Polymer Dynamics. V. The Shear Dependent Properties of Linear Polymers Including Intrinsic Viscosity, Flow Dichroism and Birefringence, Relaxation, and Normal Stresses

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Under the physical requirement that the contour length of a polymer molecule remains constant irrespective of shear rate in the Rouse and Zimm theories and the Harris–Hearst theory, the shear rate dependence of intrinsic viscosity, flow birefringence, flow dichroism, normal stresses, the relaxation of flow birefringence and flow dichroism, and some quantities at zero shear rate have been calculated for molecules of different stiffness ranging from the rod to the flexible coil in θ solvents. Changes of hydrodynamic interaction with shear rate are not included. Comparing the present theory with the experimental results there is satisfactory agreement for stiff molecules such as the cellulose derivatives and DNA at low shear.

I. INTRODUCTION

Harris and Hearst (HH) have recently introduced a dynamic model for a polymer molecule with local stiffness which has many properties similar to that of the Kratky and Porod wormlike coil. The model requires the introduction of a Lagrange multiplier whose magnitude is determined by the constraint that the contour length of the molecule has a fixed value L.

As described previously there is obvious correspondence between the HH theory and the Rouse and Zimm (RZ) theories. In the coil limit there is equivalence between the spring force constant of the RZ model and the Lagrange multiplier of the HH model if the Lagrange multiplier is evaluated from equilibrium properties of the coil at zero shear. We show here that the contour lengths of both the HH theory and RZ theory increase indefinitely with increasing shear rate. This is clearly a very nonphysical property of both models which we have corrected in this paper. It has become apparent to us that the Lagrange multiplier of the HH model or the spring constant of the RZ model must be a function of shear rate in order that the contour length L remains a constant for all values of shear rate. Using this idea, in this paper, we have calculated the shear rate dependences of viscosity, flow birefringence, flow dichroism, normal stresses, the relaxation process of flow birefringence and flow dichroism, and some properties at zero shear rate (for molecules of different stiffness ranging from the rod to the flexible coil) in θ solvents.

The effect of finite chain length on the intrinsic viscosity and flow birefringence of the flexible coil has been studied by Peterlin (the dumbbell model) and Reinhold and Peterlin (the Rouse model). They used the inverse Langevin function, which was introduced in the Kuhn–Gühn's treatment of finite coil deformability, and also introduced an adjustable parameter which gives the maximum extension of segment in the Rouse model. The results are similar to the present ones for the coil region if their extension parameter is chosen correctly. However, the condition of constant contour length in the present theory is a logical constraint introduced into the differential operator by a Lagrange multiplier. We believe its meaning is more clear than is the application of Langevin function to the spring force. The physical meaning of our Lagrange multiplier may be visualized in terms of springs, but, in fact, its justification as a technique is entirely mathematical. Thus, the springs maintaining the constant contour length are not real and the meaning of this theory is different from that of Reinhold and Peterlin.

It should be pointed out that the approach presented here is very different from that of Peterlin and Fixman who propose shear dependence in the θ solvents is caused by changes in hydrodynamic interaction as the distribution of the coil becomes distorted by shear. Although this phenomenon occurs, its effects are relatively small except for very flexible molecules and lead to a predicted shear dependence quite different from that of this theory. Ultimately a combination of these two concepts will be required.

II. THEORY

A. The Contour Length and Its Variation with the Shear Rate

1. The Rouse–Zimm Model

We define the contour length of the Rouse chain by

\[ L = N \langle P \rangle^{1/2} \tag{1} \]

where \( N \) is the number of springs in the chain and \( \langle P \rangle \) is the average of the mean square length of the spring:

\[ \langle P \rangle = N^{-1} \sum_{i=1}^{N} \langle r_i^2 \rangle \tag{2} \]

It follows that the condition requiring the total contour length to remain constant is equivalent to requiring

2342

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that

\[ N^{-1} \sum_{i=1}^{N} \langle l^2 \rangle \]

remain constant. If we assume laminar flow in the x direction, \( v_x \), with a constant gradient along the z axis, the diffusion equation of the chain molecule is given by

\[
\frac{\partial \phi}{\partial t} = \sum_n \left[ -k_n \frac{\partial \phi}{\partial \xi} + \frac{kT}{\mu_n} \left( \frac{\partial^2 \phi}{\partial \xi^2} + \frac{\partial^2 \phi}{\partial \xi' \partial 
\right) + \frac{\partial \phi}{\partial \xi} \right] + \frac{\beta}{\gamma_n} \left[ \xi_n \frac{\partial \phi}{\partial \xi_n} + \eta_n \frac{\partial \phi}{\partial \eta_n} + \xi_n \frac{\partial \phi}{\partial \xi_n} \right] + \frac{3 \beta}{\gamma_n} \phi, \tag{3}
\]

when \( \phi \) is the distribution function of the chain, \( \beta \) is the force constant of the spring, \( \kappa \) is the shear rate, \( \mu_n \) is the friction constant, \( \gamma_n \) and \( \gamma_n \) are the eigenvalues, and \( \xi_n, \eta_n, \) and \( \xi_n \) are the normal coordinates associated with the x, y, z coordinates, respectively.

The distribution function of the chain in the Rouse normal mode problem at steady state is

\[
\phi = \text{const} \times \exp \left\{ -\frac{\beta}{2kT} \sum_{n=1}^{N} \left[ \frac{(\xi_n - (\beta_z/\gamma_n) \xi_n)}{1 + (\beta_z/\gamma_n)^2} \right. \right. \]

\[ + \frac{\eta_n^2 + \xi_n^2}{1 + (\beta_z/\gamma_n)^2} \right. \left. \right] \right\} \tag{4}

with \( \beta_z = kN/\beta \). Therefore, the mean squares of the normal coordinates are given by

\[
\left\langle \xi_n^2 \right\rangle = (kT/\mu_n) \left[ 1 + (\beta_z/\gamma_n)^2 \right], \tag{5}
\]

\[
\left\langle \eta_n^2 \right\rangle = \left\langle \xi_n^2 \right\rangle = kT/\beta \mu_n. \tag{6}
\]

The relationship between the mean square length of the spring and the normal coordinate is

\[
\left\langle l^2 \right\rangle = \sum_n \left\{ \left\langle \xi_n^2 \right\rangle + \left\langle \eta_n^2 \right\rangle + \left\langle \xi_n^2 \right\rangle \right\} \left\{ \psi_n(i+1) - \psi_n(i) \right\} \]

or for large \( N \) in the continuum limit

\[
\left\langle l^2 \right\rangle = \sum_n \left\{ \left\langle \xi_n^2 \right\rangle + \left\langle \eta_n^2 \right\rangle + \left\langle \xi_n^2 \right\rangle \right\} \left\{ \partial \psi_n(i)/\partial t \right\}^2. \tag{7}
\]

Here, \( \psi_n(i) \) is the eigenfunction as follows:

\[
\psi_n(i) = \begin{cases} (2/N)^{1/2} \sin \left[ \frac{i}{N} (2i/N - 1) \right] & \text{if } n \text{ odd} \\
(2/N)^{1/2} \cos \left[ \frac{i}{N} (2i/N - 1) \right] & \text{if } n \text{ even.} \end{cases} \tag{8}
\]

