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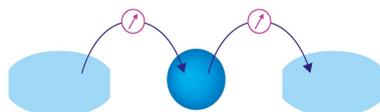
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# A Theory of the Linear Viscoelastic Properties of Dilute Solutions of Coiling Polymers

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The necessary coordination of the motions of different parts of a polymer molecule is made the basis of a theory of the linear viscoelastic properties of dilute solutions of coiling polymers. This is accomplished by use of the concept of the submolecule, a portion of polymer chain long enough for the separation of its ends to approximate a Gaussian probability distribution. The configuration of a submolecule is specified in terms of the vector which corresponds to its end-to-end separation. The configuration of a molecule which contains  $N$  submolecules is described by the corresponding set of  $N$  vectors.

The action of a velocity gradient disturbs the distribution of configurations of the polymer molecules away from its equilibrium form, storing free energy in the system. The coordinated thermal motions of the segments cause the configurations to drift toward their equilibrium distribution. The coordination is taken into account by the mathematical requirement that motions of the atom which joins two submolecules change the configurations of both submolecules. By means of an orthogonal transformation of

coordinates, the coordination of all the motions of the parts of a molecule is resolved into a series of modes. Each mode has a characteristic relaxation time. The theory produces equations by means of which the relaxation times, the components of the complex viscosity, and the components of the complex rigidity can be calculated from the steady flow viscosities of the solution and the solvent, the molecular weight and concentration of the polymer, and the absolute temperature.

Limitations of the theory may arise from the exclusion from consideration of (1) very rapid relaxation processes involving segments shorter than the submolecule and (2) the obstruction of the motion of a segment by other segments with which it happens to be in contact. Another possible cause of disagreement between the theory and experimental data is the polydispersity of any actual polymer; this factor is important because the calculated relaxation times increase rapidly with increasing molecular weight.

## INTRODUCTION

THE unusual elastic and flow properties of systems containing linear polymeric molecules arise from three factors: (1) the length of the polymer molecules, (2) the flexibility of the molecular chains, and (3) the interactions of the segments of a polymer molecule with other segments of the same and other polymer molecules.<sup>1</sup> For such a threadlike molecule to move through its surroundings it must *coordinate* the thermal motions of relatively short segments of the chain.<sup>2</sup> In diffusion and steady flow experiments, only the resultant of the coordinated segmental motions is measured; theories of such phenomena can be developed without analysis of the motions of the molecule as the sum of the motions of its parts. Certain other properties, such as creep, stress relaxation, and dynamic viscosity and rigidity, are functions of time or frequency.<sup>3</sup> Theories of these phenomena must take into account the neces-

sary coordination of the motions of the segments of the polymer molecules.

The physical concept which is the basis of the theory presented here is that a velocity gradient in a solution of a linear polymer continuously alters the distribution of configurations of the polymer molecules. The coordinated thermal motions of the segments of the polymer molecules cause the configurations to drift continuously toward their most probable distribution. The calculation resolves the coordination of the motions of the parts of a polymer molecule into a series of modes; each mode has a characteristic relaxation time. Direct contacts of a segment with segments of other molecules and with remotely connected segments of the same molecule are considered as contributing to the viscous forces which oppose the thermal motions. In its present form the theory does not take into account the obstruction of the motions of a segment by other segments with which it happens to be in contact. Consequently, the agreement between the present theory and experimental data may be expected to be reasonably satisfactory only for dilute solutions of polymers in which intermolecular contacts are relatively infrequent. Modification of the theory to take better account of the effects of interactions should improve the agreement for dilute solutions and make possible the application of the results to the properties of concentrated solutions and of undiluted polymer.

## MOTION OF THE LIQUID

It will be assumed that the shearing stress is applied to the liquid by a plane surface lying in the plane  $z=0$  of a right-handed system of Cartesian coordinates. The surface executes simple harmonic motions in the  $x$  direction with an angular frequency  $\omega$  and a maximum

<sup>1</sup> Relaxation processes arising from chemical scission of the polymer chains at elevated temperatures [see e.g., A. V. Tobolsky and R. D. Andrews, *J. Chem. Phys.* **13**, 3 (1945)] are not considered in this calculation.

<sup>2</sup> W. Kauzmann and H. Eyring, *J. Am. Chem. Soc.* **62**, 3113 (1940).

<sup>3</sup> See e.g., W. Philippoff, *Physik. Z.* **35**, 884, 900 (1934); A. P. Aleksandrov and Y. S. Lazurkin, *J. Tech. Phys. (USSR)* **9**, 1249, 1261, 1267 (1939); Gehman, Woodford, and Stambaugh, *Ind. Eng. Chem.* **33**, 1032 (1941); H. Lederman, *Elastic and Creep Properties of Filamentous Materials and Other High Polymers* (Textile Foundation, Washington, 1943); Andrews, Hofman-Bang, and Tobolsky, *J. Polymer Sci.* **3**, 669 (1948); Mason, Baker, McSkimin, and Heiss, *Phys. Rev.* **73**, 1074, 1873 (1948); *ibid.* **75**, 936 (1949); Marvin, Fitzgerald, and J. Ferry, *J. Appl. Phys.* **21**, 197 (1950); A. W. Nolle, *J. Polymer Sci.* **5**, 1 (1950); Ferry, Fitzgerald, Johnson, and Grandine, *J. Appl. Phys.* **22**, 717 (1951); H. Lederman and R. G. Smith, *Phys. Rev.* **81**, 303 (1951); R. S. Marvin, *Ind. Eng. Chem.* **44**, 696 (1952); Ferry, Fitzgerald, Grandine, and Williams, *Ind. Eng. Chem.* **44**, 703 (1952); R. D. Andrews, *Ind. Eng. Chem.* **44**, 707 (1952).

velocity  $v_0$ . The liquid is assumed to extend to infinity in the direction of  $z$  positive. Under these conditions the motion of the liquid<sup>4</sup> can be represented by

$$\dot{x} = v_0 e^{-\Gamma z} e^{i\omega t}, \quad \dot{y} = 0, \quad \dot{z} = 0, \quad \Gamma = (i\omega\rho_l/\eta)^{1/2}. \quad (1)$$

In these equations  $i$  is  $(-1)^{1/2}$ ,  $\rho_l$  is the density of the liquid and  $\eta$  is its viscosity. For polymer solutions it is necessary to replace  $\eta$  by the complex viscosity,<sup>5</sup>  $\eta^* = \eta_1 - i\eta_2$ . The concept of a complex viscosity has meaning only when steady-state conditions have been established under the influence of a sinusoidally varying shearing stress. The real and imaginary parts of the complex viscosity correspond to the components of the shearing stress which are, respectively, in phase and out of phase with the resultant gradient of velocity.

