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## Dynamics of Polymer Molecules in Dilute Solution: Viscoelasticity, Flow Birefringence and Dielectric Loss

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The problem of the motions of a chain molecule diffusing in a viscous fluid under the influence of external forces or currents is considered for a particular model. This model is a chain of beads connected by ideal springs. Hydrodynamic interaction between the beads is introduced in the approximate form due to Kirkwood and Riseman. It is possible to solve this problem exactly with the use of a transformation to a set of normal coordinates. The viscosity, birefringence of flow, and dielectric and tensile relaxation behavior are calculated explicitly. The intrinsic viscosity in steady flow is somewhat different from the Kirkwood-Riseman result, and there is no change of viscosity with shear rate. The spectrum of relaxation times is similar to that found by Rouse and by F. Bueche, but has its maximum at a lower frequency than those obtained by Kuhn and Kuhn and by Kirkwood and Fuoss in other ways.

**T**HERE is an interesting group of properties of flexible polymer molecules all of which involve the motion of the molecule through a viscous medium under the simultaneous influence of an external force field and of Brownian motion. In viscous and elastic deformation and orientation in flow the external forces are supplied by the flowing medium, while in dielectric behavior the forces are electrical. When reduced to mathematical terms, however, all of these phenomena correspond to the solutions of diffusion problems in the multidimensional configuration space of the chain. For the model discussed below, at least, the equations can be thrown in diagonal form and separated by a linear transformation of the coordinates. In this paper we find transformations for linear chains with hydrodynamic interactions and use them to solve fluid flow and mechanical and electrical response problems with the applied forces varying with time.

The fundamental ideas are not new. Alfrey<sup>1</sup> more than ten years ago recognized that a coordinate transformation was at the heart of the problem and he proposed an approximate set of normal coordinates. The discovery of an exact set applicable to three-dimensional chains was recently made independently by Rouse<sup>2</sup> and by F. Bueche,<sup>3</sup> though the use of the corresponding set for one-dimensional chains goes back at least to the Bernoullis in the early eighteenth century.<sup>4</sup> However, a set valid in the presence of hydrodynamic interaction (in a simplified form) appears to be original with this paper. While Rouse explicitly introduces Brownian motion and Bueche does not, we show in this paper that the results are equivalent in many cases.

A number of investigators have treated various aspects of the same problem. In extensive series of papers, W. Kuhn, F. Grün, and H. Kuhn<sup>5-12</sup> have

discussed most of the properties considered here, but with the handicap of not having the transformation to normal coordinates available. Hence, most of their results are approximate. On the other hand, they were able to introduce "internal viscosity" into their model chain, which we have been unable to do. The treatment of diffusion in multidimensional chain space was pioneered by Kirkwood and Fuoss<sup>13</sup> and Kirkwood,<sup>14</sup> but again without the use of normal coordinates. Kramers<sup>15</sup> gave another approach to the problem of diffusion under stationary conditions.

The discussion of hydrodynamic interaction for macromolecules in stationary flow was first done by Burgers,<sup>16</sup> whose methods were later adopted by Hermans,<sup>17</sup> Peterlin,<sup>18</sup> and Kirkwood and Riseman.<sup>19</sup> We use the Kirkwood and Riseman method here.

Lack of space forbids the discussion of many other interesting contributions. We have not attempted to make in this paper more than casual comparison of our results either to those of other theories or to experiment. A critical study of the latter would amount to a long communication in itself.

### I. FORMULATION OF THE PROBLEM

We adopt a model similar to those of Rouse<sup>2</sup> and Bueche.<sup>3</sup> This is a chain of  $N$  identical segments joining

<sup>7</sup> W. Kuhn and H. Kuhn, *Helv. Chim. Acta* **28**, 1533 (1945).<sup>8</sup> W. Kuhn and H. Kuhn, *Helv. Chim. Acta* **29**, 71 (1946).<sup>9</sup> W. Kuhn and H. Kuhn, *Helv. Chim. Acta* **29**, 609 (1946).<sup>10</sup> W. Kuhn and H. Kuhn, *Helv. Chim. Acta* **29**, 830 (1946).<sup>11</sup> W. Kuhn, *Helv. Chim. Acta* **31**, 1092 (1948).<sup>12</sup> W. Kuhn, *Helv. Chim. Acta* **31**, 1259 (1948); **33**, 2057 (1950).<sup>13</sup> J. G. Kirkwood and R. M. Fuoss, *J. Chem. Phys.* **9**, 328 (1941).<sup>14</sup> (a) J. G. Kirkwood, *Rec. trav. chim.* **68**, 649 (1949); (b) J. G. Kirkwood, *J. Polymer Sci.* **12**, 1 (1954).<sup>15</sup> H. A. Kramers, *J. Chem. Phys.* **14**, 415 (1946).<sup>16</sup> J. M. Burgers, *Second Report on Viscosity and Plasticity of the Amsterdam Academy of Sciences* (Nordemann, Publishing Company, New York, 1938).<sup>17</sup> J. J. Hermans, *Rec. trav. Chim.* **63**, 219 (1944).<sup>18</sup> A. Peterlin, *Les grosses molécules en solution* (Collège de France, Paris, 1948); "L'interaction hydrodynamique des segments de la grosse molécule," *Dissertation, Academia Scientiarum et Artium Solvenica, Ljubljana*, 1950.<sup>19</sup> J. G. Kirkwood and J. Riseman, *J. Chem. Phys.* **16**, 565 (1948).<sup>1</sup> T. Alfrey, *J. Chem. Phys.* **12**, 374 (1944).<sup>2</sup> P. E. Rouse, Jr., *J. Chem. Phys.* **21**, 1272 (1953).<sup>3</sup> F. Bueche, *J. Chem. Phys.* **22**, 603 (1954).<sup>4</sup> L. Brillouin, *Wave Propagation in Periodic Structures* (McGraw-Hill Book Company, Inc., New York, 1946) (Dover Publications, Inc., New York, 1953).<sup>5</sup> W. Kuhn and F. Grün, *Kolloid Z.* **101**, 248 (1942).<sup>6</sup> W. Kuhn and H. Kuhn, *Helv. Chim. Acta* **26**, 1394 (1943).

$N+1$  identical beads with complete flexibility at each bead. Each segment is supposed to have a Gaussian probability function,  $w(l_x, l_y, l_z)$ , for the distribution of the components of the length  $l$  of the segment:

$$w(l_x, l_y, l_z) = a \exp(-3l_x^2 - 3l_y^2 - 3l_z^2)/2b^2, \quad (1)$$

where  $a$  and  $b$  are constants;  $b^2$  is the mean of  $l^2$ . Each bead is distinguished by an index  $j$  running from 0 to  $N$ .

The chain is suspended in a viscous liquid with which it is supposed to interact through the beads only; this interaction at the  $j$ th bead consists of a force with components  $F_{xj}$ ,  $F_{yj}$ ,  $F_{zj}$  exerted on the liquid by the bead. The force is assumed to be proportional to the velocity of the bead through the fluid:

$$\begin{aligned} F_{xj} &= \rho(\dot{x}_j - v_{xj}'), \\ F_{yj} &= \rho(\dot{y}_j - v_{yj}'), \\ F_{zj} &= \rho(\dot{z}_j - v_{zj}'), \end{aligned} \quad (2)$$

where  $\rho$  is a friction constant, the dot denotes a time derivative, and  $v_{xj}'$ ,  $v_{yj}'$ ,  $v_{zj}'$  are the velocity components that the fluid would have at the position of  $j$  if the bead were absent.

The chain segments exert forces on the beads. The  $x$ -component of the mean force exerted on  $j$  by the segment from  $j-1$  to  $j$  is<sup>3,6</sup>

$$-(3kT/b^2)(x_j - x_{j-1}). \quad (3)$$

To justify this, we note that the distribution of the  $x$ -components of the length of a Hooke's law spring of force constant  $3kT/b^2$  is

$$w(l_x) = a' \exp(-3kTl_x^2/2b^2kT), \quad (4)$$

by Boltzmann's expression. This is the same as the factor dealing with  $l_x$  in Eq. (1). Hence the segments are mechanically equivalent to springs with the appropriate force constant.