The average of the mean square length of the spring is obtained by using Eqs. (2) and Eqs. (5)-(7):

\[
\langle P \rangle \approx (3kT/\beta) N^{-1} \sum_n (\mu_n)^{-2} \left[ 1 + \frac{3}{2} (\gamma_n^2 - \beta_z^2) \right] \times \sum_i \left\{ \partial \psi_n(i)/\partial t \right\}^2. \tag{9}
\]

Using \( \mu_n = \gamma_n = \pi N^2/2N^2 \) and Eq. (8) we have for the free draining coil

\[
\langle P \rangle = (3kT/\beta) \left[ 1 + \left( 3N^2/135 \right) (\beta_z^2) \right] \]

\[
= (3kT/\beta) \left[ 1 + (4/15N) (\beta_z^2) \right] \]

\[
= (3kT/\beta) \left[ 1 + (\pi^2/135N) (\tau_{1\beta})^2 \right]. \tag{10}
\]

Here, we have used the following relationships between \( \beta_z \) and \( \beta_p \) and \( \tau_{1\beta} \):

\[
\beta_p = \frac{M [\eta]_{\beta_0} \mu_n}{RT} = \left( \sum_n \gamma_n \psi_n(i+1) - \psi_n(i) \right) \tag{11}
\]

and

\[
\tau_{1\beta} = \beta_z/\gamma_1. \tag{12}
\]

where \( M \) is the molecular weight, \( [\eta] \) is the intrinsic viscosity, \( \eta_0 \) is the solvent viscosity, and \( \tau_1 \) is the first relaxation time. Using the values of \( \gamma_n \) calculated by Zimm et al., we have for the nondraining coil

\[
\langle P \rangle = (3kT/\beta) \left[ 1 + 1.227 \times 10^{-2} N^2 \beta_z^2 \right] \]

\[
= (3kT/\beta) \left[ 1 + 0.1365 (\beta_z^2/\beta) \right] \]

\[
= (3kT/\beta) \left[ 1 + (0.765/N) (\tau_{1\beta})^2 \right]. \tag{13}
\]
Although the $\langle \tilde{p} \rangle$ of the free draining and nondraining coils show entirely different dependences on $N$ in terms of $\beta_n$, it is noteworthy that both of them show the same functional relationship in terms of $\beta_n$ and moreover, give almost the same numerical values in terms of $\tau_k$. Therefore, we will use $\tau_k$ as the reduced shear in the following calculation. The quantity $\tau_k$ is simply related to $\beta_p$ which can be obtained experimentally, i.e.,

$$\beta_p = \frac{\gamma_1}{\sum_n (1/\gamma_n)} [\gamma_1 \frac{1}{\sum_n (1/\gamma_n)}] \tau_k.$$

The condition requiring the total contour length to remain constant is

$$\langle \tilde{p} \rangle = (3kT/\beta) [1 + a(\tau_k^2/\gamma_0^2)] = \langle \tilde{p} \rangle_0 = 3kT/\beta_0,$$  \hspace{1cm} (14)

where the constant $a$ is 0.722 for the free draining and 0.765 for the nondraining and $\beta_0$ is the force constant at the zero shear rate. Then we have the following equation for the variation of $\beta$ in terms of $x = \beta/\beta_0$ with shear rate $\kappa$:

$$x^3 - 2x^2 - a(\tau_k^2/\gamma_0^2) = 0.$$  \hspace{1cm} (15)

Here, $\tau_H$ is the first relaxation time at the zero shear rate. The cubic equation can be easily solved and the relationship between $\log(\beta/\beta_0)$ and $\log(\tau_k^2/\gamma_0^2)$ is shown in Fig. 1.

2. The Harris–Hearst Model

The contour length of the Harris–Hearst model, which is more clearly defined than that of RZ model, is given by

$$\langle L \rangle = \int_{-L/2}^{L/2} ds \lim_{s \to 0} \frac{d}{ds} \langle \mathbf{x}(s) \cdot \mathbf{x}(s') \rangle,$$  \hspace{1cm} (16)

where $\mathbf{x}(s)$ is the vector from the center of chain to the point of contour length $s$.

We have in the normal mode problem

$$\langle L \rangle = \sum_n \{ \langle \xi_n^2 \rangle + \langle \gamma_n^2 \rangle + \langle \xi_n^2 \rangle \}$$

$$\times \int_{-L/2}^{L/2} \left( \frac{\partial \psi_n(s)}{\partial s} \right)^2 ds.$$  \hspace{1cm} (17)

We have formerly the same distribution function for the HH model in normal coordinates as Eq. (4) for the RZ model if we use the bending force constant $\alpha$ in place of $\beta$. The same equation for the mean square of the normal coordinates as Eqs. (5) and (6) applies:

$$\langle \xi_n^2 \rangle = (kT/\alpha_n) [1 + 2(\beta_{HH}^2/\gamma_n^2)],$$

$$\langle \gamma_n^2 \rangle = \langle \xi_n^2 \rangle = kT/\alpha_n,$$  \hspace{1cm} (5')

with $\beta_{HH} = sf/2\alpha$. Thus Eq. (17) reduces to

$$\langle L \rangle = \frac{3kT}{\alpha} \sum_n (\mu_n)^{-1} [1 + \frac{1}{3} (\gamma_n^2)^{-1} \beta_{HH}^2]$$

$$\times \int_{-L/2}^{L/2} \left( \frac{\partial \psi_n(s)}{\partial s} \right)^2 ds.$$  \hspace{1cm} (18)

The eigenvalues for the HH model are

$$\mu_n L^4 = \nu_n L^4 + (\Delta L^2) v_{1n} L^2 = \nu_{2n} L^4 - (\Delta L^2) v_{2n}^2 L^2,$$

$$\gamma_n L^4 = \mu_n L^4 (1 + I_n)$$  \hspace{1cm} (19)

with

$$I_n = \frac{1}{2} \int_{-L/2}^{L/2} \int_{-L/2}^{L/2} \Psi_n(s') \Psi_n(s) ds ds'$$

and

$$\Lambda = \beta/\alpha.$$  \hspace{1cm} (20)

For the convenience of the calculation, we rewrite Eq. (17) with dimensionless parameters

$$\langle L \rangle = 4(\lambda L) \sum_n \left( \frac{1}{\mu_n L^4} \right) [1 + \frac{1}{3} \left( \frac{(\beta_{HH} L)^2}{(\gamma_n L^4)^2} \right)]$$

$$\times H_n(v_1 L, v_2 L).$$  \hspace{1cm} (21)

Here, we used the relationship $3kT/\alpha = 4\lambda$, where $1/\lambda$ is the statistical length, and

$$L^2 \int_{-L/2}^{L/2} \left( \frac{\partial \psi_n(s)}{\partial s} \right)^2 ds = H_n(v_1 L, v_2 L).$$

The condition of constant contour length is

$$1 = 4(\lambda L) \sum_n \left( \frac{1}{\mu_n L^4} \right) [1 + \frac{1}{3} \left( \frac{(\beta_{HH} L)^2}{(\gamma_n L^4)^2} \right)] H_n.$$  \hspace{1cm} (22)

The variations of the Lagrange multiplier or force constant $\Delta L^2$ with $\beta_{HH} L^2$ were calculated for various contour lengths and stiffness of the molecules by solving Eq. (21) with the computer. Here we assumed $I_n$ is independent of shear rate for the convenience of calculation considering that the dependence of $I_n$ on $\Delta L^2$ is small.