The waves represented by Eq. (1) are strongly damped. For toluene at 30°C, the viscosity is 0.606 centipoise and the density is 0.856 g/ml; according to Eq. (1) the distance in which the amplitude of the velocity is reduced by a factor  $e^{-1}$  is 0.0034 cm if the applied frequency is 200 cycles per sec. At a frequency of 60 kc this distance is only 0.00019 cm. The very rapid attenuation of these waves prevents reflected waves of appreciable amplitude even in relatively thin layers of liquid. Accordingly, only the outgoing wave need be considered and Eq. (1) applies.

The gradient of velocity varies rapidly with  $z$ , the distance from the oscillating surface. For mathematical reasons it is necessary to assume in this calculation that, at any instant, the velocity gradient,  $\alpha = \partial\dot{x}/\partial z$ , has a single value over the entire volume pervaded by a polymer molecule. The variation of  $\alpha$  with  $z$  is expressed in terms of  $\epsilon$ , the distance from the arbitrary plane  $z = z_0$ , by the equation

$$\alpha_{z=z_0+\epsilon} = -v_0\Gamma e^{-\Gamma z_0} e^{i\omega t} [1 - \Gamma\epsilon + \Gamma^2\epsilon^2/2 \dots]. \quad (2)$$

The value of  $|\alpha|$  will vary less than five percent from its value at  $z = z_0$  in the range for which  $|\Gamma\epsilon| < 0.05$ . The range to which  $\epsilon$  is restricted by this condition decreases with increasing frequency. For a very dilute solution in toluene, the condition restricts  $|\epsilon|$  to values below 700Å at an applied frequency of 60 kc. The assumption would be reasonably satisfactory under these conditions for molecular configurations whose extension did not exceed 1400Å. The root-mean-square separation of the ends of the polystyrene molecules in a toluene solution of a polymer with a molecular weight of  $1.61 \times 10^6$  was found by Outer, Carr, and Zimm<sup>6</sup> to be about 1300Å. The imperfection of the assumption at high frequencies for solutions of very long molecules in solvents of low viscosity is apparent. Data available at

present<sup>7</sup> indicate that this does not produce large discrepancies between theory and observation.

#### MODEL OF POLYMER MOLECULE

The kinetic theory of the equilibrium elastic modulus of rubber<sup>8</sup> is based upon finding an approximate value of the probability  $p(x, y, z) dx dy dz$  that one end of a molecule will be in the volume element  $dx dy dz$  in the neighborhood of  $(x, y, z)$  when the other end is fixed at the origin of coordinates. For a chain of  $n$  freely jointed links, each of length  $l$ , the result is

$$p(x, y, z) dx dy dz = (b^3/\pi^3) \exp[-b^2(x^2 + y^2 + z^2)] dx dy dz,$$

where  $b^2$  has the value  $3/(2nl^2)$ . In obtaining this result it is assumed that this probability is proportional to the number of configurations available to the molecule when its ends are in the specified positions. This assumption is satisfactory if the group of molecules corresponding to each value of the end-to-end vector is randomly distributed over the set of available configurations. This condition is attained at equilibrium, i.e., at very long times. It is not attained when a rubber or a solution of a linear polymer is subjected to a force or a deformation which changes with time. Under such conditions the configurations of the molecules are continuously altered in a systematic way. As a result the configurations of the group of molecules which have any particular end-to-end vector are not randomly distributed over all possible configurations consistent with the length of the end-to-end vector. This makes it necessary to specify the configurations of the molecules in more detail than is required in the equilibrium theory, in which the end-to-end vector suffices.

A complete description of the configuration of each molecule requires the specification of the orientation of each chemical bond in the molecular chain. Such a description was used by Kirkwood<sup>9</sup> in a completely general theory of the viscoelastic properties of solutions of linear polymers. The results of the calculation are in a form which cannot readily be used for calculation or comparison with experimental data.

In the calculation presented here mathematical simplicity is achieved with some loss in generality by use of a less detailed description of the configuration of a molecule. The molecule is divided up into  $N$  equal submolecules. Each submolecule is a portion of polymer chain just long enough so that, at equilibrium, the separation of its ends obeys, to a first approximation, a Gaussian probability function; i.e., if one end of a submolecule is located at the origin of a system of Cartesian coordinates, the probability  $\psi(x, y, z) dx dy dz$  that the other end will be in the volume element  $dx dy dz$  lying between  $x$  and  $x+dx$ ,  $y$  and  $y+dy$ ,  $z$  and  $z+dz$  is

<sup>4</sup> H. Lamb, *Hydrodynamics* (Dover Publications, New York, 1945), p. 619.

<sup>5</sup> A. Gemant, *Trans. Faraday Soc.* **31**, 1582 (1935).

<sup>6</sup> Outer, Carr, and Zimm, *J. Chem. Phys.* **18**, 830 (1950).

<sup>7</sup> P. E. Rouse, Jr., and K. Sittel, *J. Appl. Phys.* (to be published).

<sup>8</sup> L. R. G. Treloar, *Physics of Rubber Elasticity* (Oxford University Press, London, 1949).

<sup>9</sup> J. G. Kirkwood, *Rec. Trav. Chim. Pays-Bas* **68**, 649 (1949).

given approximately by

$$\psi(x, y, z) dx dy dz = (\beta/\pi)^3 \times \exp[-\beta(x^2 + y^2 + z^2)] dx dy dz. \quad (3)$$

In this expression  $\beta = 3/(2\sigma^2)$ , where  $\sigma^2$  is the mean-square separation of the ends of a submolecule.

In this calculation each submolecule has its own private system of Cartesian coordinates. The origin of the system of the  $j$ th submolecule is located at the atom which joins the  $(j-1)$ th and the  $j$ th submolecules; the axes are oriented parallel to the corresponding axes of the system used to describe the motion of the liquid. The coordinates  $x_j, y_j, z_j$  give the location in this private system of the atom which connects the  $j$ th and  $(j+1)$ th submolecules. The configuration of a molecule composed of a series of  $N$  submolecules is described by specifying the components of each of the set of  $N$  vectors which give the position of the end of each submolecule with respect to the end of the preceding submolecule. This is equivalent to representing the configuration by a point in a "phase space" of  $3N$  dimensions.