In addition to the mechanical forces, there is an effective force resulting from Brownian motion. We define a distribution function  $\psi(x_0, y_0, \dots, z_N)$ , which is a function of all the coordinates, such that

$\psi(x_0, y_0, \dots, z_N)$  is the probability of finding each bead  $j$  with coordinates between  $x_j$  and  $x_j + dx_j$ , correspondingly  $y_j$  and  $z_j$ .

Then the theory of Brownian motion<sup>20,21</sup> tells us that the beads move as if an additional force were present with components

$$-kT\partial \ln\psi/\partial x_j, \quad -kT\partial \ln\psi/\partial y_j, \quad -kT\partial \ln\psi/\partial z_j. \quad (5)$$

In sum, we now have for the  $x$ -components of the average forces on the liquid:

$$F_{x0} = -kT\partial \ln\psi/\partial x_0 - (3kT/b^2)(x_0 - x_1), \quad (6a)$$

$$F_{xj} = -kT\partial \ln\psi/\partial x_j - (3kT/b^2)(-x_{j-1} + 2x_j - x_{j+1}), \quad (0 < j < N), \quad (6b)$$

$$F_{xN} = -kT\partial \ln\psi/\partial x_N - (3kT/b^2)(x_N - x_{N-1}), \quad (6c)$$

with similar expressions for the other components.

We assume that the effect of a force on the motion of a fluid is given by the Kirkwood-Riseman<sup>19</sup> approximate form of the Oseen interaction formula:

$$v_{xj}' = v_{xj} + \sum_{j \neq k} T_{jk} F_k, \quad (7)$$

where  $v_{xj}$  is the  $x$ -component of the velocity that the fluid would have in the absence of all forces from the chain, and the interaction coefficients  $T_{jk}$  are given by

$$T_{jk} = 1/(6\pi^3)^{1/2} \eta b (|j-k|)^{-1/2}, \quad (8)$$

with  $\eta$  the viscosity of the fluid. The same form holds for the  $y$ - and  $z$ -components.

The equation of motion (strictly speaking, of average motion, with the average over the vagaries of Brownian disturbance) is now obtained by combining Eqs. (2), (6), and (7):

$$\begin{aligned} \dot{x}_j &= v_{xj} - D\partial \ln\psi/\partial x_j - \sigma(-x_{j-1} + 2x_j - x_{j+1}) \\ &\quad - \rho \sum_{k \neq j} T_{jk} [D\partial \ln\psi/\partial x_k + \sigma(-x_{k-1} \\ &\quad \quad \quad + 2x_k - x_{k+1})], \quad 0 < j < N, \end{aligned} \quad (9)$$

where  $D = kT/\rho$  and  $\sigma = 3kT/b^2\rho$ . The expressions for  $j=0$  and  $N$  are slightly modified as in Eqs. (6a) and (6c). The expressions for  $\dot{y}_j$  and  $\dot{z}_j$  are of the same form.

From this point it is but a simple step to derive the differential equation of diffusion. It is convenient to introduce a vector and matrix notation.<sup>22</sup> Let the  $(N+1)$ -dimensional column vector  $x$  be defined as

$$\mathbf{x} = \begin{pmatrix} x_0 \\ x_1 \\ \cdot \\ \cdot \\ x_N \end{pmatrix} \quad (10)$$

with similar definitions for  $y$ ,  $z$ ,  $v_x$ , etc. Also introduce the matrices  $\mathbf{A}$  and  $\mathbf{H}$  of order  $N+1$ :

$$\mathbf{A} = \begin{pmatrix} 1 & -1 & 0 & 0 & \cdots & 0 & 0 & 0 \\ -1 & 2 & -1 & 0 & \cdots & 0 & 0 & 0 \\ 0 & -1 & 2 & -1 & \cdots & 0 & 0 & 0 \\ 0 & 0 & -1 & 2 & \cdots & 0 & 0 & 0 \\ & & & & \cdots & & & \\ 0 & 0 & 0 & 0 & \cdots & -1 & 2 & -1 \\ 0 & 0 & 0 & 0 & \cdots & 0 & -1 & 1 \end{pmatrix}, \quad (11)$$

<sup>20</sup> M. C. Wang and G. E. Uhlenbeck, *Revs. Modern Phys.* **17**, 323 (1945).

<sup>21</sup> S. Chandrasekhar, *Revs. Modern Phys.* **15**, 1 (1943).

<sup>22</sup> Kirkwood (reference 14) has used a tensor notation for the same quantities. In his case the use of generalized curvilinear coordinates made desirable explicit recognition of the tensor properties of the operators. In our case the transformation to normal coordinates emphasizes essentially matrix manipulations.

while  $\mathbf{H}$  has elements  $H_{jk}$  as follows:

$$H_{jj}=1, \quad (12a)$$

$$H_{jk}=\rho T_{jk}, \quad j \neq k. \quad (12b)$$

The operator  $(3kT/b^2)\mathbf{A}$  transforms a position vector into a mechanical force vector, while  $(1/\rho)\mathbf{H}$  is the hydrodynamic mobility operator, i.e., it transforms a force vector into a velocity vector. The equation of motion, Eq. (9), can be transcribed into vector notation:

$$\begin{aligned} \partial \mathbf{x} / \partial t &= \mathbf{v}_x + (1/\rho)\mathbf{H} \cdot \mathbf{F}_x \\ &= \mathbf{v}_x - D\mathbf{H} \cdot (\partial / \partial \mathbf{x}) \ln \psi - \sigma \mathbf{H} \cdot \mathbf{A} \cdot \mathbf{x}, \end{aligned} \quad (13)$$

with

$$\partial / \partial \mathbf{x} = \begin{pmatrix} \partial / \partial x_0 \\ \partial / \partial x_1 \\ \vdots \\ \partial / \partial x_N \end{pmatrix} \quad (14)$$

and corresponding equations for the  $y$ - and  $z$ -velocities.

The unknown function  $\psi$  is to be determined from the equation of continuity:

$$\partial \psi / \partial t = -\text{div} \psi [(\partial \mathbf{x} / \partial t) + (\partial \mathbf{y} / \partial t) + (\partial \mathbf{z} / \partial t)]. \quad (15)$$

The divergence operator in matrix notation is

$$\text{div} = \partial / \partial \mathbf{x}^T + \partial / \partial \mathbf{y}^T + \partial / \partial \mathbf{z}^T, \quad (16)$$

where the superscript  $T$  indicates the transpose of the given vector. In this way we obtain a linear second-order differential equation for  $\psi$ :

$$\begin{aligned} \partial \psi / \partial t &= \sum_{u=x,y,z} \{ -(\partial \psi / \partial \mathbf{u})^T \cdot \mathbf{v}_u - \psi (\partial / \partial \mathbf{u})^T \cdot \mathbf{v}_u \\ &+ D(\partial / \partial \mathbf{u})^T \cdot \mathbf{H} \cdot (\partial \psi / \partial \mathbf{u}) + \sigma (\partial \psi / \partial \mathbf{u})^T \cdot \mathbf{H} \cdot \mathbf{A} \cdot \mathbf{u} \\ &+ \sigma \psi (\partial / \partial \mathbf{u})^T \cdot \mathbf{H} \cdot \mathbf{A} \cdot \mathbf{u} \}. \end{aligned} \quad (17)$$

This is in agreement with the form taken by the general equation given by Kirkwood<sup>14</sup> for the case of our particular model.

When the external currents  $\mathbf{v}_u$  are zero there is a simple solution,  $\Psi_0$ , of Eq. (17). Direct substitution will verify that the equation is satisfied by

$$\begin{aligned} \Psi_0 &= \exp(-\sigma/2D)(\mathbf{x}^T \cdot \mathbf{A} \cdot \mathbf{x} + \mathbf{y}^T \cdot \mathbf{A} \cdot \mathbf{y} + \mathbf{z}^T \cdot \mathbf{A} \cdot \mathbf{z}) \\ &= \exp(-3/2b^2) \left\{ \sum_{j=0}^{N-1} [(x_j - x_{j+1})^2 \right. \\ &\quad \left. + (y_j - y_{j+1})^2 + (z_j - z_{j+1})^2] \right\}. \end{aligned} \quad (18)$$

This is what is expected, given Eq. (1) for the probability distribution of the individual segments.

