Table V
Reduced Moments of Distributions for Self-Avoiding Walks of *n* Steps on a Tetrahedral Lattice

	n	M_4	M_6	M_8
Total distribution statistics	18	2.4802	8.8920	39.541
Exact	18	2.4785	8.8814	39.497
	19	2.4897	8.9926	40.446
	20	2.4972	9.0752	41.193
Fixed coordinate statistics	21	2.495	9.068	41.25
	22	2.519	9.292	43.04
	23	2.522	9.326	43.36
	24	2.523	9.359	43.78
Total distribution statistics	24	2.531	9.429	44.31
	30	2.562	9.751	47.27
	∞^a	2.65	10.8	58.0

^{a} Taken from ref 7.

quite accurate for values of n up to 24. (We are less sure of the results for $n = 30$.) A comparison of the exact and statistical values, displayed in Tables II and III, supports this conclusion.

Another check on the general validity is obtained by considering the total number of walks calculated in two different ways. In preparing Tables II and III, we used the numbers of fringe walks, for which we have exact formulas, to establish weight factors. Alternatively, we could examine the overall attrition attending interstride exclusions. Suppose after 18 steps we try t different six-step strides, chosen randomly, to bring each walk up to 24 steps. If there are s successes, then we could calculate the total number of walks for $n = 24$ as follows:

$$N_{24} = N_{18} 948(s/t) \tag{2}$$

The factor 948 appears because there are precisely that many six-step strides of which t are tried. The computation can, of course, be generalized to cover the addition of more than one stride. Under those circumstances, we would calculate for p additional strides

$$N_{n+6p} = N_n \prod_i (948 s_i/t_i) \tag{3}$$

where i denotes an added stride.

Since we know N_{18} exactly, we used eq 2 and found that $N_{24} = 2.1521 \times 10^{11}$; this is about 0.06% less than the number calculated using the weight factor obtained from exact formulas for fringe configurations. The results for N_{30} and the distribution associated with $n = 30$ are, of course, less reliable than those for $n = 24$. Nevertheless, we feel that the method used is not only valid but highly effective, and only more computation time is necessary to reach high precision. Once accurate values are obtained for $n = 30$, extrapolation can be carried out with greater confidence than heretofore.

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Viscoelastic Properties of Straight Cylindrical Macromolecules in Dilute Solution

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ABSTRACT: The rotatory diffusion coefficient, intrinsic viscosity, and rigidity of straight cylindrical macromolecules are evaluated by an application of the Oseen–Burgers procedure of hydrodynamics. Plots of the reduced intrinsic viscosity and rigidity against the reduced frequency are rather insensitive to the change in the ratio of length to diameter. In particular, the high frequency limit of the latter is exactly independent of the molecular weight and takes the Kirkwood–Auer limiting value of 3/5 for an infinitely long rod.

In previous papers,[1] the steady state transport coefficients of stiff chains have been evaluated by an application of the Oseen–Burgers procedure of classical hydrodynamics to wormlike cylinder models with some comments[2] on Ullman's treatment[3] of the same problem. For example, the phenomenological friction constant per unit chain contour length remains in his final results, though his equations in the nondraining limit are equivalent to ours. In the present paper, it is shown that the kernels of his[4] and our integral equations are also different in the case of the rotatory diffusion, dynamic viscosity, and rigidity of rodlike or straight cylindrical macromolecules.

The present work has also been motivated by the very recent experimental results. The data obtained by Nemoto[5] for tobacco mosaic virus show that the high frequency limit of the reduced intrinsic rigidity is independent of the molecular weight and takes the Kirkwood–Auer limiting value[6] of 3/5 for an infinitely long rod. However, the Ullman theory[4] predicts values of the corresponding limit appreciably dependent on the molecular weight and smaller than the Kirkwood–Auer value. This disagreement may arise from the inadequacy of Ullman's trick or mistakes in his numerical solution, or from both. Further, the recent data obtained by Record et al.[7] for rodlike DNA fragments show that our equation[1a] for the sedimentation coefficient of wormlike chains extrapolates well to the rod region down to the molecular length about ten times as long as the molecular diameter. Thus it is of interest to apply our procedure[1] also to an analysis of the dynamic mechanical behavior of rodlike macromolecules in dilute solution.