It is assumed that the probability,  $\Psi_i d\phi_i$ , of a molecule having a configuration corresponding to a point in the volume element  $d\phi_i$  lying between  $x_1$  and  $x_1 + dx_1$ ,  $y_1$  and  $y_1 + dy_1$ ,  $z_1$  and  $z_1 + dz_1$ ,  $x_2$  and  $x_2 + dx_2$ ,  $\dots$ ,  $z_N$  and  $z_N + dz_N$  is proportional to the number of configurations of the molecule which are represented by points in that element of volume. This number of configurations is the product of the numbers of configurations of each of the submolecules having the requisite end-to-end separations; it follows that

$$\begin{aligned} \Psi_i d\phi_i &= \prod_{j=1}^N \psi(x_j, y_j, z_j) dx_j dy_j dz_j \\ &= (\beta/\pi)^{3N/2} \exp\left[-\beta \sum_{j=1}^N (x_j^2 + y_j^2 + z_j^2)\right] \\ &\quad \times dx_1 dy_1 dz_1 dx_2 \dots dz_N. \end{aligned} \quad (4)$$

This assumption is equivalent to the assumption that the configurations of the group of submolecules which, at any instant, have a particular end-to-end separation are randomly distributed over all available configurations consistent with that end-to-end separation. The significance of this assumption for a dynamic measurement made at the angular frequency  $\omega$  can be seen by considering a group of submolecules each of whose ends are fixed at points the separation of which is small compared to the length of a fully extended submolecule. A small, rapid increase in the separation of the fixed ends of each submolecule will result in the submolecules having configurations which are not randomly distributed over the available configurations. After a time the thermal motions will re-establish a random distribution. If this time is small compared to  $\omega^{-1}$  the assumption will be valid.

## MOTION OF THE POLYMER MOLECULES

A velocity gradient in a solution of a linear polymer produces motions of the polymer molecules which are resolved in this calculation into two components; (1) a motion of the atom at each junction between two submolecules with a velocity equal to that of the surrounding liquid, and (2) the coordinated Brownian motions of the segments of each polymer molecule by which the configurations drift toward their equilibrium distribution. The justification of this procedure rests on the flexibility of the polymer molecules. For each part of a molecule to move with the velocity of the surrounding liquid the configuration of the molecule must be able to change as rapidly as required by the gradient of velocity of the liquid. If the polymer molecule were not sufficiently flexible to allow this rapid change of configuration, the presence of a gradient of velocity in the solution would always entail motion of the solvent relative to the atomic groups of the polymer chain. The relative motions would cause dissipation of energy and the contribution of the polymer to the real part of the complex viscosity would remain large at all frequencies. Actually, the experimental data<sup>7,10,11</sup> indicate that at high frequencies the viscous losses caused by the polymer molecules approach zero. For example, Mason<sup>10</sup> reports measurements made on a solution in cyclohexane of a polyisobutylene with a molecular weight of  $3.93 \times 10^6$ ; the solution contained one gram of polymer per 100 ml and had a relative viscosity in steady flow of 30. At 14 megacycles, "the indicated viscosity is only about 10 percent higher than that for the pure solvent alone."<sup>10</sup>

These data strongly support the validity of the assumption that the *primary* effect of the velocity gradient is to carry each segment of each polymer molecule along with the liquid, at least for velocity gradients of the magnitudes encountered in these measurements.

In the calculation the motions of the polymer molecules are expressed in terms of the motions of their representative points in the configuration space. The value of  $(\dot{x}_j)_\alpha$ , the component in the  $x_j$  direction of the velocity of a point caused directly by the velocity gradient  $\alpha$  of the liquid, is equal to the difference between the  $x$  components of the velocity of the liquid at the two ends of the  $j$ th submolecule. Thus

$$(\dot{x}_j)_\alpha = z_j \partial \dot{x} / \partial z = \alpha z_j. \quad (5)$$

Since the velocity of the liquid has a nonvanishing component only in the  $x$  direction, the components  $(\dot{y}_j)_\alpha$  and  $(\dot{z}_j)_\alpha$  are zero.

The calculation of the second component of the motions of the polymer molecules—the diffusional motion by which their distribution of configurations moves toward its equilibrium form—is the central

<sup>10</sup> W. P. Mason, *Piezoelectric Crystals and Their Applications to Ultrasonics* (D. Van Nostrand Company, Inc., New York, 1950), p. 351.

<sup>11</sup> Baker, Mason, and Heiss, *J. Polymer Sci.* **8**, 129 (1952).

part of the theory. This calculation requires first the evaluation of the effect of the perturbation of the distribution of configurations of the polymer molecules upon the thermodynamic potentials of the molecules. This is accomplished by calculating the effect of the velocity gradient  $\alpha$  upon the entropy of the  $\nu$  polymer molecules contained in a volume  $V$  of solution. The procedure is a generalization of the one used by Wall<sup>12</sup> in his calculation of the entropy changes produced by elongation of a piece of rubber. The average number of molecules whose representative points lie in the volume element  $d\phi_i$  at equilibrium is  $n_i = \nu \Psi_i d\phi_i$ . If the number of representative points in  $d\phi_i$  under the influence of the perturbing velocity gradient is  $s_i$ , the change in entropy of the volume  $V$  of solution is given by Wall's equation<sup>12</sup>

$$\Delta S = k \sum_i s_i \ln(n_i/s_i). \quad (6)$$

The increase in the Helmholtz free energy is  $\Delta A = -T\Delta S$ , since it is assumed that all configurations have the same internal energy.

The change in the free energy of the system caused by entrance of a molecule into  $d\phi_i$  is

$$\mu_i = \partial(\Delta A)/\partial s_i = kT[1 + \ln(s_i/n_i)]. \quad (7)$$

The quantity  $\mu_i$  is the thermodynamic potential of the polymer molecules in the volume element  $d\phi_i$ .