## II. TRANSFORMATION TO NORMAL COORDINATES

Solution of Eq. (17) is facilitated by a change of coordinates that diagonalizes the quadratic forms occurring in the differential equation. This transforma-

tion is constructed from the characteristic vectors of the matrix  $\mathbf{H} \cdot \mathbf{A}$ .

Let the  $N+1$  eigenvectors and eigenvalues of  $\mathbf{H} \cdot \mathbf{A}$  be  $\alpha_k$  and  $\lambda_k$ , respectively,

$$\mathbf{H} \cdot \mathbf{A} \cdot \alpha_k = \lambda_k \alpha_k, \quad 0 \leq k \leq N. \quad (19)$$

Form a square matrix  $\mathbf{Q}$  whose  $N+1$  columns are the eigenvectors  $\alpha_k$ . Let  $\mathbf{Q}^{-1}$  be its inverse,

$$\mathbf{Q}^{-1} \cdot \mathbf{Q} = \mathbf{I} = \mathbf{Q} \cdot \mathbf{Q}^{-1}, \quad (20)$$

where  $\mathbf{I}$  is the unit matrix. Then it follows immediately that  $\mathbf{H} \cdot \mathbf{A}$  is diagonalized by the similarity transformation:

$$\mathbf{Q}^{-1} \cdot \mathbf{H} \cdot \mathbf{A} \cdot \mathbf{Q} = \mathbf{\Lambda}, \quad (21)$$

where  $\mathbf{\Lambda}$  is the diagonal matrix of the  $\lambda_k$ .

The same matrix  $\mathbf{Q}$  can also be used to diagonalize the matrices  $\mathbf{H}$  and  $\mathbf{A}$  separately, though not by similarity transformations. We first establish that

$$\alpha_k^T \cdot \mathbf{A} \cdot \mathbf{H} = (\mathbf{H}^T \cdot \mathbf{A}^T \cdot \alpha_k)^T = (\mathbf{H} \cdot \mathbf{A} \cdot \alpha_k)^T = \lambda_k \alpha_k^T, \quad (22)$$

since  $\mathbf{H}$  and  $\mathbf{A}$  are symmetric. Hence

$$\alpha_k^T \cdot \mathbf{A} \cdot \mathbf{H} \cdot \mathbf{A} \cdot \alpha_l = (\alpha_k^T \cdot \mathbf{A} \cdot \mathbf{H}) \cdot \mathbf{A} \cdot \alpha_l = \lambda_k \alpha_k^T \cdot \mathbf{A} \cdot \alpha_l. \quad (23)$$

Also,

$$\alpha_k^T \cdot \mathbf{A} \cdot \mathbf{H} \cdot \mathbf{A} \cdot \alpha_l = \alpha_k^T \cdot \mathbf{A} \cdot (\mathbf{H} \cdot \mathbf{A} \cdot \alpha_l) = \lambda_l \alpha_k^T \cdot \mathbf{A} \cdot \alpha_l. \quad (24)$$

Equations (23) and (24) can both be true only if

$$\alpha_k^T \cdot \mathbf{A} \cdot \alpha_l = 0, \quad k \neq l \quad (25)$$

unless  $\lambda_k = \lambda_l$ . Therefore, if all the eigenvalues are distinct (as turns out to be the case),  $\mathbf{A}$  is diagonalized by the congruent transformation,

$$\mathbf{Q}^T \cdot \mathbf{A} \cdot \mathbf{Q} = \mathbf{M}, \quad (26)$$

where  $\mathbf{M}$  has nonzero elements  $\mu_k$  on the diagonal only.

Now multiply Eq. (26) from the left with  $\mathbf{M}^{-1}$  and compare with Eq. (19). The formal result is

$$\mathbf{Q}^{-1} = \mathbf{M}^{-1} \cdot \mathbf{Q}^T \cdot \mathbf{A}. \quad (27)$$

This allows us to construct most of  $\mathbf{Q}^{-1}$  without the need of inverting  $\mathbf{Q}$ . The exception is the first row of  $\mathbf{Q}^{-1}$ , which is indeterminate in Eq. (27) since the element  $\mu_0$  turns out to be zero.

Define a set of  $N+1$  vectors  $\beta_k$  as the column vectors of  $\mathbf{Q}^{-1T}$ . Then comparison of Eqs. (20) and (21) shows that the  $\beta_k$  are the eigenvectors of  $\mathbf{A} \cdot \mathbf{H}$  with eigenvalues  $\lambda_k$ . With these we can also diagonalize  $\mathbf{H}$  by a congruent transformation. If we find  $\mathbf{A} \cdot \mathbf{Q}$  from Eq. (26) and substitute it in Eq. (21), we find

$$\mathbf{Q}^{-1} \cdot \mathbf{H} \cdot \mathbf{Q}^{-1T} = \mathbf{M}^{-1} \cdot \mathbf{\Lambda} = \mathbf{N}, \quad (28)$$

where  $\mathbf{N}$  is diagonal with elements  $\nu_k$ ,

$$\nu_k = \beta_k^T \cdot \mathbf{H} \cdot \beta_k, \quad (29a)$$

$$= \lambda_k / \mu_k. \quad (29b)$$

The element  $\nu_0$  is indeterminate in Eq. (29b), since

both  $\lambda_0$  and  $\mu_0$  are zero. On the other hand, while Eq. (29a) is valid by definition for all  $k$ , it requires the inversion of  $\mathbf{Q}$  to determine the  $\beta_k$ .

If we multiply Eq. (28) from the left with  $\mathbf{N}^{-1}$  and compare to Eq. (20), we can show that

$$\alpha_k = (1/\nu_k)\mathbf{H} \cdot \beta_k, \quad (30)$$

from which we can derive a third expression for  $\nu_k$ :

$$1/\nu_k = \alpha_k^T \cdot \mathbf{H}^{-1} \cdot \alpha_k. \quad (31)$$

This is valid for all  $k$  including zero, but requires the inversion of  $\mathbf{H}$ .

The only properties of the matrices  $\mathbf{A}$  and  $\mathbf{H}$  that have been used to obtain these diagonal forms are the properties of symmetry and of distinctness of the eigenvalues; the latter will be demonstrated later when the eigenvalues are actually computed. It should be noted that the product matrix  $\mathbf{H} \cdot \mathbf{A}$  is not in general symmetric and  $\mathbf{Q}$  is not orthogonal. The eigenvector sets  $\alpha_k$  and  $\beta_k$  are not self-orthogonal but are bi-orthogonal with each other. The exception occurs when  $\mathbf{H}$  is the unit matrix (the "free-draining" case discussed below). In this case  $\mathbf{Q}$  is orthogonal and the two sets of eigenvectors are identical.

Two other properties of  $\mathbf{A}$  are worth noting here. First  $\mathbf{A}$  is factorable,

$$\mathbf{A} = \mathbf{a}^T \cdot \mathbf{a}, \quad (32)$$

where

$$\mathbf{a} = \begin{pmatrix} 1 & -1 & 0 & 0 & \dots & 0 \\ 0 & 1 & -1 & 0 & \dots & 0 \\ & & \dots & & & \\ 0 & \dots & 0 & 1 & -1 & 0 \\ 0 & \dots & 0 & 0 & 1 & -1 \\ 0 & \dots & 0 & 0 & 0 & 0 \end{pmatrix}. \quad (33)$$

The coordinates that Rouse<sup>2</sup> uses may be obtained from ours by operation with  $\mathbf{a}$ .

A second important property of  $\mathbf{A}$  is its possession of a zero eigenvalue, since the determinant of  $\mathbf{A}$  vanishes. This may be demonstrated by adding all the rows except the first of the determinant to the first row, whereupon the first row is reduced to zero. As a consequence  $\mathbf{H} \cdot \mathbf{A}$  also has a zero eigenvalue. The eigenvector in each case is a constant vector, corresponding to a simple translation in space. We will designate  $\lambda_0$  as the vanishing eigenvalue of  $\mathbf{H} \cdot \mathbf{A}$ .