Basic Equations

Consider a straight cylinder of length L and diameter d in the unperturbed flow field $\mathbf{v}^0$ of a solvent with viscosity coefficient η_0. Suppose that the center of mass of the cylinder is fixed at the origin of a spherical polar coordinate system (r, θ, φ) with the cylinder axis in the r direction, and let $\mathbf{e}_r$, $\mathbf{e}_\theta$, and $\mathbf{e}_\varphi$ be the unit vectors in the r, θ, and φ directions, respectively. Following the Oseen–Burgers procedure,[1] 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 $(-L/2 \le x \le L/2)$ from the origin. Let $\mathbf{a}$ 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

$$|\mathbf{a}| = a = \tfrac{1}{2}d \qquad \mathbf{e}_r \cdot \mathbf{a} = 0 \tag{1}$$

Let $\mathbf{R}$ be the distance between the contour points x and y. For an instantaneous orientation of the cylinder, the velocity $\mathbf{v}(P)$ of solvent at the point P relative to the velocity $\mathbf{u}(P)$ of the cylinder at P may then be expressed as

$$\mathbf{v}(P) = \mathbf{v}^0(P) - \mathbf{u}(P) + \int_{-L/2}^{L/2} \mathbf{T}(\mathbf{R} - \mathbf{a}) \cdot \mathbf{f}(y)\,\mathrm{d}y \tag{2}$$

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.

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; that is

$$\langle \mathbf{v}(P) \rangle_{\mathbf{a}} = 0 \tag{4}$$

for

$$-L/2 \le x \le L/2$$

where $\langle\ \rangle_{\mathbf{a}}$ designates the average over $\mathbf{a}$, assuming its uniform distribution subject to the conditions given by eq 1. Since the unperturbed flow field is assumed to be nonexistent or linear in space and the velocity $\mathbf{u}(P)$ is derived from the angular velocity of the cylinder, we have

$$\langle \mathbf{v}^0(P) \rangle_{\mathbf{a}} = \mathbf{v}^0(x) \qquad \langle \mathbf{u}(P) \rangle_{\mathbf{a}} = \mathbf{u}(x) \tag{5}$$

Therefore eq 2 reduces to

$$\int_{-L/2}^{L/2} \langle \mathbf{T}(\mathbf{R} - \mathbf{a}) \rangle_{\mathbf{a}} \cdot \mathbf{f}(y)\,\mathrm{d}y = \mathbf{u}(x) - \mathbf{v}^0(x) \tag{6}$$

where $\langle \mathbf{T}(\mathbf{R} - \mathbf{a}) \rangle_{\mathbf{a}}$ is easily found to be

$$\langle \mathbf{T}(\mathbf{R} - \mathbf{a}) \rangle_{\mathbf{a}} = \frac{1}{8\pi\eta_0 |\mathbf{R} - \mathbf{a}|}\left[\mathbf{I} + \frac{2R^2\mathbf{e}_r\mathbf{e}_r + a^2(\mathbf{e}_\theta\mathbf{e}_\theta + \mathbf{e}_\varphi\mathbf{e}_\varphi)}{2(R^2 + a^2)}\right] \tag{7}$$