The tendency of the free energy of the system to seek a minimum value provides the directing force which impels the configurations of the molecules toward their most probable distribution. The thermal motions of the submolecules produce a flow along each of the coordinates used in describing the configurations. The velocity of the flow along a particular coordinate is taken as the product of the mobility of the end of a submolecule and the negative of the total change in thermodynamic potential of the molecule resulting from a displacement along that coordinate. The validity of this procedure relies upon the legitimacy of the use of thermodynamic functions outside of equilibrium conditions. The conditions under which procedures of this kind are permissible have been discussed by several authors.<sup>13</sup> Comparison of their conclusions with the present calculation suggests that the procedure will give a valid result if the perturbation of the distribution of configurations is small. This condition can be stated quantitatively in terms of an expansion of  $s_i$  as a power series in  $\alpha$ ,

$$s_i = n_i(1 + \alpha f + \alpha^2 g + \alpha^3 h + \dots).$$

The perturbation is sufficiently small if all terms of the expansion which contain powers of  $\alpha$  higher than the first can be neglected. The potential  $\mu$  of a molecule can then be written

$$\mu = kT[1 + \ln(1 + \alpha f)], \quad (8)$$

<sup>12</sup> F. T. Wall, *J. Chem. Phys.* **10**, 132, 485 (1942).  
<sup>13</sup> S. R. de Groot, *Thermodynamics of Irreversible Processes* (North-Holland Publishing Company, Amsterdam, 1951), pp. 11, 221.

where  $\mu$  and  $f$  are functions of the  $3N$  coordinates. If  $\alpha$  is a sinusoidal function of time,  $\alpha = \alpha_0 e^{i\omega t}$ ,  $\mu$  and  $f$  will be complex, while if  $\alpha$  is a constant (steady flow),  $\mu$  and  $f$  will be real.

The calculation of the rate of the configurational diffusion of the polymer molecules is based on consideration of the  $s_i$  molecules whose configurations at the time  $t$  correspond to points in the volume element  $d\phi_i$ ; although  $d\phi_i$  is infinitesimal in volume, the number  $s_i$  can be made large enough for statistical treatment by letting the volume  $V$  of solution be very large. Motion of the point representing one of these molecules along the  $x_j$  coordinate can take place by the displacement in the  $x$  direction of the end either of the  $(j-1)$ th submolecule or of the  $j$ th submolecule. Motion of the end of the  $(j-1)$ th submolecule, with the ends of all other submolecules held fast, changes the values of  $x_{j-1}$  and  $x_j$  by amounts which are equal in magnitude and opposite in sign. The average velocity of the representative points along the  $x_j$  coordinate resulting from thermal motions of the end of the  $(j-1)$ th submolecule of each of the  $s_i$  molecules is

$$(\dot{x}_j)_{j-1} = -B \left[ \frac{\partial \mu}{\partial x_j} - \frac{\partial \mu}{\partial x_{j-1}} \right].$$

The symbol  $B$  represents the mobility of the end of a submolecule; it will be discussed in the following paragraph. In addition to  $(\dot{x}_j)_{j-1}$ , an average velocity of the representative points along the  $x_j$  coordinate results from thermal motions of the end of the  $j$ th submolecule of each of the  $s_i$  molecules. It is

$$(\dot{x}_j)_j = -B \left[ \frac{\partial \mu}{\partial x_j} - \frac{\partial \mu}{\partial x_{j+1}} \right].$$

The sum of these velocities is the total velocity of diffusion of the points in  $d\phi_i$  along the  $x_j$  coordinate.

$$(\dot{x}_j)_D = -B \left[ -\frac{\partial \mu}{\partial x_{j-1}} + 2\frac{\partial \mu}{\partial x_j} - \frac{\partial \mu}{\partial x_{j+1}} \right]. \quad (9)$$

Similar equations will hold for  $(\dot{y}_j)_D$  and  $(\dot{z}_j)_D$ .

The meaning of the mobility  $B$  can be made clear by consideration of a large number of polymer chains each equal in length to two submolecules. Choose a distance,  $a$ , which is small compared to the length of two fully extended submolecules. Fix one end of each chain at the origin of a private system of Cartesian coordinates; fix the other end at the point  $(a, 0, 0)$  of the local coordinate system. The central atom of each chain marks the end of a submolecule. At equilibrium the central atoms have coordinates which are distributed approximately in accordance with the probability density

$$p(x, y, z) = (2\beta/\pi)^{3/2} \exp\{-2\beta[(x-a/2)^2 + y^2 + z^2]\},$$

and the average velocity of central atoms located in the neighborhood of  $(x, y, z)$  of their respective coordinate systems is zero. If the central atom of each chain is now subjected to a small steady force  $\delta F$ , these atoms will have a small average velocity  $\delta v$  in the direction of the force. It is required that  $\delta F$  be so small that the configurations of the submolecules will always be randomly distributed over the available configurations. The value of  $\delta v$  will change as the distribution of the central atoms becomes significantly different from the equilibrium distribution. The initial value of the ratio of the velocity to the force  $(\delta v/\delta F)_0$ , is the mobility  $B$  of the end of a submolecule. It is clear that  $B$  depends upon the viscous forces exerted by the medium along the entire length of chain between the two fixed ends. If the length of chain included in a submolecule were increased above the minimum length which will obey Eq. (3), the viscous forces acting along the chain would be proportionately increased. Thus the mobility  $B$  would be inversely proportional to the length of chain included in the submolecule.

The viscous reaction of the medium to motions of the polymer segments depends, of course, on the local concentration of polymer segments. Since this must fluctuate with time and, further, must depend somewhat on the position of the submolecule along the chain, the value of  $B$  in Eq. (9) is an average over all the submolecules in the solution.