The matrix  $\mathbf{Q}$  is used to transform coordinates from  $\mathbf{x}$ ,  $\mathbf{y}$ ,  $\mathbf{z}$  to  $\xi$ ,  $\eta$ ,  $\zeta$ , according to the equations:

$$\mathbf{x} = \mathbf{Q} \cdot \xi, \quad (34a)$$

$$\xi = \mathbf{Q}^{-1} \cdot \mathbf{x}. \quad (34b)$$

By the usual rules for transforming partial derivatives, we also find

$$\partial/\partial \mathbf{x} = \mathbf{Q}^{-1T} \cdot \partial/\partial \xi, \quad (35a)$$

$$\partial/\partial \xi = \mathbf{Q}^T \cdot \partial/\partial \mathbf{x}. \quad (35b)$$

The transformations connecting  $\mathbf{y}$  and  $\mathbf{z}$  with  $\eta$  and  $\zeta$

and their derivatives are identical in form to Eqs. (34)–(35).

### III. SOLUTION OF THE DIFFERENTIAL EQUATION

In order to transform the velocities  $\mathbf{v}_u$  to the new coordinates, it is necessary to state them explicitly. We assume laminar flow with a gradient effectively constant over a domain of molecular dimensions. This assumption would not be valid above some frequency dependent on the density and viscosity of the particular fluid, however it allows us to write:

$$\begin{aligned} v_{xj} &= \kappa z_j, \\ v_{yj} &= 0 = v_{zj}, \end{aligned} \quad (36)$$

with the shear rate,  $\kappa$ , a harmonic function of time:

$$\kappa = \kappa_0 \exp(i\omega t). \quad (37)$$

In the new coordinates,  $\xi$ ,  $\eta$ , and  $\zeta$ , the differential Eq. (17) becomes

$$\partial\psi/\partial t = -\kappa\zeta^T \cdot (\partial\psi/\partial \xi) + \sum_{u=\xi,\eta,\zeta} \sum_k [D\nu_k \partial^2 \psi / \partial u_k^2 + \sigma \lambda_k (u_k \partial \psi / \partial u_k + \psi)]. \quad (38)$$

We assume as a solution a power series in  $\kappa$  of the form

$$\psi = \Psi_0 \sum_{n=0}^{\infty} \psi^n \kappa^n, \quad (39)$$

with  $\psi_0$  equal to unity. In the new coordinates Eq. (18) becomes (except for a normalization constant):

$$\Psi_0 = \exp(-\sigma/2D) \left[ \sum_{k=1}^N \mu_k (\xi_k^2 + \eta_k^2 + \zeta_k^2) \right] \quad (40)$$

and

$$\partial\Psi_0/\partial u_k = -(\sigma/D)\mu_k u_k \Psi_0, \quad u = \xi, \eta, \zeta. \quad (41)$$

Now if we equate the coefficients of  $\kappa^n$  in Eq. (38), we obtain the set of equations

$$\begin{aligned} i\omega\psi_n = \sum_{k=1}^N [(\sigma/D)\mu_k \xi_k \zeta_k \psi_{n-1} - \zeta_k \partial\psi_{n-1}/\partial \xi_k \\ + \sum_{u=\xi,\eta,\zeta} (D\nu_k \partial^2 \psi_n / \partial u_k^2 \\ - \sigma \lambda_k u_k \partial \psi_n / \partial u_k)], \quad n \geq 1. \end{aligned} \quad (42)$$

In particular, the equation for  $\psi_1$  is

$$\begin{aligned} i\omega\psi_1 = \sum_{k=1}^N \{(\sigma/D)\mu_k \xi_k \zeta_k + \sum_{u=\xi,\eta,\zeta} \\ \times (D\nu_k \partial^2 \psi_1 / \partial u_k^2 - \sigma \lambda_k u_k \partial \psi_1 / \partial u_k)\}. \end{aligned} \quad (43)$$

Equation (43) is solved by a bilinear form in the products  $\xi_k \zeta_l$ . On substitution it is found that the coefficients of the nondiagonal terms are zero. Hence the result is

$$\psi_1 = \sum_{k=1}^N c_k \xi_k \zeta_k, \quad (44a)$$

$$c_k = \mu_k / 2D \lambda_k (1 + i\omega / 2\sigma \lambda_k). \quad (44b)$$

This is a particular solution of Eq. (43) consistent with the boundary condition of integrability when multiplied by  $\Psi_0$ , and hence it is the solution of importance for the physical problem.

Equations (42) form a set of recursion relations from which  $\psi_2, \psi_3$ , etc. can be calculated from  $\psi_1$ . For many purposes this is not necessary, since certain integrals of  $\psi$  can be obtained exactly without finding  $\psi$  itself. In view of its interpretation in terms of probability,  $\psi$  must be normalized so that

$$\int \psi d\xi_0 \cdots d\xi_N = J^{-1}, \quad (45)$$

where  $J$  is the Jacobian of the coordinate set  $\xi, \eta, \zeta$ . Also  $\psi$  must vanish at infinity. Now, making use of these relations, one can multiply Eq. (38) by  $\xi_k \zeta_k, \xi_k^2, \eta_k^2$ , or  $\zeta_k^2$  and integrate over the space coordinates with the aid of integration by parts to obtain first-order differential equations with the time as the only independent variable. These are easily solved. Some results of importance are:

$$J \int \xi_k \zeta_k \psi d\xi_0 \cdots d\xi_N = \kappa D / \mu_k \sigma (2\sigma \lambda_k + i\omega), \quad (46)$$

$$J \int \xi_k^2 \psi d\xi_0 \cdots d\xi_N = (D / \mu_k \sigma) [1 + \kappa^2 / (2\sigma^2 \lambda_k^2 - \omega^2 + 3i\sigma \lambda_k \omega)], \quad (47)$$

$$J \int \eta_k^2 \psi d\xi_0 \cdots d\xi_N = D / \mu_k \sigma, \quad (48)$$

$$J \int \zeta_k^2 \psi d\xi_0 \cdots d\xi_N = D / \mu_k \sigma. \quad (49)$$

In these equations transient terms containing

$$\exp(-2\sigma \lambda_k t)$$

have been omitted; otherwise the solutions are exact consequences of the original assumptions and valid for any value of  $\kappa$ .

#### IV. VISCOSITY AND FLOW BIREFRINGENCE

The intrinsic viscosity, or limiting viscosity number,  $[\eta]$ , is defined as

$$[\eta] = \lim_{c \rightarrow 0} (\eta_s - \eta) / \eta c, \quad (50)$$

where  $c$  is the concentration of the solute in mass per unit volume,  $\eta_s$  the viscosity of the solution, and  $\eta$  that of the solvent. On the other hand,  $[\eta]$  is given by<sup>15,19</sup>

$$[\eta] = - (N_a / M \eta \kappa) \left\langle \sum_{j=0}^N z_j F_{xj} \right\rangle_{Av}, \quad (51)$$

where  $N_a$  is Avogadro's number and  $M$  is the molecular weight of the solute, and the averaging is to be done

over all configurations of the chain with the distribution function  $\psi$ .

Equation (6) for the forces can be rewritten in matrix form as

$$\mathbf{F}_x = -kT(\partial/\partial \mathbf{x}) \ln \psi - (kT\sigma/D) \mathbf{A} \cdot \mathbf{x}. \quad (52)$$

Since  $\psi$  vanishes at infinity, the first term on the right drops out on integration. Thus one finds, for example,

$$\int_{-\infty}^{\infty} \psi \mathbf{F}_x dx_0 \cdots dz_N = - (kT\sigma/D) \int_{-\infty}^{\infty} \mathbf{A} \cdot \mathbf{x} \psi dx_0 \cdots dz_N. \quad (53)$$

With this and the aid of the transformation  $\mathbf{Q}$  and Eq. (26) we find:

$$\langle \sum_j z_j F_{xj} \rangle_{Av} = - (kT\sigma/D) \sum_{k\mu k} J \int \psi \xi_k \zeta_k d\xi_0 \cdots d\xi_N. \quad (54)$$