For the flexible coil region and rod limit in the free draining cases, we can obtain the analytical expression for the contour length by using the approximate eigenvalues and eigenvectors. This calculation is very useful to get perspective into this problem since we can expect the equations to be almost the same in terms of $\tau_k$ irrespective of draining as seen in the RZ model. The eigenvalues and approximate eigenvectors for the free draining coil are

$$\mu_n L^4 = \gamma_n L^4 = (\pi n)^4 + (\Delta L^2) (\pi n)^2,$$  \hspace{1cm} (22)

$$\psi_n(s) = 2(L/\pi)^{1/2} \sin[\pi n(L/\pi) s] \quad n \text{ odd},$$

$$= 2(L/\pi)^{1/2} \cos[\pi n(L/\pi) s] \quad n \text{ even}.$$  \hspace{1cm} (23)

By the substitution of Eqs. (22) and (23) into Eq. (20), we have at the limit of the free draining flexible coil:

$$\langle L \rangle = \frac{2\lambda L}{(\Lambda)^{1/2} L} \left[ 1 + \frac{1}{8} \left( \frac{(\beta_{HH} L)^2}{(\gamma_n L^4)^2} \right) \right]$$

$$= \frac{2\lambda L}{(\Lambda)^{1/2} L} \left[ 1 + \frac{4n^2}{270} (\tau_k^2)^{1/2} \right].$$  \hspace{1cm} (24)

where $\tau_k = \beta_{HH} L^2/\gamma_n L^4$, which is similar to Eq. (12). The condition of the constant contour length in terms of
$y = \Delta L^2/\Lambda \sigma^2$ gives

$$y^2 - y - 270 (\sigma \bar{\nu}^2/\lambda L) = 0.$$  \hspace{1cm} (25)

Here, we used the relationship $(\Lambda \sigma)^{1/2} L = 2 \lambda L$ since $\Lambda \sigma = \lambda L^2/\sigma$. For the free draining rod, the first eigenvalue and $H_1$ are

$$\mu_1 L^4 = \gamma_1 L^4 = 12 \lambda_0 L^2 + (\Lambda L^2) (12 \lambda_0 L^2)^{1/2}, \quad H_1 = 12.$$  \hspace{1cm} (26)

Since the contribution of the higher eigenvalues is negligible relative to the first one, we have

$$\langle L \rangle = 48 (\Lambda L^2) L \left[ 12 \lambda_0 L^2 + (\Lambda L^2) (12 \lambda_0 L^2)^{1/2} \right]^{-1} + \frac{3}{2} \left( \beta BH \right) \left[ 12 \lambda_0 L^2 + (\Lambda L^2) (12 \lambda_0 L^2)^{1/2} \right]^{-1}.$$  \hspace{1cm} (27)

The condition of constant contour length is

$$s^2 - s^2 - 3 \tau_0 \bar{\nu}^2 = 0,$$  \hspace{1cm} (28)

where

$$s = \mu_1 L^4 / 12 \lambda_0 L^2 = 1 + [12 \lambda_0 L^2 / 12 \gamma_1].$$  \hspace{1cm} (29)

Equations (27) and (28) predict that $\Delta L^2/\Lambda \sigma^2$ is a unique function of $\tau_0 \bar{\nu}^2/\lambda L$ for the coil and of $\tau_0 \bar{\nu}^2$ for the rod. The variations of the force constant with shear rate for the HH model are shown by plotting $\log(\Delta L^2/\Lambda \sigma^2)$ against $\log(\tau_0 \bar{\nu}^2/\lambda L)$ for $\lambda L \geq 1$ and $\log(\tau_0 \bar{\nu}^2)$ for the rod limit in Fig. 1. The computer result for the nondraining case almost agrees with that for the free draining case. They are also in good agreement with the result of Eq. (25) for the coil limit if $\lambda L > 49$ and with that of Eq. (28) for the rod limit unless $\log(\tau_0 \bar{\nu}^2)$ is small where the approximation in Eq. (28) becomes poor. The effect of the diameter of the backbone, $h$, on the results is not large except for low $\lambda L$. The HH model at the coil limit gives almost the same dependence of the force constant on the molecular weight and shear rate as the RZ model does, although there are slight numerical differences between them due to differences in the definition of their contour lengths.

**Fig. 2.** The non-Newtonian viscosity of polymers having various $\lambda L$. The curves are the computer results at non-draining for $\lambda L = 10^{-3}$, 1, 10, 49, $10^6$, $4 \times 10^5$, $10^6$, and $10^8$ from bottom to top.
B. The Non-Newtonian Viscosity

Defining the relative intrinsic viscosity \( \eta_{rel} \) as the ratio of the intrinsic viscosity at the finite shear rate \( \dot{\gamma} \) to that at zero shear rate, we have the following relationship for each of the models:

\[
[\eta]_{rel} = \left[ \eta \right]/\left[ \eta \right]_0 = (\beta^{-1})_\dot{\gamma}/(\beta^{-1})_0 = 1/x
\]

for the RZ model,

\[
[\eta]_{rel} = [\eta]_x/[\eta]_0 = \sum_n \left( \gamma_n L^4 \right)x^{n-1}/\sum_n (\gamma_n L^4) x^{-1}
\]

\[
= \sum_n \left[ (\gamma_n L^4)^2 + (\Delta L^2)^2 (\gamma_n L^4)^2 (1+I_n) \right]^{-1}
\]

\[
= \sum_n \left[ (\gamma_n L^4)^2 + (\Delta L^2)^2 (\gamma_n L^4)^2 (1+I_n) \right]^{-1}
\]

for the HH model. Since \( x \) is expressed in terms of \( (\tau_{10k})^2/N \) for the RZ model, \( [\eta]_{rel} \) is a function of \( (\tau_{10k})^2/N \) or \( \beta_{10}^2/N \) irrespective of the drainage, where \( \beta_{10} \) is the value of \( \beta_{10} \) calculated when \( [\eta] = [\eta]_0 \) is substituted into Eq. (11). The right term of Eq. (31) is equal to \( 1/\gamma \) in the coil limit and is equal to \( 1/\gamma \) in the rod limit for the HH model. Hence, \( [\eta]_{rel} \) is a function of \( (\tau_{10k})^2/N \) or \( \beta_{10}^2/N \) for the coil limit and is a function of \( \eta_{rel} \) or \( \beta_{10} \) for the rod limit.