The set of  $N$  partial differential equations which give the components of the motion of the polymer molecules in the various  $x$  directions can be summarized in the form of a matrix<sup>14</sup> equation.

$$\mathbf{x}_t = \alpha \mathbf{z} - B\mathbf{A}\{\nabla_x \mu\}. \quad (10a)$$

In this equation  $\mathbf{x}_t$ ,  $\mathbf{z}$ , and  $\{\nabla_x \mu\}$  are column vectors with the forms

$$\begin{aligned} \mathbf{x}_t &= \{\dot{x}_1, \dot{x}_2, \dot{x}_3, \dots, \dot{x}_N\}, \\ \mathbf{z} &= \{z_1, z_2, z_3, \dots, z_N\}, \\ \{\nabla_x \mu\} &= \{\partial\mu/\partial x_1, \partial\mu/\partial x_2, \partial\mu/\partial x_3, \dots, \partial\mu/\partial x_N\}. \end{aligned}$$

and  $\mathbf{A}$  is the square matrix of order  $N$

$$\mathbf{A} = \begin{pmatrix} 2 & -1 & 0 & 0 & 0 & \dots & 0 & 0 & 0 \\ -1 & 2 & -1 & 0 & 0 & \dots & 0 & 0 & 0 \\ 0 & -1 & 2 & -1 & 0 & \dots & 0 & 0 & 0 \\ 0 & 0 & -1 & 2 & -1 & \dots & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 2 & \dots & 0 & 0 & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \dots & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \dots & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \dots & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & 0 & 0 & \dots & 2 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & \dots & -1 & 2 & -1 \\ 0 & 0 & 0 & 0 & 0 & \dots & 0 & -1 & 2 \end{pmatrix}$$

The sets of equations for the motions in the  $y$  directions

and  $z$  directions are written in the analogous forms

$$\mathbf{y}_t = -B\mathbf{A}\{\nabla_y \mu\}, \quad (10b)$$

$$\mathbf{z}_t = -B\mathbf{A}\{\nabla_z \mu\}. \quad (10c)$$

The solution of the problem requires a transformation of the original system of  $3N$  coordinates into a system in which the component of the velocity of diffusion along each coordinate is a function of the partial derivative of  $\mu$  with respect to that coordinate alone. This is performed by determining the orthogonal matrix  $\mathbf{R}$  such that

$$\mathbf{R}^{-1}\mathbf{A}\mathbf{R} = \mathbf{\Lambda} = [\lambda_p \delta_{pq}], \quad (11)$$

where  $\lambda_p$  is the  $p$ th eigenvalue of the set of  $N$  eigenvalues of  $\mathbf{A}$  and  $\delta_{pq}$  is the Kronecker delta.

$$\delta_{pq} = \begin{cases} 0; & p \neq q \\ 1; & p = q. \end{cases}$$

The eigenvalues  $\lambda_p$  of the matrix  $\mathbf{A}$  are related to the index  $p$  and the number of submolecules  $N$  by the equation

$$\lambda_p = 4 \sin^2 \frac{p\pi}{2(N+1)}. \quad (11a)$$

As the new coordinates we take the system  $u_1, v_1, w_1, \dots, u_p, v_p, w_p, \dots, u_N, v_N, w_N$ , which are related to the original coordinates by the three sets of equations

$$\mathbf{u} = \mathbf{R}^{-1}\mathbf{x}, \quad (12a)$$

$$\mathbf{v} = \mathbf{R}^{-1}\mathbf{y}, \quad (12b)$$

$$\mathbf{w} = \mathbf{R}^{-1}\mathbf{z}. \quad (12c)$$

Multiplying Eq. (10a) by  $\mathbf{R}^{-1}$  and making use of the fact that  $\mathbf{R}\mathbf{R}^{-1} = \mathbf{E}$ , the unit matrix, produces the equation

$$\mathbf{R}^{-1}\mathbf{x}_t = \alpha \mathbf{R}^{-1}\mathbf{z} - B\mathbf{R}^{-1}\mathbf{A}\mathbf{R}\mathbf{R}^{-1}\{\nabla_x \mu\}. \quad (13)$$

From Eq. (12a) it can be shown that

$$\{\nabla_x \mu\} = \tilde{\mathbf{R}}^{-1}\{\nabla_u \mu\}, \quad (14)$$

where

$$\{\nabla_u \mu\} = \{\partial\mu/\partial u_1, \partial\mu/\partial u_2, \partial\mu/\partial u_3, \dots, \partial\mu/\partial u_N\}.$$

Since  $\mathbf{R}$  is orthogonal (14) can be written

$$\mathbf{R}^{-1}\{\nabla_x \mu\} = \{\nabla_u \mu\},$$

and Eq. (13) becomes

$$\mathbf{u}_t = \alpha \mathbf{w} - B\mathbf{\Lambda}\{\nabla_u \mu\}. \quad (15a)$$

Application of the treatment given (10a) to (10b) and (10c) gives the result,

$$\mathbf{v}_t = -B\mathbf{\Lambda}\{\nabla_v \mu\}, \quad (15b)$$

$$\mathbf{w}_t = -B\mathbf{\Lambda}\{\nabla_w \mu\}. \quad (15c)$$

<sup>14</sup> The matrix notation and terminology used here are taken from H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand Company, Inc., New York, 1943), Chapter 10.

The effect of the orthogonal transformation on the expression for  $\Psi$ , the probability density of configurations, can be seen by noting that the coordinates appear only in the term

$$\sum_{j=1}^N (x_j^2 + y_j^2 + z_j^2).$$

This summation is the square of the length of the vector drawn to the representative point from the origin of configuration space. Since the length of a vector is unchanged by an orthogonal transformation, the expression for  $\Psi$  in the new coordinates is

$$\Psi(u_1, v_1, w_1, u_2, \dots, w_N) = (\beta/\pi)^{3N/2} \exp\left[-\beta \sum_{p=1}^N (u_p^2 + v_p^2 + w_p^2)\right]. \quad (16)$$

The volume element  $dx_1 dy_1 dz_1 dx_2 \dots dz_N$  transforms into the volume element  $du_1 dv_1 dw_1 du_2 \dots dw_N$ . The transformation, therefore, leaves unchanged both the equilibrium density of points in configuration space

$$\rho_0 = n_i/d\phi_i = \nu\Psi, \quad (17)$$

and the density at time  $t$

$$\rho = s_i/d\phi_i = n_i(1 + \alpha f)/d\phi_i = \nu\Psi(1 + \alpha f). \quad (18)$$

The function  $f$  can be found by solving the equation of continuity

$$\dot{\rho} = -\text{div}(\rho\mathbf{V}), \quad (19)$$

where  $\mathbf{V}$ , the vector velocity of the representative points is given by Eqs. (15a), (15b), and (15c). The divergence of the flux density is

$$\text{div}(\rho\mathbf{V}) = \sum_{p=1}^N \left[ \frac{\partial(\rho\dot{u}_p)}{\partial u_p} + \frac{\partial(\rho\dot{v}_p)}{\partial v_p} + \frac{\partial(\rho\dot{w}_p)}{\partial w_p} \right]. \quad (20)$$

We will evaluate first  $\partial(\rho\dot{u}_p)/\partial u_p$ . From (15a) and (18)

$$\rho\dot{u}_p = \nu\Psi(1 + \alpha f) \left[ \alpha w_p - B\lambda_p \frac{\partial\mu}{\partial u_p} \right].$$