The optical properties of the solution are determined by the polarizability tensor,  $\Gamma$ . Kuhn and Gr $\ddot{u}$  n<sup>5</sup> have given a formula for the polarizability tensor of a "statistical chain element" which should be applicable to one of our segments. Let  $\gamma_1$  be the polarizability component along the vector between the ends of the segment and  $\gamma_2$  be the value of the two equal components normal to this vector, then Kuhn and Gr $\ddot{u}$  n give

$$\begin{aligned} \gamma_1 &= p + 2ql^2, \\ \gamma_2 &= p - ql^2, \end{aligned} \quad (55)$$

where  $p$  and  $q$  are constants depending on the constitution of the system and  $l$  is the length of the segment. The polarizability of the whole molecule is the sum of the polarizabilities of the separate segments; the average of this is  $\Gamma$ . When all the individual tensors are referred to the  $x, y, z$  coordinate system and added, and matrix notation introduced with the aid of the matrices  $\mathbf{A}$  and  $\mathbf{a}$ , Eqs. (32) and (33), the following appears:

$$\begin{aligned} \Gamma &= (N+1)(p-q)1 + q \\ &\times \begin{bmatrix} \langle \mathbf{x}^T \cdot \mathbf{A} \cdot \mathbf{x} \rangle_{Av} & \langle \mathbf{x}^T \cdot \mathbf{A} \cdot \mathbf{y} \rangle_{Av} & \langle \mathbf{x}^T \cdot \mathbf{A} \cdot \mathbf{z} \rangle_{Av} \\ \langle \mathbf{y}^T \cdot \mathbf{A} \cdot \mathbf{x} \rangle_{Av} & \langle \mathbf{y}^T \cdot \mathbf{A} \cdot \mathbf{y} \rangle_{Av} & \langle \mathbf{y}^T \cdot \mathbf{A} \cdot \mathbf{z} \rangle_{Av} \\ \langle \mathbf{z}^T \cdot \mathbf{A} \cdot \mathbf{x} \rangle_{Av} & \langle \mathbf{z}^T \cdot \mathbf{A} \cdot \mathbf{y} \rangle_{Av} & \langle \mathbf{z}^T \cdot \mathbf{A} \cdot \mathbf{z} \rangle_{Av} \end{bmatrix}. \end{aligned} \quad (56)$$

If we consider a light beam progressing along the  $y$ -axis, as is usual in flow-birefringence experiments, the electric vectors in the  $x$ - $z$ -plane are the only ones of interest, and we may omit the second row and column of the tensor in Eq. (56). Let the smaller angle between the principal axes of  $\Gamma$  and the  $x$ -axis be  $\chi$  (the "extinction angle"). By the usual procedures for diagonalizing a tensor we find:

$$\tan 2\chi = 2 \langle \mathbf{x}^T \cdot \mathbf{A} \cdot \mathbf{z} \rangle_{Av} / (\langle \mathbf{x}^T \cdot \mathbf{A} \cdot \mathbf{x} \rangle_{Av} - \langle \mathbf{z}^T \cdot \mathbf{A} \cdot \mathbf{z} \rangle_{Av}). \quad (57)$$

The difference of the polarizabilities along the principal axes,  $\Delta\Gamma$ , is:

$$\begin{aligned} \Delta\Gamma &= q [ (\langle \mathbf{x}^T \cdot \mathbf{A} \cdot \mathbf{x} \rangle_{Av} - \langle \mathbf{z}^T \cdot \mathbf{A} \cdot \mathbf{z} \rangle_{Av})^2 \\ &\quad + 4 (\langle \mathbf{x}^T \cdot \mathbf{A} \cdot \mathbf{z} \rangle_{Av})^2 ]^{1/2}. \end{aligned} \quad (58)$$

The magnitude of the birefringence of the solution,

$\Delta n$ , is proportional to this expression times the number of molecules per unit volume,  $cN_a/M$ .

Use of the transformation  $\mathbf{Q}$  and Eq. (26) allows the averages to be evaluated by means of Eqs. (46)–(49). The results are:

$$[\eta] = (N_a b^2 \rho / 6M\eta) \sum_{k=1}^N 1/\lambda_k (1 + i\omega\tau_k), \quad (59)$$

$$\tan 2\chi = \frac{\sum_{k=1}^N \tau_k / (1 + i\omega\tau_k)}{\kappa \sum_{k=1}^N \tau_k^2 / (1 - 2\omega^2 \tau_k^2 + 3i\omega\tau_k)}, \quad (60)$$

$$\Delta n = (q' c N b^2 [\eta]_{\kappa\eta} / MRT) (1 + \frac{1}{4} \tan^2 2\chi)^{\frac{1}{2}}, \quad (61)$$

where  $q'$  is an optical constant characteristic of the system and  $R$  is the gas constant, and the relaxation times,  $\tau_k$ , are given by

$$\tau_k = 1/2\sigma\lambda_k = M\eta[\eta]_0 / RT\lambda_k \left( \sum_{k=1}^N 1/\lambda_k \right), \quad (62)$$

with  $[\eta]_0$  the intrinsic viscosity at  $\omega=0$ .

It is noteworthy that the intrinsic viscosity is independent of the velocity gradient,  $\kappa$ . This result is not in accord with experiment for the case of flexible chains. Since the only approximation that has been made in the mathematics is the use of the Kirkwood-Riseman interaction tensor, this result must reflect either the inadequacy of the Kirkwood-Riseman approximation or a defect in the model. Kuhn and Kuhn<sup>7</sup> attribute the change of viscosity with gradient to lack of complete flexibility in the chain. Another possible source of difficulty is the assumption of a perfect Gaussian form for the distribution function of the individual segments, Eq. (1). Bueche<sup>23</sup> has given an approximate treatment based on what appears to be the same model, but with different results. We are unable to decide among these possibilities without further study.

We should also note that Eq. (61) has been previously derived by Kuhn and Kuhn<sup>6</sup> for the case of steady flow ( $\omega=0$ ).

## V. THE EIGENVALUE PROBLEM

The solution of the equations of motion now rests on the solution of the eigenvalue problem,

$$\mathbf{H} \cdot \boldsymbol{\alpha} = \lambda \boldsymbol{\alpha}. \quad (19)$$

We are particularly interested in the case of large  $N$ , and then in the smaller values of  $\lambda$ . In this case the components  $\alpha_j$  of  $\boldsymbol{\alpha}$  vary slowly with the index  $j$  so that they may be represented by a continuous function,  $\alpha(s)$ :

$$\alpha_j = (2/N)^{\frac{1}{2}} \alpha(s), \quad (63)$$

with the relations between indices  $i$  and  $j$  and the variables  $r$  and  $s$  given by

$$(2i/N) - 1 = r, \quad (64a)$$

$$(2j/N) - 1 = s. \quad (64b)$$

The matrix operators now find approximate representation in terms of integral transform operators:

$$\sum_{i=0}^N = (N/2) \int_{-1}^1 ds, \quad \sum_{j=0}^N = (N/2) \int_{-1}^1 dr, \quad (65)$$

$$\mathbf{a} = (-2/N) \int_{-1}^1 ds \delta(r-s) (d/ds), \quad (66)$$

$$\mathbf{A} = (-4/N^2) \int_{-1}^1 ds \delta(r-s) (d^2/ds^2), \quad (s \neq 1), \quad (67a)$$

$$= (-2/N) \int_{-1}^1 ds \delta(r-s) (d/ds), \quad (s = -1), \quad (67b)$$

$$= (2/N) \int_{-1}^1 ds \delta(r-s) (d/ds), \quad (s = 1), \quad (67c)$$

$$\mathbf{H} = \int_{-1}^1 ds \delta(r-s) + h \int_{-1}^1 ds (|r-s|)^{-\frac{1}{2}}. \quad (68)$$

In the last equation the quantity  $h$  is

$$h = N^{\frac{1}{2}} \rho / (12\pi^3)^{\frac{1}{2}} b \eta. \quad (69)$$

$\delta(x)$  is the Dirac delta function.

The eigenvalue equation now becomes

$$\begin{aligned} A_r \alpha(r) + h \int_{-1}^1 \alpha''(s) (|r-s|)^{-\frac{1}{2}} ds + N \alpha'(r) [2(r-1)]^{-\frac{1}{2}} \\ - N \alpha'(r) [2(1+r)]^{-\frac{1}{2}} = (-N^2 \lambda / 4) \alpha(r), \quad (70) \\ A_r = d^2/dr^2, \quad (r \neq 1), \\ = (N/2) d/dr, \quad (r = -1), \\ = -(N/2) d/dr, \quad (r = 1). \end{aligned}$$

Equation (70) shows that  $\alpha'(r)$  must be very small when  $r = \pm 1$ . Therefore it appears we can replace the above by the equation,

$$\alpha''(r) + h \int_{-1}^1 \alpha''(s) (|r-s|)^{-\frac{1}{2}} ds = (-N^2/4) \lambda \alpha(r), \quad (71)$$

plus the boundary conditions,

$$\alpha'(\pm 1) = 0. \quad (72)$$

The eigenvalues depend upon the parameter  $h$ , which is a measure of the strength of the hydrodynamic interaction. Two limiting cases may be distinguished for convenience:

<sup>23</sup> F. Bueche, J. Chem. Phys. 22, 1570 (1954).