In Fig. 2, \( [\eta]_{rel} \) is plotted against \( \log \beta_{10} \) for the various values of \( \lambda L \) and also numerical values of \( [\eta]_{rel} \) are listed in Table I. The result in the rod limit is in good agreement with the non-Newtonian viscosity of rigid ellipsoids having large axial ratio. The present theory predicts the effect of stiffness on the non-Newtonian viscosity from the flexible coil to rigid rod. For the stiff molecule the \( [\eta]_{rel} \) drops at lower values of \( \beta_{10} \) than for the flexible molecule. This result is entirely different from many theories so far published but the result in the coil limit is similar to the results of Cerf, and of Reinhold and Peterlin. The physical meaning of their model is different from ours because Cerf introduced "the internal viscosity" to the RZ model as a parameter of stiffness and Reinhold and Peterlin used the inverse Langevin function in place of the Hookian spring and introduced an additional arbitrary parameter as mentioned in the Introduction.

C. Flow Birefringence and Flow Dichroism

The optical properties of the polymer in solution are determined by the polarizability or absorption coefficient tensor of the segments. The tangent vector on the chain, \( t \), is given by the following equation according to the HH theory:

\[
t = \partial x/\partial s = \sum_n \epsilon_n [\partial \psi_n(s)/\partial s],
\]

where \( x \) is the vector from the center of the chain to the point \( s \) and the \( \epsilon_n \)'s are the amplitudes.

The direction cosines of the vectors \( l \), \( m \), and \( n \) referenced to \( x \), \( y \), and \( z \) are given in the normal coordinate problem by

\[
l = t \cdot i = \sum_n \xi_n [\partial \psi_n(s)/\partial s],
\]

\[
m = t \cdot j = \sum_n \eta_n [\partial \psi_n(s)/\partial s],
\]

\[
n = t \cdot k = \sum_n \zeta_n [\partial \psi_n(s)/\partial s].
\]

Now we define \( \epsilon_{1l} \) as the polarizability or absorption coefficient component per unit length along the segment and \( \epsilon_{1s} \) as the value of two equal components normal to this vector. Using these quantities defined above, the tensor of polarizability or absorption coefficient which is averaged over all configurations of the polymer is given by

\[
\epsilon_{1l} + (\epsilon_{1l} - \epsilon_{1s}) \left( \begin{array}{ccc}
\langle P \rangle & \langle ml \rangle & \langle ln \rangle \\
\langle ml \rangle & \langle m^2 \rangle & \langle mn \rangle \\
\langle ln \rangle & \langle mn \rangle & \langle n^2 \rangle 
\end{array} \right),
\]

where \( I \) is the unit tensor and \( \langle \cdot \rangle \) means the average over all configurations of the polymer chain.

We obtain the following relationship between the average quantities of the direction cosines used later and the normal coordinates from Eq. (33):

\[
\langle P^2 \rangle = L^{-1} \int_{-L/2}^{L/2} \sum_n \xi_n^2 \left( \frac{\partial \psi_n(s)}{\partial s} \right)^2 ds,
\]

\[
\langle n^2 \rangle = L^{-1} \int_{-L/2}^{L/2} \sum_n \eta_n^2 \left( \frac{\partial \psi_n(s)}{\partial s} \right)^2 ds,
\]

\[
\langle ln \rangle = L^{-1} \int_{-L/2}^{L/2} \sum_n \xi_n \eta_n \left( \frac{\partial \psi_n(s)}{\partial s} \right)^2 ds.
\]

Here, \( \langle \xi_n^2 \rangle \) and \( \langle \eta_n^2 \rangle \) are already given by Eqs. (5)' and (6)', and \( \langle \xi_n \eta_n \rangle \) is also easily calculated using the distribution function (4):

\[
\langle \xi_n \eta_n \rangle = \langle kT/\alpha \mu \gamma_n \rangle \beta_{HH}.
\]

The expression of the flow birefringence or flow dichroism depends on the relationship between the direction of flow, light beam, and the measurement.

When the light beam progresses along the \( y \) axis, the difference of the intrinsic polarizabilities or absorption coefficients along the principle axes is

\[
\Delta \Gamma = (\epsilon_{1l} - \epsilon_{1s}) L [\langle P^2 \rangle - \langle n^2 \rangle + 4(\langle ml \rangle)^2]^{1/2}
\]

and also the extinction angle \( \chi \) which is defined as the smaller angle between the principle axis and \( x \) axis is

\[
tan 2\chi = 2(\langle ln \rangle - \langle P^2 \rangle - \langle n^2 \rangle). \quad (38)
\]

By substitution of Eqs. (5)' and (6)', (35), and (36) into Eqs. (37) and (38) we have

\[
tan 2\chi = \frac{\sum H_n(\mu_s L^2)(\gamma_n L^2)/(\mu_s L^2)(\gamma_n L^2)^2)(\beta_{HH} L^4)}{\sum [\mu_n L^2]}.
\]


and
\[ \Delta \Gamma = \frac{8}{3} (\epsilon_1 - \epsilon_2) \lambda \mathcal{L} \left[ \sum_n H_n / (\mu_n L^4) (\gamma_n L^4) \right] \times (\cosec 2\chi) (\beta_{HH} L^4). \] (40)

The magnitude of the intrinsic birefringence of the solution is given by
\[ \Delta n = \Delta \Gamma (CN_A / M) \frac{3}{2} \pi \left[ (n_0^2 + 2)^2 / 6n_0 \right]. \] (41)

Here, $C$ is the concentration (g/ml), $M$ is the molecular weight, $N_A$ is the Avogadro number, and $n_0$ is the refractive index of solvent.

Thus
\[ \Delta n = 4 (N_A B / M_L) C (\lambda L) \sum_n \left[ H_n / (\mu_n L^4) (\gamma_n L^4) \right] \times (\cosec 2\chi) (\beta_{HH} L^4) \] (42)

with
\[ B = \frac{3}{2} \pi \left[ (n_0^2 + 2)^2 / 9 n_0 \right] (\epsilon_1 - \epsilon_2) \]
and
\[ M_L = M / L. \]

By substituting Eqs. (22) and (23) into Eqs. (39) and (42), we have the following equations in the coil limit:
\[ \tan 2\chi = \frac{\sum_n (\gamma_n L^4)^{-1}}{\sum_n (\gamma_n L^4)^{-2} (\beta_{HH} L^4)} \] (43)
and
\[ \Delta n = (N_A C / M) (B / L) \sum_n (\gamma_n L^4)^{-1} (\cosec 2\chi) (\beta_{HH} L^4). \] (44)

Equation (44) shows that the optical anisotropy of the principle axes $(\gamma_1 - \gamma_2)$ is proportional to $1/\lambda (\epsilon_1 - \epsilon_2)$ in the coil limit. Kuhn and Grün8 derived the relationship (45a) between the optical anisotropy of the Gaussian chain and that of its structural unit, $(\epsilon_1 - \epsilon_2)$. Gotlib7 also obtained the relationship (45b) for the wormlike coil in the coil limit:
\[ \gamma_1 - \gamma_2 = (3/5) (\epsilon_1 - \epsilon_2), \] (45a)
\[ \gamma_1 - \gamma_2 = (1/2\lambda) (\epsilon_1 - \epsilon_2). \] (45b)

The numerical difference between the optical anisotropy in Eq. (44) and Eq. (45) probably is caused by the different averaging processes of optical vector. That is, the end-to-end distance is fixed in both the Kuhn–Grün and Gotlib averaging processes but not in the present one. By substitution of Eq. (45a) in Eq. (44), Eq. (44) at low shear agrees with the result of the RZ model having the Kuhn–Grün optical segments.7 When the light beam progresses along the $y$ axis and polarization or adsorption coefficient is observed along the $x$ and $z$ axes, the difference $\Delta \epsilon = \epsilon_x - \epsilon_z$ is given by
\[ \Delta \epsilon = -(\epsilon_1 - \epsilon_2) L \left[ (n^2 - 1)^2 \right]. \] (46)

This equation is almost equal to Eq. (37) if the extinction angle is almost equal to zero as assumed for very high molecule weight DNA at high shear rate. When we define the average adsorption coefficient as $\bar{\epsilon} = (\epsilon_1 + 2\epsilon_2) / 3$, we obtain an equation for flow di-
Table II. The extinction angle. The variation of log[\cot 2\chi] of the polymer having various L with the reduced shear rate, log\beta_p.