Since we are interested here only in first-order effects we can disregard terms containing powers of  $\alpha$  higher than the first. Then, using (8),

$$\rho\dot{u}_p = \alpha\nu\Psi[w_p - D_p \partial f / \partial u_p], \quad (21)$$

in which the symbol  $D_p$  replaces the product  $BkT\lambda_p$ . Differentiation with respect to  $u_p$  gives

$$\frac{\partial(\rho\dot{u}_p)}{\partial u_p} = -\alpha\nu\Psi \left\{ D_p \frac{\partial^2 f}{\partial u_p^2} + 2\beta u_p \left( w_p - D_p \frac{\partial f}{\partial u_p} \right) \right\}. \quad (22a)$$

Similarly, we find from (15b) and (15c)

$$\frac{\partial(\rho\dot{v}_p)}{\partial v_p} = -\alpha\nu\Psi D_p \left[ \frac{\partial^2 f}{\partial v_p^2} - 2\beta v_p \frac{\partial f}{\partial v_p} \right], \quad (22b)$$

$$\frac{\partial(\rho\dot{w}_p)}{\partial w_p} = -\alpha\nu\Psi D_p \left[ \frac{\partial^2 f}{\partial w_p^2} - 2\beta w_p \frac{\partial f}{\partial w_p} \right]. \quad (22c)$$

For a sinusoidal oscillation  $\alpha = \alpha_0 e^{i\omega t}$  the time derivative of the density is

$$\dot{\rho} = i\omega\alpha\nu\Psi f. \quad (23)$$

Substitution of (22a), (22b), (22c), and (23) in (19) and solving for  $f$  gives

$$f = \sum_{p=1}^N \frac{u_p w_p}{2D_p(1 + i\omega\tau_p)}, \quad (24)$$

where

$$\tau_p = (4\beta D_p)^{-1} = \sigma^2(6BkT\lambda_p)^{-1}. \quad (24a)$$

The thermodynamic potential and the velocity of diffusion at any point in configuration space can be evaluated from this expression for the perturbation of the distribution of configurations.

### THE VISCOELASTIC PROPERTIES

The shearing stress which will produce a velocity gradient  $\alpha = \alpha_0 e^{i\omega t}$  in a liquid with a complex viscosity  $\eta^* = \eta_1 - i\eta_2$  is

$$S = \text{Re}\{\eta^* \alpha\} = \alpha_0[\eta_1 \cos\omega t + \eta_2 \sin\omega t].$$

The rate at which work is done by application of this shearing stress to a unit volume of solution is

$$P = S\alpha_0 \cos\omega t = \alpha_0^2[\eta_1 \cos^2\omega t + \eta_2 \sin\omega t \cos\omega t]. \quad (25)$$

The complex viscosity imparted to a solution by the polymer molecules can be calculated by calculating the rate of input of free energy into the polymer molecules as a result of the motion of each part of each molecule with the velocity of the surrounding liquid. The average rate per molecule of doing work on the molecules whose representative points lie in  $d\phi_i$  is given by the scalar product of two vectors, both of which are functions of the  $3N$  coordinates of configuration space. The first of these is  $\mathbf{V}_i$ , the velocity of the liquid, which, in the transformed coordinates, is given by

$$\dot{u}_p = \alpha_0 w_p \cos\omega t, \quad \dot{v}_p = 0, \quad \dot{w}_p = 0. \quad (26)$$

The other vector in the scalar product is  $\nabla\mu$ , the gradient of the thermodynamic potential. Since the velocity of the liquid has nonvanishing components only in the  $u$ -directions, only the components of  $\nabla\mu$  in the  $u$ -directions will appear in the scalar product. These components are found from (8) and (24) to be

$$\frac{\partial\mu}{\partial u_p} = \frac{\alpha_0 k T w_p}{2D_p(1 + \omega^2 \tau_p^2)} (\cos\omega t + \omega\tau_p \sin\omega t), \quad (27)$$

in which only first-order terms in  $\alpha$  have been retained. Combining (26) and (27) we find for the scalar product

$$\mathbf{V}_i \cdot \nabla\mu = \alpha_0^2 k T \sum_{p=1}^N \frac{w_p^2 (\cos^2\omega t + \omega\tau_p \sin\omega t \cos\omega t)}{2D_p(1 + \omega^2 \tau_p^2)}. \quad (28)$$

The number of molecules per unit volume of solution is  $n = \nu/V$ ; the number of these molecules whose representative points are in the volume element  $d\phi_i$  at the time  $t$  is  $n\Psi(1+\alpha f)d\phi_i$ . Multiplying this number by (28) and integrating over configuration space gives the rate at which the shearing stress does work upon the polymer molecules in a unit volume of solution. The result is

$$P_m = \alpha_0^2 nkT\sigma^2 \sum_{p=1}^N \frac{\cos^2\omega t + \omega\tau_p \sin\omega t \cos\omega t}{6D_p(1+\omega^2\tau_p^2)},$$

in which terms containing powers of  $\alpha$  higher than the second have been disregarded. Adding to this expression the energy input into the solvent,  $P_s = \eta_s \alpha_0^2 \cos^2\omega t$ , and comparing the result with (25) shows that

$$\eta_1 = \eta_s + \frac{nkT\sigma^2}{6} \sum_{p=1}^N \frac{1}{D_p(1+\omega^2\tau_p^2)}, \quad (29a)$$

$$= \eta_s + nkT \sum_{p=1}^N \frac{\tau_p}{1+\omega^2\tau_p^2}, \quad (29b)$$

$$\eta_2 = \frac{nkT\sigma^2}{6} \sum_{p=1}^N \frac{\omega\tau_p}{D_p(1+\omega^2\tau_p^2)}, \quad (29c)$$

$$= nkT \sum_{p=1}^N \frac{\omega\tau_p^2}{1+\omega^2\tau_p^2}. \quad (29d)$$

$\eta_s$  is the viscosity of the solvent.