$h \ll 1$ , the "free-draining" case. The values of  $\lambda$  of Eq. (71) are

$$\lambda_k = \pi^2 k^2 / N^2, \quad (73)$$

where  $k$  is any integer including 0. The corresponding eigenfunctions,  $\alpha_k(\mathbf{r})$ , are

$$\begin{aligned} \alpha_k(\mathbf{r}) &= \cos(\pi k r / 2), & k\text{-even}, \\ \alpha_k(\mathbf{r}) &= \sin(\pi k r / 2), & k\text{-odd}. \end{aligned} \quad (74)$$

The sums needed for Eqs. (59)–(60) can be found in tables of the Riemann zeta function:

$$\sum_{k=1}^{\infty} \lambda_k^{-1} = N^2 / 6, \quad (75)$$

$$\sum_{k=1}^{\infty} \lambda_k^{-2} = N^4 / 90. \quad (76)$$

From Eqs. (59)–(60), for the case of steady flow,  $\omega = 0$ , we get

$$[\eta]_0 = N_a N^2 b^2 \rho / 36 M \eta, \quad (77)$$

$$\tan 2\chi_0 = 5RT / 2M [\eta]_0 \kappa \eta, \quad (78)$$

while the relaxation times are given by

$$\tau_k = 6M \eta [\eta]_0 / \pi^2 RT k^2. \quad (79)$$

Equation (77) is the well-known result for this case, while Rouse<sup>2</sup> has obtained Eq. (79). Peterlin<sup>18</sup> gives an equation similar to (78) for the extinction angle, but the coefficient is unity instead of 5/2. This is the result we would have gotten if there had been only one relaxation time.

$h \gg 1$ , the "non-free-draining" case. The integral equation that results is solved in the following paper. The eigenvalues  $\lambda_k$  are related to numbers  $\lambda_k'$  by the equation:

$$\lambda_k = (4h / N^2) \lambda_k', \quad (80)$$

and the  $\lambda_k'$  are tabulated in the following paper. The eigenfunctions are expressed as a Fourier series of which the largest term is still that given by Eq. (74).

The intrinsic viscosity is

$$[\eta] = (\pi^3 N_a L^3 / 4 \cdot 3^3 M) \sum_{k=1}^N 1 / \lambda_k' (1 + i\omega \tau_k), \quad (81)$$

with

$$L = N^{1/2} b, \quad (82)$$

$$\tau_k = M \eta [\eta]_0 / 0.586 RT \lambda_k', \quad (83)$$

and  $[\eta]_0$  is the intrinsic viscosity at  $\omega = 0$ . The following results, evaluated by numerical summation, give the results that apply to steady flow:

$$\sum_1^{\infty} \lambda_k'^{-1} = 0.586 \quad (84)$$

$$\sum_1^{\infty} \lambda_k'^{-2} = 0.0703 \quad (85)$$

$$[\eta]_0 = 2.84 \times 10^{23} L^3 / M, \quad (86)$$

$$\tan 2\chi_0 = 4.88 RT / M [\eta]_0 \kappa \eta. \quad (87)$$

The value of  $6.02 \times 10^{23}$  has been used for Avogadro's number in these expressions.

Equations identical to the last two except for the constants, have been given by Kuhn and Kuhn,<sup>6-8</sup> Peterlin,<sup>18</sup> and Kirkwood and Riseman.<sup>19</sup> Kuhn and Kuhn's and Peterlin's model differs from ours, while Kirkwood and Riseman's model is ostensibly the same as ours. Equation (77) for the free-draining case has been derived previously by Kramers<sup>15</sup> and by Rouse<sup>2</sup> with explicit consideration of Brownian motion, and by Debye,<sup>24</sup> Huggins,<sup>25</sup> and others without consideration of Brownian motion.

It is remarkable that almost the same results are found whether Brownian motion is considered or not, since it makes a large difference in the case of elongated rigid molecules. The explanation appears when we calculate the velocities of the beads from the equations of motion, Eq. (13). Applying  $\mathbf{Q}$  to this equation, we get:

$$\dot{u}_k = v_{uk} - D v_k (\partial \ln \psi / \partial u_k) - \sigma \lambda_k u_k, \quad u = \xi, \eta, \zeta. \quad (88)$$

If we restrict ourselves to the first power of  $\kappa$ , we can use Eq. (44), and get, for  $k \neq 0$ ,

$$\dot{\xi}_k = \kappa \zeta_k [1 - 1/2(1 + i\omega \tau_k)] \quad (89a)$$

$$\dot{\eta}_k = 0 \quad (89b)$$

$$\dot{\zeta}_k = -\kappa \xi_k / 2(1 + i\omega \tau_k). \quad (89c)$$

The angular velocity,  $\dot{\theta}_j$ , of a bead,  $j$ , about a  $y$ -axis through the origin of coordinates is

$$\dot{\theta}_j = (z_j \dot{x}_j - x_j \dot{z}_j) / (x_j^2 + z_j^2). \quad (90)$$

To locate the origin of coordinates we must understand the eigenvectors  $\alpha_0$  and  $\beta_0$ . The elements of  $\alpha_0$  are all the same arbitrary constant, whose value may be conveniently chosen to be  $1/N^{1/2}$ . Then by Eq. (63) the function  $\alpha_0(\mathbf{r})$  is:

$$\alpha_0(\mathbf{r}) = \frac{1}{2}^{1/2}. \quad (91)$$

From Eqs. (30) and (31) we can show that, for the two cases considered in the foregoing,

$$\beta_0(\mathbf{r}) = \frac{1}{2}^{1/2}, \quad (h=0), \quad (92a)$$

$$\beta_0(\mathbf{r}) = 2^{1/2} \Gamma(5/4) / \Gamma(1/2) \Gamma(3/4) (1-r^2)^{1/4}, \quad (h \gg 1), \quad (92b)$$

and

$$v_0 = 1, \quad (h=0), \quad (93a)$$

$$v_0 = 8^{1/2} \pi \Gamma(5/4) h / \Gamma(1/2) \Gamma(3/4), \quad (h \gg 1), \quad (93b)$$

where  $\Gamma$  is the usual gamma function.<sup>26</sup>

<sup>24</sup> P. Debye, J. Chem. Phys. **14**, 636 (1946).

<sup>25</sup> M. L. Huggins, J. Phys. Chem. **42**, 911 (1938); **43**, 439 (1939).

<sup>26</sup> The inversion of  $\mathbf{H}$  to obtain Eqs. (92) and (93) is not a trivial matter for the non-free-draining case. I am indebted to Dr. P. L. Auer and Dr. C. S. Gardner for a private communication containing this result. The validity of Eq. (30) with Eq. (92) can be directly established by replacing  $r$  with the substitution  $r = (p-1)/(p+1)$  and using contour integration along a branch cut on the positive real axis of  $p$  and a circle at infinity (see reference 28).

The vector  $\alpha_0$  represents a simple translation of the molecule by an amount  $1/N^{\frac{1}{2}}$ . The meaning of  $\beta_0$  is exposed by Eq. (30) and the physical interpretation of  $(1/\rho)\mathbf{H}$  as the operator that converts force into velocity;  $\beta_0$  is the force vector that is produced by a uniform translational velocity of the molecule relative to the fluid with a magnitude  $N^{\frac{1}{2}}/\rho\nu_0$ .