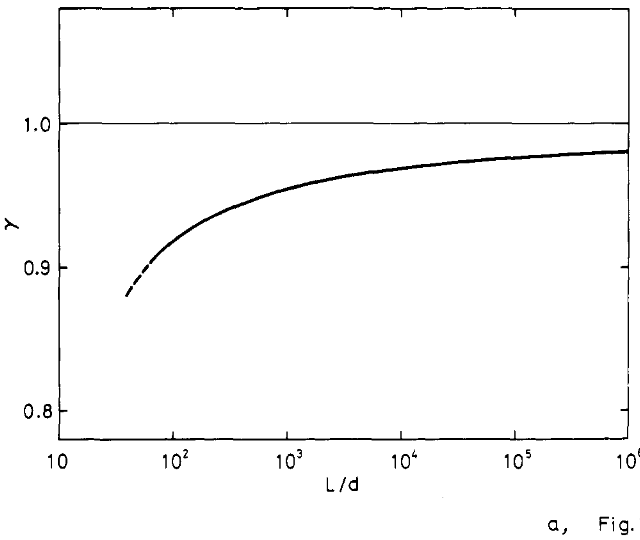

Figure 1. The parameter γ plotted against the logarithm of L/d.

The integral eq 6 is our basic equation determining the frictional force. Note that the usual configurational preaveraging of the Oseen tensor has not been made in eq 7. In what follows, the variables x and y are measured in units of $L/2$, for simplicity.

Rotatory Diffusion Coefficient

For a calculation of the rotatory diffusion coefficient $D^{\theta\theta}$ (or the rotatory friction coefficient) defined by Kirkwood and Auer,[6,8] we may assume that $\mathbf{f}(x) = f(x)\mathbf{e}_\theta$, $\mathbf{v}^0 = 0$, and $\mathbf{u}(x) = \Omega x \mathbf{e}_\theta$ with Ω the angular velocity of the cylinder. If we put

$$f(x) = 4\pi\eta_0 L\Omega\psi_1(x) \tag{8}$$

we obtain

$$D^{\theta\theta} = 3kT/\pi\eta_0 L^3 F_1 \tag{9}$$

where k is the Boltzmann constant, T is the absolute temperature, and F_1 is defined by

$$F_1 = 3\int_{-1}^{1} x\psi_1(x)\,\mathrm{d}x \tag{10}$$

The function $\psi_1(x)$ is determined from eq 6 or

$$\int_{-1}^{1} K_1(x, y)\psi_1(y)\,\mathrm{d}y = x \tag{11}$$

where

$$K_1(x, y) = \frac{1}{[(x - y)^2 + \sigma^2]^{1/2}}\left\{1 + \frac{\sigma^2}{2[(x - y)^2 + \sigma^2]}\right\} \tag{12}$$

with

$$\sigma = d/L \tag{13}$$

The asymptotic analytical solution of the integral eq 11 for $L \to \infty$ may be found by a Legendre polynomial expansion method.[1b] The result is

$$\lim_{L\to\infty} F_1^{-1} = \ln(L/d) + 2\ln 2 - 11/6 \tag{14}$$

where the constant $(11/6) - 2\ln 2 = 0.4470$ is in good agreement with Broersma's value[9] of 0.447 for the corresponding constant.

The numerical solution for F_1 has also been obtained following the procedure of Schlitt[10] and Ullman[4] with the use

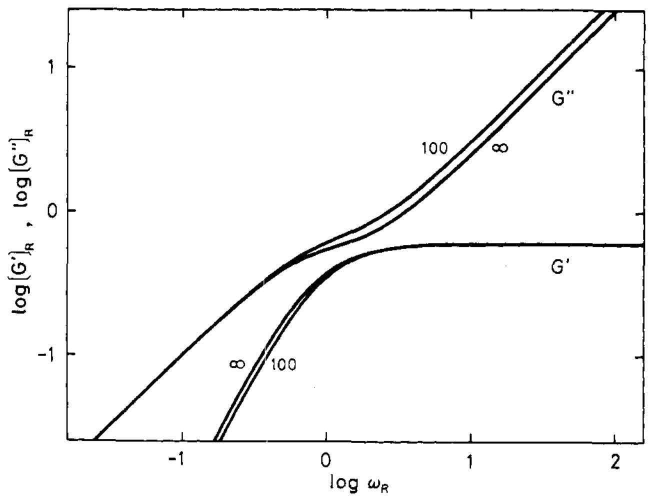

Fig. 2

Figure 2. Log $[G']_R$ and log $[G'']_R$ plotted against log ω_R. The numbers attached to the curves indicate the values of L/d.