These results can also be expressed in terms of a complex shear modulus,<sup>15</sup>  $G^* = G_1 + iG_2 = i\omega\eta^*$ . The components of  $G^*$  are

$$G_1 = nkT \sum_{p=1}^N \frac{\omega^2\tau_p^2}{1+\omega^2\tau_p^2} \quad (30a)$$

$$G_2 = \omega\eta_s + nkT \sum_{p=1}^N \frac{\omega\tau_p}{1+\omega^2\tau_p^2}. \quad (30b)$$

The relaxation times,  $\tau_p$ , in these equations are obtained from (11a) and (24a).

$$\tau_p = \sigma^2 \left[ \frac{24BkT \sin^2 \frac{p\pi}{2(N+1)}}{2(N+1)} \right]^{-1} \quad p=1, 2, \dots, N. \quad (31)$$

Each relaxation time corresponds to a particular mode of coordination of the motions of the segments of the molecule. The longest relaxation time is that for  $p=1$ . The ratio between successive relaxation times is large for small values of  $p$ , decreases with increasing  $p$ , and approaches unity as  $p$  approaches  $N$ .

In steady flow,  $\omega=0$ , both components of  $G^*$  and the imaginary part of  $\eta^*$  vanish. The real part of  $\eta^*$  becomes the steady-flow viscosity,  $\eta_0$ . From (29b) and (31), we

have

$$\begin{aligned} \eta_0 &= \eta_s + \frac{n\sigma^2}{24B} \sum_{p=1}^N \left[ \frac{\sin \frac{p\pi}{2(N+1)}}{2(N+1)} \right]^{-2} \\ &= \eta_s + \frac{n\sigma^2 N(N+2)}{36B}. \end{aligned} \quad (32)$$

Each relaxation time makes a contribution of  $nkT\tau_p$  to  $\eta_0$ . The contribution of  $\tau_1$ , the longest relaxation time, is

$$n\sigma^2 \left[ \frac{24B \sin^2 \frac{\pi}{2(N+1)}}{2(N+1)} \right]^{-1}.$$

The ratio of this contribution to the entire calculated contribution of the polymer is

$$3 \left[ \frac{2N(N+2) \sin^2 \frac{\pi}{2(N+1)}}{2(N+1)} \right]^{-1} \cong \frac{6(N+1)^2}{\pi^2 N(N+2)} \cong \frac{6}{\pi^2}.$$

This result indicates that the longer relaxation times account for practically all of the viscosity. The short relaxation times, although many in number if  $N$  is large, account for only a small part of the total viscosity.

This conclusion is important because the use of the submolecule as the fundamental relaxing unit excludes from consideration any processes involving segments of the chain shorter than the submolecule. Such processes would take place more rapidly than processes requiring the coordination of longer sections of the chain and would, therefore, be expected to give rise to shorter relaxation times. Accordingly, the relative contribution of these processes to the steady-flow viscosity would be expected to be negligible as compared to the contribution of the processes included by the theory.

The shortest relaxation time included by the theory is  $\tau_N$ ; from (31) we have  $\tau_N \cong \sigma^2 / (24BkT)$  if  $N \gg 1$ . At frequencies for which  $\omega\tau_N > 0.1$  the excluded processes will be expected to make an appreciable contribution to the real part of the complex shear modulus. The frequency  $\omega_l$ , at which  $\omega_l\tau_N = 0.1$ , will mark the upper limit of applicability of the theory. Let the relaxation time  $\tau_l$  be the one for which  $\omega_l\tau_l = 1$ . We then have  $\tau_l = 10\tau_N$ , which leads to

$$\sigma^2 \left[ \frac{24BkT \sin^2 \frac{l\pi}{2(N+1)}}{2(N+1)} \right]^{-1} \cong 10\sigma^2 [24BkT]^{-1},$$

or

$$l \cong N/5.$$

Thus the relaxation times for which  $p < N/5$  account for the dispersion of the viscoelastic properties up to frequencies within approximately one decade of the range in which excluded processes should begin to contribute to the real part of the modulus. For the

<sup>15</sup> R. L. Wegel and H. Walther, *Physics* 6, 141 (1935).

relaxation times for which  $p < N/5$  Eq. (31) simplifies to

$$\tau_p \approx \frac{\sigma^2(N+1)^2}{6\pi^2 p^2 BkT} \approx \frac{\sigma^2 N^2}{6\pi^2 p^2 BkT}. \quad (33)$$

Combining (32) and (33) gives

$$\tau_p = \frac{6(\eta_0 - \eta_s)}{\pi^2 p^2 nkT}. \quad (34)$$

Substitution of (34) in (29b) and (30a) gives

$$\eta_1 = \eta_s + \frac{6(\eta_0 - \eta_s)}{\pi^2} \sum_{p=1}^N \frac{p^2}{p^4 + \omega^2 \tau_1^2}, \quad \omega \tau_1 < \frac{N^2}{250}, \quad (35)$$

$$G_1 = nkT \sum_{p=1}^N \frac{\omega^2 \tau_1^2}{p^4 + \omega^2 \tau_1^2}, \quad \omega \tau_1 < \frac{N^2}{250}. \quad (36)$$

The summations in (35) and (36) have been evaluated (Table I) for ten values of  $\omega \tau_1$  between 0.1 and 100. If these summations are replaced by integrals from  $p=0.5$  to  $p=\infty$  and the results simplified by assuming  $\omega \tau_1 \gg 0.5$ , we obtain

$$\eta_1 = \eta_s + \frac{3(\eta_0 - \eta_s)}{\pi(2\omega \tau_1)^{\frac{1}{2}}}, \quad 2 < \omega \tau_1 < \frac{N^2}{250}, \quad (37)$$

and

$$G_1 = nkT \left[ \frac{\pi}{2} \left( \frac{\omega \tau_1}{2} \right)^{\frac{1}{2}} - 0.5 \right], \quad 5 < \omega \tau_1 < \frac{N^2}{250}. \quad (38)$$

The lower limits of the indicated ranges of applicability of these equations are based on the requirement that values calculated from these equations agree within approximately 0.1 percent with corresponding values obtained from Eqs. (35) and (36). The upper limit is set by the requirement that no relaxation times for which  $p > N/5$  should make an appreciable contribution. The limit of applicability of Eqs. (29) and (30) is one decade higher, i.e.,  $\omega \tau_1 < N^2/25$ ; it is set by the use of the submolecule as the fundamental relaxing unit.