The relation of these to the coordinates  $\xi_0$ ,  $\eta_0$ , and  $\zeta_0$  is shown by Eqs. (34a)-(b), since  $\alpha_0$  is the first column of  $\mathbf{Q}$  and  $\beta_0^T$  the first row of  $\mathbf{Q}^{-1}$ ; by these equations  $\xi_0$  represents a translation of the whole molecule by the amount  $\xi_0/N^{\frac{1}{2}}$  in the  $x$ -direction. Also we can define a center of resistance, whose  $x$ -coordinate is  $x_r$ , as that point about which the net torque vanishes when the force vector  $\beta_0$  arising from uniform translation is applied to the molecule and an equivalent total force is applied to the point. In symbols,

$$\beta_0^T \cdot (\mathbf{x} - x_r \mathbf{1}) = 0, \quad (94)$$

where  $\mathbf{x}$  is an arbitrary vector,  $\mathbf{1}$  is the unit vector and the left-hand side of the equation is the net torque. Since

$$\mathbf{1} = N^{\frac{1}{2}} \alpha_0, \quad (95a)$$

the solution is

$$\xi_0 = N^{\frac{1}{2}} x_r. \quad (95b)$$

Hence,  $\xi_0$  with  $\eta_0$  and  $\zeta_0$  measures the position of the center of resistance. If these are made zero, then the center is at the origin.

In this way, with the use of Eqs. (34a)-(b), we get from Eqs. (89a), (b), (c) and Eq. (90) for the case of steady flow,  $\omega = 0$ ,

$$\dot{\theta}_j = \kappa/2; \quad (96)$$

$\dot{\theta}_j$  is now the angular velocity of  $j$  about the center of resistance. This is just the rate of rotation of a *rigid* spherically symmetric structure, and it is just the value usually assumed if Brownian motion is not explicitly taken into account. With this rate of rotation the average forces are given correctly by Eq. (2) and  $[\eta]$  can then be found by solving Eq. (7) and using Eq. (51). The solution of Eqs. (2) and (7) is essentially the process used by Kirkwood and Riseman. However, these authors assumed that the molecule rotates around its center of mass, rather than its center of resistance. This probably accounts for the numerical difference in the results. Where we have 2.84 in Eq. (86), Kirkwood and Riseman originally had 3.6; this was recently corrected by Kirkwood, Zwanzig, and Plock<sup>27</sup> to 3.36.<sup>28</sup> A recent experimental value<sup>29</sup> is 2.5. In the free-draining case the two centers are the same, so that our results are identical with those of Debye,<sup>23</sup> for example.

The number  $\nu_0$  is related to the translational diffusion

<sup>27</sup> Kirkwood, Zwanzig, and Plock, *J. Chem. Phys.* **23**, 213 (1955).  
<sup>28</sup> P. L. Auer and C. S. Gardner [*J. Chem. Phys.* **23**, 1545 (1955)] have obtained a value of 2.90 from a recalculation of the Kirkwood-Riseman result.

<sup>29</sup> Newman, Krigbaum, Laugier, and Flory, *J. Polymer Sci.* **14**, 451 (1954).

constant. In Eq. (38) the diffusion constant associated with  $\partial^2\psi/\partial\xi_0^2$  is  $D\nu_0$ , but  $\xi_0$  is  $N^{\frac{1}{2}}$  times the magnitude of a translation of the center of resistance, so that the diffusion constant for translation is  $D\nu_0/N$ . For the free-draining case then we have:

$$D\nu_0/N = kT/N\rho, \quad (97a)$$

and for the non-free-draining case, from Eq. (93b),

$$D\nu_0/N = 0.192kT/N^{\frac{1}{2}}b\eta. \quad (97b)$$

Kirkwood and Riseman give the same results, except for a slight difference in the constant in Eq. (97b) for which they have 0.188 instead of 0.192. A recent paper<sup>14b</sup> shows that 0.188 is the correct result when a more exact form is used for the interaction coefficients Eq. (8).

From Eqs. (89a), (b), (c) it can be shown how the motion changes with frequency,  $\omega$ . At  $\omega = 0$ ,

$$\dot{x}_j = \dot{z}_{xj}/2, \quad (98a)$$

$$\dot{z}_j = -\dot{z}_{xj}/2,$$

so that energy is lost as the fluid slips by the bead. As  $\omega$  approaches infinity, however,

$$\begin{aligned} \dot{x}_j &= \dot{v}_{xj}, \\ \dot{z}_j &= \dot{v}_{zj} = 0. \end{aligned} \quad (98b)$$

The bead moves with the same velocity as the fluid and there is no energy loss; hence the intrinsic viscosity is zero.

## VI. TENSILE AND DIELECTRIC RELAXATION

The first-order effect of an electric field on our model is the same as that produced by a tensile stress applied to the ends, so that the two are naturally treated together.

If equal and opposite forces in the  $x$ -direction and of magnitude  $f$  are applied to the ends of the chain, the  $x$ -component of the force vector is

$$\mathbf{F}_x = -kT(\partial/\partial\mathbf{x}) \ln\psi - (3kT/b^2)\mathbf{A} \cdot \mathbf{x} - f\mathbf{e}, \quad (99)$$

where  $\mathbf{e}$  is the vector

$$\mathbf{e} = \begin{pmatrix} -1 \\ 0 \\ 0 \\ \cdot \\ \cdot \\ \cdot \\ 0 \\ 1 \end{pmatrix}. \quad (100)$$

For the dielectric case we assume that an extension  $x$  of segment produces a proportionate electric dipole moment  $\mu x$ . Then by averaging with Boltzmann's factor we find that the average moment in a field  $E$  is  $\mu^2 Eb^2/3kT$ ; hence the average extension in  $x$ , call it  $\bar{x}$ , is

$$\bar{x} = \mu Eb^2/3kT. \quad (101)$$

For the mean force exerted on  $j$  by the segment from  $j-1$  to  $j$  we have, instead of Eq. (3),

$$-(3kT/b^2)(x_j - x_{j-1} - \bar{x}). \quad (102)$$

From this we get the  $x$ -component of the force vector to be

$$\mathbf{F}_x = -kT(\partial/\partial \mathbf{x}) \ln \psi - (3kT/b^2)(\mathbf{A} \cdot \mathbf{x} + \bar{x}\mathbf{e}), \quad (103)$$

of the same form as Eq. (99) but with  $f$  replaced by  $3kT\bar{x}/b^2 = \mu E$ . Therefore, except for the latter substitution, the two problems are identical.

The analog of Eq. (17) is identical to (17) in all respects except for the first two terms on the right-hand side, which are replaced by

$$(f/\rho)(\partial\psi/\partial \mathbf{x})^T \cdot \mathbf{H} \cdot \mathbf{e}. \quad (104)$$

On transformation with  $\mathbf{Q}$ , this becomes

$$(f/\rho)(\partial\psi/\partial \boldsymbol{\xi})^T \cdot \mathbf{N} \cdot \boldsymbol{\varepsilon}, \quad (105)$$

where the vector  $\boldsymbol{\varepsilon}$  is the transform of  $\mathbf{e}$  according to

$$\boldsymbol{\varepsilon} = \mathbf{Q} \cdot \mathbf{e}. \quad (106)$$

We should note that Eq. (105) with (106) is valid for any force vector  $\mathbf{e}$ , not only for the particular one given by Eq. (100).

The quantity of interest is the mean extension of the whole chain,  $\langle x_N - x_0 \rangle_{Av}$ . This can be found without actually solving the partial differential equation; it is necessary only to multiply it by  $\xi_k$  and integrate over all the space coordinates, as was done to obtain Eqs. (46-49). In this way one derives

$$\partial \Xi_k / \partial t + \sigma \lambda_k \Xi_k = - (f/\rho) \nu_k \epsilon_k, \quad (107)$$

where

$$\Xi_k = \int \cdots \int \xi_k \psi d\xi_0 \cdots d\xi_N. \quad (108)$$

The general solution is

$$\Xi_k = \nu_k \epsilon_k e^{-\sigma \lambda_k t} \left[ \int e^{\sigma \lambda_k t} (-f/\rho) dt + C \right], \quad (109)$$

where  $C$  is the constant of integration. The coordinate of any bead is given by

$$\langle x_j \rangle_{Av} = \sum_{k=0}^N Q_{jk} \Xi_k \quad (110)$$

by Eq. (34a). These equations again are valid for any arbitrary force vector  $\mathbf{e}$ , as long as it is independent of the space coordinates, though it may depend on the time. The quantities  $\epsilon_k$  are the scalar products of  $\mathbf{e}$  with the eigenvectors  $\boldsymbol{\alpha}_k$  which form the rows of  $\mathbf{Q}^T$ . Thus our Eq. (107) is analogous to Bueche's equation (5),<sup>3</sup> while our Eq. (110) corresponds in form to his Eq. (3). This analogy is not generally valid except for linear functions of the coordinates.