of a FACOM 230-75 digital computer at this university. The results may be expressed empirically in the form

$$F_1^{-1} = \ln \sigma^{-1} + c_{10} + c_{11}\sigma + c_{12}\sigma^2 + c_{13}\sigma^3 \quad (15)$$

with

$$c_{10} = -0.481312$$
$$c_{11} = -38.9683$$
$$c_{12} = 3691.64 \quad (16)$$
$$c_{13} = -128,672$$

for

$$\sigma \leq 1.6 \times 10^{-2}$$

Equations 15 with 16 can yield the numerical solutions within 1% error in the indicated range of σ. For larger σ, errors in the numerical solution become large. Although the procedure of Schlitt causes smaller errors, especially in the rod region, than does the procedure previously used, the value of c_{10} in eq 15 does not exactly agree with the corresponding value in eq 14. This disagreement should also be regarded as arising from the fact that eq 15 is just an empirical fit to the numerical solutions.

Intrinsic Viscosity and Rigidity

Suppose that $\mathbf{v}^0$ is an oscillating shear flow with gradient κ and angular frequency ω. Then the orientational distribution function for the cylinder and the velocity $\mathbf{u}(x)$ under the influence of its Brownian motion are well known.[6] The r component of $\mathbf{f}(x)$ is given by

$$\mathbf{f}(x)\cdot\mathbf{e}_r = -2\pi\eta_0 L\kappa\psi_2(x)\sin^2\theta\sin 2\varphi \quad (17)$$

where $\psi_2(x)$ satisfies the integral eq 11 with the kernel

$$K_2(x,y) = \frac{1}{[(x-y)^2+\sigma^2]^{1/2}}\left[1 + \frac{(x-y)^2}{(x-y)^2+\sigma^2}\right] \quad (18)$$

The θ and φ components may be expressed in terms of $\psi_1(x)$, the results being omitted.

With these modifications of the Kirkwood–Auer theory and the definition

$$F_2 = 6\int_{-1}^{1} x\psi_2(x)\,dx \quad (19)$$

the real parts $[\eta']$ and $[G']$ of the intrinsic viscosity and rigidity and the relaxation time τ are obtained as

$$[\eta'] = [G'']/\omega\eta_0 = \frac{\pi N_A L^3}{90M}\left(F_2 + \frac{3F_1}{1+\omega^2\tau^2}\right) \quad (20)$$

$$[G'] = \frac{3RT}{5M}\left(\frac{\omega^2\tau^2}{1+\omega^2\tau^2}\right) \quad (21)$$

$$\tau = 1/6D^{\theta\theta} = 5\gamma\eta_0 M[\eta]_0/4RT \quad (22)$$

with

$$\gamma = 4F_1/(3F_1 + F_2) \quad (23)$$

where N_A is the Avogadro number, R is the gas constant, M is the molecular weight of the cylinder, and $[\eta]_0$ is the zero-frequency intrinsic viscosity

$$[\eta]_0 = \frac{\pi N_A L^3}{90M}(3F_1 + F_2) \quad (24)$$

The asymptotic analytical solution for F_2 is easily found to be

$$\lim_{L\to\infty} F_2^{-1} = \ln(L/d) + 2\ln 2 - 17/6 \quad (25)$$

so that we have from eq 14, 24, and 25

$$\lim_{L\to\infty}[\eta]_0 = \frac{2\pi N_A L^3}{45M}\,\frac{1}{\ln(L/d) + 2\ln 2 - (25/12)} \quad (26)$$

If the Oseen tensor is preaveraged as done previously,[1b] in eq 26 the factor 2/45 and the constant (25/12) − 2 ln 2 = 0.6970 are replaced by 1/24 and (7/3) − 2 ln 2 = 0.9470, respectively.

