(y)\, dx\, dy \quad \text{(A18)}$$

Thus we obtain the asymptotic form,

$$[\eta] = \frac{\pi N_A \mu^2 L^2}{9M} a_{11}^{-1} \quad \text{(A19)}$$

with

$$a_{11} = \frac{8}{3|\mu|L}\left[\ln\left(\frac{|\mu|L}{d}\right) + 2\ln 2 - \frac{7}{3} - c_0 + 2|\mu|(1-\mu^2)c_1 + |\mu|c_5 + O(\nu^{-1}L^{-1})\right] \quad \text{(A20)}$$

Equation A19 with A20 gives eq 79.

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