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<th>L</th>
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\[ \Delta \varepsilon / \varepsilon = - \frac{\langle \varepsilon_h \rangle \langle L^4 \rangle}{\langle L \rangle} \times \frac{1}{n} \sum \left( H_n / \mu_n L^4 \right) (\gamma_n L^4)^2 (\beta_{HH} L)^2. \] (47)

When an unpolarized light beam progresses along the \( x \) axis and adsorption is observed along the \( z \) axis, the difference of adsorption coefficient of the flowing \( A_{\|} \) and the stationary solution \( A \) is given by\(^{19}\)

\[ (A_{\|} - A) / A = \Delta A / A = - \frac{(\varepsilon_{11} - \varepsilon_{12})}{6\varepsilon} \times \frac{(4\lambda L)}{\sum \mu_n L^4} \frac{H_n}{\mu_n L^4} \times \left[ 1 + \left( \frac{\beta_{HH} L^6}{(\gamma_n L^4)^2} \right) \right] - 1. \] (48)

Since the eigenvalue is a function of shear rate as described in Sec. II A, we obtained the shear rate dependence of flow birefringence and flow dichroism using the computer. The numerical results of these quantities are shown in Figs. 3–6 and Table II and III. It is noteworthy that we have almost the same dependence of birefringence and dichroism in terms of \( \tau_{HH} \) irrespective of draining. As shown in Figs. 3–5, flow birefringence and flow dichroism do not increase infinitely as the original RZ theory\(^{7}\) predicts and also the shape and position of those curves depend on the stiffness of molecules. The similar saturation effect was obtained in the Reinhold and Peterlin theory.\(^{9}\) The extinction angle \( \chi \) decreases more rapidly with in-

Fig. 5. The comparison between the theory and the experimental data of flow dichroism\(^{10}\) of DNA solutions at high shear rate. The curves are the computer results of Eq. (48) at non-drainage with the same optical values obtained in Fig 4 for \( L = 25, 10^6, \) and \( 4 \times 10^6 \), respectively. The symbols (.), (.), and (.) are the data for \( \lambda_0 = 25 \text{ c.} \) half molecule, \( \lambda_0 = 25 \text{ c.} \) and \( T = 4 \) in 0.1 M NaCl buffer solution.
increasing stiffness. The variation of $\chi$ with shear rate at the rod limit is similar to that of the rotational ellipsoid having the infinite axial ratio\textsuperscript{20} but does not exactly agree with it because of the preaveraging of the Oseen tensor. The initial slope of the curve of $\chi$ vs $\kappa$ is given by

$$-(d\chi/d\kappa)_{\kappa=0} = D(\eta)[n]_{\eta} M/2RT.$$ \hfill (49)

Here, $D$ increases with increasing stiffness from the value of 0.2 for the flexible coil to the value 1.0 for the rod as seen in Table IV. The value of the rod limit is not equal to that of the rotational ellipsoid having the infinite axial ratio (1.25).\textsuperscript{20} Determining the intrinsic birefringence at zero shear rate by

$$[n] = \lim_{C \to 0, \kappa \to 0} (\Delta n/C\eta_{0}),$$ \hfill (50)

the ratio of $[n]$ to the intrinsic viscosity $[\eta]$ is given by

$$\frac{[n]}{[\eta]} = \frac{4B}{kT} \frac{\lambda L}{L} \left[ \frac{\sum_n H_n/(\mu_s L^4) (\gamma_L L^4)}{\sum_n (1/\gamma_L L^4)} \right]_{\kappa=0}.$$ \hfill (51)

For the free draining case we have the following equations at the limits of flexible coil and rigid rod:

$$\frac{[n]}{[\eta]} = (B/kT) \lambda^{-1},$$ \hfill (52)

$$\frac{[n]}{[\eta]} = (B/kT) \lambda, \quad \text{at rod limit.} \hfill (53)$$

A similar result has been obtained by Gotlib and Svetlov\textsuperscript{20} who used a free draining wormlike chain, but the numerical values are 2 and $\frac{2}{3}$ times larger than their result in the coil and rod limit, respectively. The differences may be related to the different optical constants as mentioned before. Since the computer results show that $[n]/[\eta]$ is not affected by the amount of drainage, the ratio of $[n]/[\eta]$ to $(\sum_n H_n/\mu_s L^4)(\gamma_L L^4)_{\kappa=0}$ at the coil limit is

$$\frac{[n]}{[\eta]} = 4(\lambda L)^2 \frac{\sum_n H_n/(\mu_s L^4) (\gamma_L L^4)}{\sum_n (1/\gamma_L L^4)}_{\kappa=0}.$$ \hfill (54)

<table>
<thead>
<tr>
<th>$\lambda L$</th>
<th>$10^{-3}$</th>
<th>1</th>
<th>10</th>
<th>49</th>
<th>$4 \times 10^{3}$</th>
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Fig. 6. The variations of the extinction angle, \( \log[\cot 2\chi] \), with shear rate. The curves are the computer results at nondrainage for \( \lambda L = 10^{-3}, 1, 10, 49, 4 \times 10^3, 10^4, \) and \( 10^4 \) from top to bottom at low shear rate.

Since this ratio is a function of \( \lambda L \) as shown in Fig. 7 we can determine \( 1/\lambda \) from this equation.