The numerical solutions for F_2 may be expressed in the form

$$F_2^{-1} = \ln\sigma^{-1} + c_{20} + c_{21}\sigma + c_{22}\sigma^2 + c_{23}\sigma^3 \quad (27)$$

with

$$c_{20} = -1.48618$$
$$c_{21} = -61.1872$$
$$c_{22} = 6734.48 \quad (28)$$
$$c_{23} = -240,760$$

for

$$\sigma \leq 1.6 \times 10^{-2}$$

where the same comments as in eq 15 and 16 apply. The values of γ calculated from eq 23 with eq 15 and 27 are plotted against the logarithm of L/d in Figure 1. The asymptotic limit for $L \to \infty$ is seen to be rather slowly approached.

Now we define the reduced quantities

$$[G']_R = [G']M/RT$$
$$[G'']_R = [G'']M/RT \quad (29)$$

and

$$\omega_R = \omega\eta_0 M[\eta]_0/RT \quad (30)$$

so that

$$\omega\tau = \tfrac{5}{4}\gamma\omega_R \equiv \xi \quad (31)$$

We then have

$$[G']_R = \frac{3}{5}\left(\frac{\xi^2}{1+\xi^2}\right)$$

$$[G'']_R/\omega_R = 1 - \frac{3\gamma}{4}\left(\frac{\xi^2}{1+\xi^2}\right) \quad (32)$$

It is seen that

$$\lim_{\omega \to \infty} [G']_R = 3/5$$
$$\lim_{\omega \to 0} [G'']_R/\omega_R = 1 \qquad (33)$$

These limiting values are independent of γ or M and are identical with the corresponding Kirkwood–Auer limiting values for large M.

Figure 2 shows double-logarithmic plots of $[G']_R$ and $[G'']_R$ against ω_R for $L/d = \infty$ and 100, where we have used the values of γ obtained in Figure 1. The plots are seen to be rather insensitive to the change in the value of L/d. We note that a curve of $[G']_R$ for a given L/d can be obtained by displacing that for $L/d = \infty$ by log γ^{-1} in the abscissa direction, and the high frequency part of a curve of $[G'']_R$ for a given L/d by displacing that for $L/d = \infty$ by log $(4 - 3\gamma)$ in the ordinate direction.

Discussion

As in the previous case of wormlike cylinders,[1] the hydrodynamic behavior of the straight cylinder may be described in terms of only its molecular weight M and dimensions L and d. The results involve no phenomenological friction constant per unit contour length as introduced by Ullman. This is natural from the general point of view of classical hydrodynamics of rigid continuous bodies. Although we have ignored end effects, one way of taking them into account is the following. We may add one-half of an oblate ellipsoid with major semiaxis a and minor semiaxis l to each end of the cylinder, so that the cylinder surface becomes continuous everywhere. The kernels of the integral equations may then be modified in such a way that d depends on x near $x = \pm 1$. In the limit of $l \to 0$, however, such end effects have no influence on the present results. The same argument applies also to the previous work.[1]

According to the present formulation, $D^{\theta\theta}$ and $[G']$ may be expressed in terms of the solution of the same integral equation. Thus the high frequency limit of $[G']_R$ becomes exactly independent of M and takes the Kirkwood–Auer limiting value of 3/5. This simple conclusion cannot be obtained if $D^{\theta\theta}$ and $[G']$ are calculated in a different scheme following the procedure of Kirkwood and Auer, as done by Ullman and Hearst and Tagami.[11,12] The reason is that the Kirkwood–Auer equation for $D^{\theta\theta}$ for rodlike bead models is exactly correct and becomes equivalent to the result from the integral equation only in the limit of $L \to \infty$.[8]

References and Notes

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