For the tensile and dielectric problems we let  $f = f_0 \times \exp(i\omega t)$  and  $E = E_0 \exp(i\omega t)$ . The results for the

mean extension and electric moment (per unit field) of the molecule are:

$$\langle x_N - x_0 \rangle_{Av} \exp(-i\omega t) = \frac{b^2 f}{3kT} \sum_{k=1}^N \frac{(Q_{Nk} - Q_{0k})^2}{\mu_k (1 + i\omega/\sigma \lambda_k)}, \quad (111)$$

$$p = \frac{\mu \langle x_N - x_0 \rangle_{Av}}{E} = \frac{\mu^2 b^2}{3kT} \sum_{k=1}^N \frac{(Q_{Nk} - Q_{0k})^2}{\mu_k (1 + i\omega/\sigma \lambda_k)}. \quad (112)$$

The quantity  $p$  is the mean electric moment per molecule per unit applied field; its relation to the dielectric constant is discussed by Kirkwood and Fuoss.<sup>13</sup> The quantity  $\mu^2 b^2$  is the mean square moment of a segment. It is shown in the following paper that

$$\mu_k = \pi^2 k^2 / N^2, \quad (113)$$

approximately in the non-free-draining case, while in the free-draining case  $\mu_k$  is the same as  $\lambda_k$  and is given exactly by this expression. Likewise, with the same qualifications for the two cases,

$$Q_{Nk} - Q_{0k} = 2^3 / N^{\frac{1}{2}}, \quad k\text{-odd}, \quad (114a)$$

$$= 0, \quad k\text{-even}, \quad (114b)$$

from Eqs. (74) and (63). Hence for both the free- and non-free-draining cases the mean polarization per unit field is given by

$$p = (\mu^2 b^2 / 3kT) \sum_{k\text{-odd}} (8N / \pi^2 k^2) / (1 + i\omega \tau_k'), \quad (115)$$

with  $\tau_k' = 1/\sigma \lambda_k = 2\tau_k$ . The mean polarization per unit field at  $\omega = 0$  can be shown with the aid of the theory of the zeta-function to be  $\mu^2 b^2 / 3kT$ , as it should be if there is no restriction on the orientations of the various segments.

These expressions may be compared with the ones derived by Kirkwood and Fuoss,<sup>13</sup> Kirkwood,<sup>30</sup> and Kuhn and Kuhn<sup>9-12</sup> for the polarization and extension of a chain of freely rotating bonds. While the spectrum of relaxation times covers a comparable range, the Kirkwood and Fuoss and Kuhn and Kuhn expressions for the polarization have a maximum contribution from a relaxation process with time constant of order  $\tau_1'/N$  instead of  $\tau_1'$ , as we have. The same is true in the tensile problem. It does not seem to be an easy matter to trace this difference to its source.

It remains to discuss what structure is necessary in a real molecule to give an electric moment proportional to the mean segment extension, as assumed above. If each bond of the real chain corresponding to the model segment has a moment parallel to the bond then, of course, the vector sum of the moment is proportional to the vector sum of the bond lengths, i.e., the extension. However, if the moment is in a side group with respect to which the chain is symmetrical, then the mean moment of the chain at all moderate extensions must vanish. This is in accord with Kuhn's

<sup>30</sup> J. G. Kirkwood, J. Chem. Phys. 14, 51 (1946).

result.<sup>11</sup> In such a case the relaxation of the dipole moment must proceed by processes involving no change in mean length, and which are entirely outside the scope of our bead and segment model. This is unfortunately the case for the substituted polyvinyl chains on which most of the experimental work has been done. For such chains there should be very little correlation between the mechanical and dielectric relaxation.

### VII. THE GENERAL SPECTRUM OF RELAXATION TIMES

We have just seen that two different but related sets of relaxation times,  $\tau_k$  and  $\tau_k'$ , appear in the problems discussed above. Actually there are many other sets that may appear in particular circumstances. They are the eigenvalues associated with the fundamental differential equation of the system without external forces:

$$\partial\psi/\partial t = \sum_{u=\xi,\eta,\zeta} \sum_k D\nu_k \partial^2\psi/\partial u_k^2 + \sigma\lambda_k(u_k\partial\psi/\partial u_k + \psi). \quad (116)$$

If we let

$$\psi = \Phi(\xi_0, \eta_0, \zeta_0, t) T(t) \prod_{u=\xi,\eta,\zeta} \prod_{k=1}^N \varphi_k(u_k),$$

where each function is a function only of the indicated variables, and divide Eq. (116) through by  $\psi$ , we find that the equation separates and the individual equations may be solved. In this way we find the usual diffusion equation for the coordinates of the center of resistance:

$$\partial\Phi/\partial t = D\nu_0(\partial^2\Phi/\partial\xi_0^2 + \partial^2\Phi/\partial\eta_0^2 + \partial^2\Phi/\partial\zeta_0^2), \quad (117)$$

while for the time and the internal coordinates, after some calculation, we get:

$$T(t) = \exp(-t/\tau), \quad (118)$$

$$\varphi_{uk}(u_k) = H_n(u_k(\mu_k\sigma/2D)^{1/2}) \exp(-\sigma\mu_k u_k^2/2D). \quad (119)$$

In the last equations  $H_n(x)$  is the  $n$ th Hermite polynomial,<sup>12</sup> where  $n$  is an arbitrary integer, and the relaxation time,  $\tau$ , is

$$\tau = \sum_{\text{all } uk} n_{uk}\sigma\lambda_k. \quad (120)$$

<sup>12</sup> Courant and Hilbert, *Methoden der Mathematischen Physik* (Verlag Julius Springer, Berlin, 1924); Margenau and Murphy, *The Mathematics of Physics and Chemistry* (D. van Nostrand Company, Inc., New York, 1943).

The relaxation time thus may be  $\sigma$  multiplied by an integer and any  $\lambda_k$ , or any combination of such terms. Which relaxation times appear in a given problem depend upon which of the eigenfunctions [Eq. (119)] are "excited" in this problem.

There are thus two characteristic-value problems associated with our general study; one associated with the coordinate transformation and the other associated with the differential equation. The eigenvalues of the latter problem are formed from combinations of those of the former.

### VIII. CONCLUSION

The principal result of this paper has been the demonstration of an exact solution, valid at all frequencies and strengths of the applied force or flow field, of a three-dimensional chain problem with Brownian motion and a special type of interaction. This has been possible only with the neglect of internal viscosities or forms of interaction that would introduce into the differential equation functions not linear in the coordinates. The transformation to normal coordinates is essentially a linear transformation. It seems likely, although it is only a speculation, that the independence of viscosity of shear rate is a result of this linearity. There is still a possibility that nonlinear terms could be successfully handled as perturbations, thus disclosing which features of the real situation are responsible for the observed variable viscosity, for example. In any case, we hope that the solution of this linearized problem will serve as a base of attack on others of greater generality.

*Note added in proof.*—Professor Peterlin has graciously communicated to me a solution in closed form of Eq. (38); it is

$$\psi = \exp\left\{-\frac{\sigma}{2D} \sum_{k=1}^N \frac{\mu_k}{1+\beta^2/\lambda_k^2} \left[ \xi_k^2 - \frac{2\beta\xi_k\zeta_k}{\lambda_k} + \left(1 + \frac{2\beta^2}{\lambda_k^2}\right)\zeta_k^2 + \left(1 + \frac{\beta^2}{\lambda_k^2}\right)\eta_k^2 \right]\right\},$$

where  $\beta = \kappa/2\sigma$ .

The relation of this paper to those of Kirkwood and of Rouse is not properly indicated in the text. Our study may be considered to be an application of Kirkwood's general formalism to a particular example, although we have performed the initial steps at a more elementary level and have solved the differential equations differently. Likewise, our method of handling the viscosity problem must be considered to be fundamentally the same as that of Rouse, although there are considerable differences at certain intermediate steps.

Work of a similar nature has recently been communicated by O. Nakada, *J. Phys. Soc. Japan* **10**, 804 (1955); by R. Cerf, *Compt. rend.* **241**, 496 (1955); and by L. K. H. van Beek, thesis, Leiden (1955).