D. Normal Stress

Since the HH model can be formally expressed as the same normal coordinate problem as the RZ model, the normal stresses are given by

\[
\sigma_{zz} - \sigma_{zz}^0 = (CN_AkT/M) \sum_n \left[ -1 + (\alpha/kT)\mu_n(\alpha z)^2 \right],
\]
\[
\sigma_{yy} - \sigma_{yy}^0 = (CN_AkT/M) \sum_n \left[ -1 + (\alpha/kT)\mu_n(\beta_y L)^2 \right],
\]
\[
\sigma_{xx} - \sigma_{xx}^0 = (CN_AkT/M) \sum_n \left[ -1 + (\alpha/kT)\mu_n(\alpha z)^2 \right].
\]

(55)

Substituting Eqs. (5') and (6') in Eq. (55), we have

\[
\sigma_{zz} - \sigma_{zz}^0 = 2CN_AkT \sum_n \left( 1/\gamma_n L \right)^2 (\beta_{HH} L)^2,
\]
\[
\sigma_{yy} - \sigma_{yy}^0 = \sigma_{xx} - \sigma_{xx}^0 = 0.
\]

(56)

The relationship (57) is always obtained irrespective of stiffness and drainage in this model. However, it is known that \( \sigma_{yy} - \sigma_{yy}^0 \neq \sigma_{xx} - \sigma_{xx}^0 \neq 0 \) for the rod.\(^{23}\) This discrepancy most likely comes from preaveraging of Oseen tensor in the present theory. The reduced steady state compliance \( J_{\text{sr}} \) is given by

\[
J_{\text{sr}} = (CNY_A/M)kTJ_c = \frac{\sum_n \left[ 1/(\gamma_n L)^2 \right]}{\sum_n \left[ (1/\gamma_n L)^2 \right]}.
\]

(58)

\( J_{\text{sr}} \) at zero shear rate is unity in the rod limit, decreases with increasing \( \lambda L \), and then becomes 0.20 in the coil limit. \( J_{\text{sr}} \) for the actual rod is 15/16.\(^{23}\) This discrepancy also comes from the preaveraging. Moreover, \( J_{\text{sr}} \) decreases with increasing shear rate as shown in Fig. 8.

It is noteworthy that the proportional optical constants\(^{24,25}\) between \( \Delta e \) and \( \Delta\sigma = \sigma_{zz} - \sigma_{xx} \) vary with the stiffness and shear rate in the present theory. From Eqs. (46) and (56), we have

\[
\Delta e = \frac{4}{3} \frac{(\epsilon_{\parallel} - \epsilon_{\perp})}{kT} \sum_n \left( 1/\gamma_n L \right)^2 \left( \beta_{HH} L \right)^2,
\]
\[
\Delta\sigma = \frac{\gamma_n}{3} \frac{(\epsilon_{\parallel} - \epsilon_{\perp})}{kT} \sum_n \left( 1/\gamma_n L \right)^2.
\]

(59)

The function \( K \) changes from 1/\( \lambda \) for the coil to \( L \) for rod at zero shear rate and also \( K \) markedly decreases with increasing shear rate. Thus, the flow birefringence or flow dichroism in this theory are not proportional to normal stress except for the limit of the coil. This result is caused by the nonlinearity of the elastic modulus introduced under the condition of constant contour length. It is interesting to see that the initial behavior of the function \( K \) for the rod limit is similar to that of the actual rod.\(^{20,23}\)

E. The Relaxation of Flow Birefringence and Flow Dichroism

Under the condition that \( \kappa \) is zero after \( t = 0 \) from steady shear rate the diffusion equation of the HH model is

\[
\frac{\partial \phi}{\partial t} = \sum_n \left( \frac{kT \gamma_n}{f \mu_n} \left[ \frac{\partial \phi}{\partial \xi_n^2} + \frac{\partial \phi}{\partial \eta_n^2} + \frac{\partial \phi}{\partial \zeta_n^2} \right] + \frac{\alpha}{f} \gamma_n \left[ \frac{\partial \phi}{\partial \xi_n} + \eta_n \frac{\partial \phi}{\partial \eta_n} + \zeta_n \frac{\partial \phi}{\partial \zeta_n} \right] + \frac{3 \alpha}{f} \gamma_n \phi \right).
\]

(60)

By multiplying both terms of Eq. (60) with \( \xi_n, \eta_n, \) and \( \zeta_n \), we have the following differential equations of relaxation:

\[
(d(\xi_n^2)/dt) + 2(\alpha/f) \gamma_n(\xi_n^2) = 2(kT/f)(\gamma_n/\mu_n),
\]
\[
(d(\eta_n^2)/dt) + 2(\alpha/f) \gamma_n(\eta_n^2) = 2(kT/f)(\gamma_n/\mu_n),
\]
\[
(d(\zeta_n^2)/dt) + 2(\alpha/f) \gamma_n(\zeta_n^2) = 0.
\]

(61)
We solved the differential equations under the following initial conditions:

\[
\langle \xi^2 \rangle_{t=0} = \left( kT/\alpha \mu_n \right) \left[ 1 + 2 (\beta_{HH}/\gamma_n^2) \right] \beta_{HH} \beta_{HH},
\]

\[
\langle \xi_s^2 \rangle_{t=0} = \left( kT/\alpha \mu_n \right) \beta_{HH} \beta_{HH},
\]

\[
\langle \xi^2 \rangle_{t=0} = \left( kT/\alpha \mu_n \right) \beta_{HH} \beta_{HH}
\]

where the subscript $\beta_{HH}$ denotes the quantity is evaluated at the steady-state shear rate $\beta_{HH}$, which pertains prior to stopping the flow. Thus we have

\[
\langle \xi^2 \rangle = \left( kT/\alpha \right) \left[ \mu_n^{-1} \beta_{HH} \left[ 1 - \exp \left( -t/\tau_n \right) \right] + \mu_n^{-1} \beta_{HH} \exp \left( -t/\tau_n \right) \right],
\]

\[
\langle \xi_s^2 \rangle = \left( kT/\alpha \right) \left[ \mu_n^{-1} \beta_{HH} \left[ 1 - \exp \left( -t/\tau_n \right) \right] + \mu_n^{-1} \beta_{HH} \exp \left( -t/\tau_n \right) \right],
\]

with

\[
\tau_n = \left( f/2 \alpha \right) \left( 1/\gamma_n \right) \beta_{HH}^{-1}.
\]

We can obtain the equation for the relaxation of flow birefringence and flow dichroism by using Eq. (63). The $c$- and $s$-mode birefringences measured by Thomson and Gill are

\[
\Delta J_c = \text{const} \times \sum_n \left[ \langle \xi^2 \rangle - \langle \xi_s^2 \rangle \right] (H_n/L^2),
\]

\[
\Delta J_s = \text{const} \times \sum_n \langle \xi_s^2 \rangle / (H_n/L^2).
\]

Thus the ratios of these modes at $t$ and at the initial time are

\[
\frac{\Delta J_c(t)}{\Delta J_c(0)} = \frac{\sum_n \left[ H_n / (\mu_n L^4) \right] \beta_{HH} \left[ 1 - \exp \left( -t/\tau_n \right) \right]}{\sum_n \left[ H_n / (\mu_n L^4) \right] \beta_{HH} \left[ 1 - \exp \left( -t/\tau_n \right) \right]},
\]

\[
\frac{\Delta J_s(t)}{\Delta J_s(0)} = \frac{\sum_n \left[ H_n / (\mu_n L^4) \right] \beta_{HH} \left[ 1 - \exp \left( -t/\tau_n \right) \right]}{\sum_n \left[ H_n / (\mu_n L^4) \right] \beta_{HH} \left[ 1 - \exp \left( -t/\tau_n \right) \right]}.
\]

The relaxation of flow dichroism measured by Callis and Davidson is

\[
A(t)/A(0) = \left[ A(t) - A_\infty \right] / \left[ A(0) - A_\infty \right]
\]

\[
\sum_n \left[ \frac{1}{\mu_n L^4} + \frac{2 (\beta_{HH} L^4)^2}{(\mu_n L^4) (\gamma_n L^4)^2} \right] \beta_{HH} \left[ 1 - \exp \left( -t/\tau_n \right) \right] - \left( \frac{1}{\mu_n L^4} \right) \beta_{HH} \exp \left( -t/\tau_n \right)
\]

\[
\sum_n \left[ \frac{1}{\mu_n L^4} + \frac{2 (\beta_{HH} L^4)^2}{(\mu_n L^4) (\gamma_n L^4)^2} \right] \beta_{HH} \left[ 1 - \exp \left( -t/\tau_n \right) \right] - \left( \frac{1}{\mu_n L^4} \right) \beta_{HH} \exp \left( -t/\tau_n \right)
\]

If we do not take into account the change of force constant with shear rate, Eq. (68) is equal to Eq. (66), and Eqs. (66) and (67) become the equations which were derived from the original RZ model at the critical limit. These equations predict the relaxation process from the rod limit to coil limit. The computer results of Eq. (66) for different $\lambda L$ are shown in Fig. 9.

III. COMPARISON WITH EXPERIMENTAL DATA

A. The Non-Newtonian Viscosity

Although there is much experimental data on the non-Newtonian viscosity of polymers there is very little data available to compare with the present theory since the present theory does not take into account the excluded volume effect. The unique feature of this theory is that $[\eta]_{rel}$ cannot be expressed in terms of $\beta_{\rho}$ only, even in $\theta$ solvent. The $[\eta]_{rel}$ of a polymer having a low molecular weight drops faster than that of polymer having high molecular weight, when plotted in terms of $\beta_{\rho}$. In Fig. 10 the $[\eta]_{rel}$ of cellulose nitrate are plotted against $\beta_{\rho}$ in the molecular range from $0.36 \times 10^6$ to $5.5 \times 10^6$ along with the theory since the excluded volume effect in cellulose nitrate solution is not large except for very high molecular weights. The theory is in good agreement with the data not only qualitatively but also quantitatively considering that the statistical length $1/\lambda$ is $332 \, \text{Å}$. This agreement may show that the basic idea of this theory is right for stiff chains in $\theta$ solvent. In Eq. 11 the $[\eta]_{rel}$ of $T=2$ DNA is plotted against log$\beta_{\rho}$ along with the theoretical curve for $\lambda L = 4 \times 10^4$. The molecular weight of $T=2$ DNA is $113 \times 10^6$ and the statistical length $1/\lambda$ is $1200-1300 \, \text{Å}$ in a 0.2 ionic strength buffer solution. If one ignores the excluded volume effect, although one author $(\text{JEH})$ has quoted lower values for $1/\lambda$ in the
presence of excluded volume. Thus, the number of segments \( \lambda L \) for \( T=2 \) DNA is \( 4.4\text{--}4.8\times10^2 \). Although the deviation from the data is observed at high shear rate, the theory agrees well with the experiment considering that there is an ambiguity in the value of \( [\eta]_0 \) and the excluded volume effect may play a role for \( T=2 \) DNA solution. However, we should carry out the measurement of the non-Newtonian viscosity of DNA having different molecular weights in a \( \theta \) solvent to make a definite conclusion.

The solution of polystyrene having high molecular weight at a \( \theta \) temperature\(^{19}\) shows the non-Newtonian behavior at lower shear rate than the theory can predict. The force constant of the very flexible chain does not change so markedly with shear rate and the chain is deformed easily. Hence, probably the change of hydrodynamic interaction with changing of chain configuration mainly determines the non-Newtonian viscosity as the Peterlin and Fixman theories predict.\(^{11,12}\) For the stiffer molecules, the agreement between the theory and experiment is better since neglect of the effects of excluded volume and changes in hydrodynamic interaction are better assumptions for this case.

### B. Flow Birefringence and Flow Dichroism

In Fig. 12 the theoretical value of \( \log[\cot\chi] \) is plotted against \( \log\beta_{\rho 0} \) along with the data of cellulose tricarbanilates.\(^{29}\) The theory predicts that for the stiffer molecule \( \log[\cot\chi] \) is larger at the same \( \beta_{\rho 0} \) and deviates more rapidly from linearity than for the more flexible molecule. This behavior cannot be expected from the original \( RZ \) model. This theoretical prediction is in good agreement with these data, considering ambiguities from the polydispersity and solvation of the sample and also considering that the data were not extrapolated to the intrinsic values at zero concentration.\(^{26}\) The experimental values of \( \beta_p \) were obtained from \( \beta_{\rho 0}' \), i.e.,

\[
\beta_{\rho 0}' = M (\eta - \eta_0)_{s=0}/C R T,
\]

where \( C \) is the concentration.

![Fig. 9. The theoretical relaxation curve calculated from Eq. (66) in terms of a reduced time \( t/\tau_1 \). The curves are the computer results at non-drainage for \( \lambda L = 10^5 \), 10, and \( 10^2 \) from top to bottom.](image)

![Fig. 10. The comparison between the theory and the data of the non-Newtonian viscosity of cellulose nitrate.\(^{25}\) The curves are the computer results at non-drainage for \( \lambda L = 16, 49, 10^4, 1.5 \times 10^4 \) and \( 4 \times 10^5 \) from bottom to top. The symbols \( \bullet, \triangle, \ast, \cdot, \circ, \ast, \times \) are used to represent the data of cellulose nitrate having the molecular weight of \( 0.36 \times 10^6 \) (19), \( 1.1 \times 10^6 \) (58), \( 1.9 \times 10^6 \) (100), \( 3.1 \times 10^6 \) (163), and \( 5.5 \times 10^6 \) (289), respectively. Here, the numbers in parentheses are the number of statistical segments, \( \lambda L \), obtained by assuming \( 1/\lambda = 332 \text{ Å} \).](image)

![Fig. 11. The comparison between the theory and the data of the non-Newtonian viscosity of \( T=2 \) DNA.\(^{29}\) The symbols \( \bullet, \bigtriangleup, \ast, \cdot \) and \( \circ \) are used to represent the data in NaCl buffer solution having ionic strength \( \mu = 0.2 \); in 75\% glycerol–NaCl buffer solution having \( \mu = 0.2 \); and in 0.1 M NaCl buffer solution. The symbol \( \square \) is the value obtained from the data of Ref. 31 assuming \( [\eta]_0 = 320 \text{ dl/g}. \)](image)
In Fig. 13, the theoretical values of \( \log(\cot 2\chi) \) for \( \lambda L = 4 \times 10^3 \) are compared with the data of T-2 DNA too. Here the data in aqueous glycerol solutions are plotted against \( \log \beta_{\rho0} \) where the values of \( \eta_0/C \) at finite concentration of T-2 DNA were estimated from the data of Crothers and Zimm. The agreement between the theory and the experiment is very good as shown in the figure.

The comparison of the theory with the data of polystyrene and of cellulose tricarbanilate having very high molecular weights show that the deviation of \( \log(\cot 2\chi) \) from the linearity begins faster than the theory predicts. We think that this disagreement may be occurring for the same reasons as the disagreement of the non-Newtonian viscosity of polystyrene with the theory.

Next, we compare this theory with the data of flow birefringence and flow dichroism of DNA. They depend not only on the hydrodynamic property but also on the optical property of the segment. In Fig. 4, the data of flow dichroism \( [\log(\Delta \mu/e)] \) and flow birefringence \( [\log(\Delta n \cos 2\chi)] \) for T-2 and T-4 DNA are plotted against \( \log \beta_{\rho0} \), where we used \( \beta_{\rho0} \) for the data at finite concentration in place of \( \beta_{\rho} \). For convenience of comparison, data of flow birefringence were converted to the same functional form as \( \Delta \mu/e \) by multiplying \( \Delta n \) by \( \cos 2\chi \) and shifting to fit the data of dichroism along the ordinate. Here, the optical constants in glycerol solutions were reduced to the quantities in aqueous solution by using their difference at zero shear rate. They agree with each other as shown in Fig. 4.

If we assume the optical properties of the segment are independent of shear rate (that is, the macroform anisotropy does not exist), and the microform anisotropy is independent of \( \beta_{\rho0} \), we can fit the theory with the experiment for T-4 (or T-2) and \( \lambda Lb2bc \) at not too high reduced shear \( \beta_{\rho0} \) when shifting the theoretical curves along the ordinate as shown in Fig. 4. The value of \( \lambda L \) in the theoretical curve for \( \lambda Lb2bc \) is \( 10^3 \) since the value of \( \lambda L \) of this DNA is \( 1.0 \times 10^2 \) calculated from the molecular weight of 25-26 x 10. daltons assuming that \( 1/\lambda = 1200-1300 \AA \). From this fitting, \( \log(\Delta A/A) \) under another assumption that the microform dichroism does not exist, we have \( - (e_{11} - e_{12})/\varepsilon = 0.30 \) or \( - (e_{11} - e_{22})/\varepsilon = 0.50 \) if we take into account the relationship (45a). They are much smaller than the expected 1.50 or 2.50 obtained when we assume \( e_{11} = e_{22} = 0 \). This result suggests that the base pair in DNA tilts at about 30° from the perpendicular to the chain axis if the absorption dipole moment is in the plane of the base pairs.

The flow dichroism of several DNA’s \( [\log(\Delta A/A)] \) at high shear are plotted against \( \log \beta_{\rho0} \) along the theoretical Eq. (48) in Fig. 5. The experimental result that the flow dichroism shows saturation and almost becomes constant independent of the molecular weight can be well explained by this theory. Using the same optical values obtained in Fig. 4, the theoretical curves are shown for three values of \( \lambda L \) corresponding to T-4, \( \lambda Lb2bc \), and \( \lambda Lb2bc \). The agreement is good at lower values of \( \beta_{\rho0} \) but deviations from the curves are observed at high value of \( \beta_{\rho0} \). At infinite value of \( \beta_{\rho0} \), we have \( \Delta A/A = -(e_{11} - e_{12})/(e_{11} + 2e_{22}) \), irrespective of the molecular model. From the experimental data in Fig. 5, \( \Delta A/A \) that is, \( -(e_{11} - e_{12})/(e_{11} + 2e_{22}) \) is larger than 0.27 and also \( -(e_{11} - e_{12})/(e_{11} + 2e_{22}) \) is larger.
than 0.45 if we take into account the relationship
(45a) at very high shear. They are equal to 0.5 and
0.83 when we assume $\epsilon_{\infty} = \epsilon_1 = 0$. This means that
the angle of tilt from perpendicular is less than 23$^\circ$
or 10$^\circ$ at high shear rate. This result shows the possibility
that the angle of base pair in DNA changes with the
shear rate. The results described above, however, were
obtained under the assumption that both form di-
choisms do not exist. A study on form anisotropy is
necessary to get a definite conclusion.

In Fig. 7, $([\eta]/[\eta])_s$ of polyoxypropyl-
ene glycol and polystyrene$^4$ are plotted against $\lambda L$
along with the theory. Since the experimental result is
well explained by the theory; we obtained from the
figure the molecular weight of the statistical segment
$M_s = 288$ for polyoxypropylene glycol and $M_s = 1100$
for polystyrene. These are not unreasonable numbers for
the statistical lengths of these polymers.

C. Relaxation of Flow Dichoism

The experimental results on the relaxation of DNA
by Callis and Davidson$^2$ showed that the relaxation
process is very much affected by shear rate before
stopping the flow and the contribution of higher re-
lexation times on the process increase with increasing
the shear rate. The theoretical result, however, predicts
a very small effect of shear rate on the relaxation
process. This fact shows that the present theory cannot
explain the behavior of polymer solution at high shear
rate.

IV. CONCLUSION

In the present paper, we calculated the shear-rate
dependence of various hydrodynamic properties and
some quantities at zero shear rate for molecules having
different stiffness from the rod to the flexible coil under
the condition that the contour length is constant.
We have assumed no thermodynamic interaction and
no change of hydrodynamic interaction with shear rate.
When we compared our calculation with experimental
results, we have satisfactory agreement for stiff
molecules such as the cellulose derivatives and DNA at
low shear rate but not for the flexible molecules such as
high molecular weight polystyrene.

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1 R. A. Harris and J. E. Hearst, J. Chem. Phys. 44, 2595
(1966).
2 J. E. Hearst and R. A. Harris, J. Chem. Phys. 45, 3106
(1966).
45, 537 (1966).
8 T. Peterlin, Makromol. Chem. 44–46, 538 (1961); Polymer
9 Chr. Reinhold and A. Peterlin, J. Chem. Phys. 44, 4333
(1966).
14 See the papers cited in Ref. 15.
15 I. Noda, Y. Yamada, and M. Nagasawa, J. Phys. Chem. 72,
2896 (1968).
16 C. R. Cerf, J. Phys. Radium 19, 122 (1958); Advan. Polymer
Sci. 1, 382 (1958).
18 C. S. Lee and N. Davidson, Biopolymers 6, 531 (1967).
19 R. R. Callis and N. Davidson, Biopolymers 7, 335 (1969).
19, 1101 (1951).
26 C. E. Thompson and S. J. Gill, J. Chem. Phys. 47, 5008
(1967).
27 P. R. Callis and N. Davidson, Biopolymers 8, 379 (1969).
28 V. Lohmander and A. Svenson, Makromol. Chem. 65, 202
(1963).
29 V. V. Schulz and E. Penzel, Makromol. Chem. 112, 260
(1968).
31 R. E. Chapman, Jr., L. C. Klotz, D. S. Thompson, and B. H.
34 J. B. Hays, M. E. Magar, and B. H. Zimm, Biopolymers 8,
1, 491 (1968).
36 H. Janescht-Kriegl and W. Burchard, J. Polymer Sci. 6, 1953
(1968).
37 R. E. Harrington, “The Optical-Hydrodynamic Properties
of High Molecular Weight DNA. II: The Effect of Aqueous
Glycerol Solvents,” Biopolymers (to be published).
39 D. M. Gray and I. Rubenstein, Biopolymers 6, 1605 (1968).
41 N. N. Tsvetkov, T. I. Garmonova, and R. P. Stankevitch,