It is of interest to note the following equation for the imaginary part of the complex viscosity, which was obtained from Eqs. (38) and (34).

$$\eta_2 = \frac{G_1}{\omega} = \frac{3(\eta_0 - \eta_s)}{\pi} [(2\omega \tau_1)^{-\frac{1}{2}} - (\pi \omega \tau_1)^{-1}].$$

This equation, which has necessarily the same range of validity as Eq. (38), shows that at high frequencies the calculated value of  $\eta_2$  will approach the value of  $(\eta_1 - \eta_s)$  calculated from Eq. (37).

#### DISCUSSION OF RESULTS

The result of the calculation, as expressed in Eqs. (29), (30), and (31), predicts that the viscoelastic properties of a polymer solution can be described by a

TABLE I. Theoretical values of the real parts of the complex viscosity, Eq. (35), and the complex shear modulus, Eq. (36).

$\omega \tau_1$	$(\eta_1 - \eta_s)/(\eta_0 - \eta_s)$	$G_1/(nkT)$
0.1	0.9939	0.01072
0.2	0.9762	0.04162
0.5	0.8758	0.2203
1.0	0.6861	0.5785
2.0	0.4776	1.076
5.0	0.3003	1.982
10.0	0.2135	3.012
20.0	0.1511	4.476
50.0	0.0955	7.351
100.0	0.0676	10.60

“generalized Maxwell model.”<sup>16</sup> Each Maxwell element makes a contribution of  $nkT$  to the real part of the complex shear modulus at high frequencies and each of the relaxation times depends in the same way on temperature. Thus the results are consistent with the concept of “reduced variables” introduced by Ferry.<sup>17</sup>

According to (31) the relaxation times depend upon the temperature through three factors. They are inversely proportional to the absolute temperature and to the mobility of the end of a submolecule, which increases with decreases in the viscous forces exerted by the surrounding medium. And they are directly proportional to  $\sigma^2$ , the mean-square separation of the ends of the submolecule, and consequently to  $S^2$ , the mean-square separation of the ends of the molecule;<sup>18</sup> it has been shown by Flory<sup>19</sup> and his collaborators that changes in temperature cause changes in the extension of dissolved polymer molecules which are reflected in the intrinsic viscosity of the solution.

At frequencies below the range in which processes excluded from consideration by use of the concept of the submolecule make an appreciable contribution, the relaxation times predicted by Eq. (33) do not depend upon the number of submolecules into which the chain is divided. This can be seen from the following considerations. The submolecule may be chosen longer than the minimum length which obeys, approximately, the Gaussian law. The viscous forces which reduce the mobility  $B$  are directly proportional to the length chosen; accordingly, we may write  $B = KN$ . Since  $\sigma^2 N = S^2$  Eq. (33) becomes

$$\tau_p = S^2 / (6K\pi^2 p^2 kT),$$

which contains no factors dependent upon the length of the submolecule.

The contribution of the polymer to the viscosity of

<sup>16</sup> W. Kuhn, *Z. physik. Chem.* **B42**, 1 (1939); T. Alfrey and P. Doty, *J. Appl. Phys.* **16**, 700 (1945); R. D. Andrews, *Ind. Eng. Chem.* **44**, 707 (1952).

<sup>17</sup> J. D. Ferry, *J. Am. Chem. Soc.* **72**, 3746 (1950).

<sup>18</sup> It is easily shown that  $S^2 = N\sigma^2$ .

<sup>19</sup> T. G. Fox, Jr., and P. J. Flory, *J. Phys. Colloid Chem.* **53**, 197 (1949); T. G. Fox, Jr., and P. J. Flory, *J. Am. Chem. Soc.* **73**, 1909, 1915 (1951); H. L. Wagner and P. J. Flory, *ibid.* **74**, 195 (1952); L. Mandelkern and P. J. Flory, *ibid.* **74**, 2517 (1952); Flory, Mandelkern, Kinsinger, and Shultz, *ibid.* **74**, 3364 (1952); Krigbaum, Mandelkern, and Flory, *J. Polymer Sci.* **9**, 381 (1952).

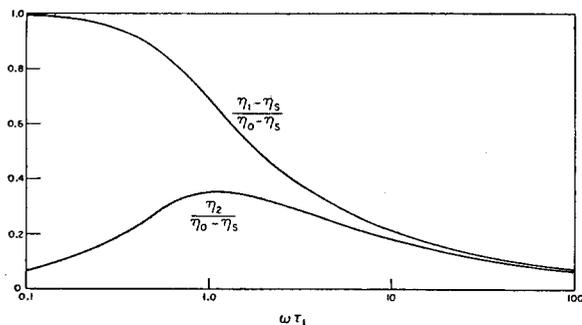


Fig. 1. Contribution of the polymer to the components of the complex viscosity relative to its contribution to the viscosity in steady flow.

the solution in steady flow is given by (32). Since  $\sigma^2 N = S^2$ , this equation can be written

$$\eta_0 - \eta_s = nNS^2 / (36B),$$

if  $N \gg 2$ . It is interesting to note that this expression has a form similar to that of the expression obtained by Debye<sup>20</sup> in his hydrodynamic calculation of the viscosity of a solution of "free-draining chains." However  $N$  is here the number of submolecules rather than the number of atomic groups, and the frictional coefficient of an atomic group is replaced by  $B^{-1}$ , the reciprocal of the mobility of the end of a submolecule.

The results are presented in Eqs. (34)–(38) in a form which can be readily used in calculation. The relaxation times as given by (34) can be calculated from the steady-flow viscosities of the solution and solvent, the molecular weight and concentration (in mass per unit volume) of the polymer, and the absolute temperature. The real parts of the complex viscosity and the complex shear modulus at the angular frequency  $\omega$  can then be calculated. The theoretical curves for the functions  $(\eta_1 - \eta_s) / (\eta_0 - \eta_s)$  and  $\eta_2 / (\eta_0 - \eta_s)$  are shown in Fig. 1. The corresponding curves for  $(G_2 - \omega\eta_s) / (nkT)$  and  $G_1 / (nkT)$  are shown in Fig. 2.

Experimental data have recently been obtained<sup>7</sup>

<sup>20</sup> P. Debye, J. Chem. Phys. 14, 636 (1946).

which indicate that these curves are at least a good first approximation to the actual viscoelastic behavior of dilute solutions of polystyrene and polyisobutylene. It is hoped that data which will provide a more exacting test will soon be available. Disagreements between theory and experiment are to be expected as the result of the following factors: (1) importance at high frequencies of processes excluded by the calculation, (2) polydispersity of any actual polymer, and (3) effects

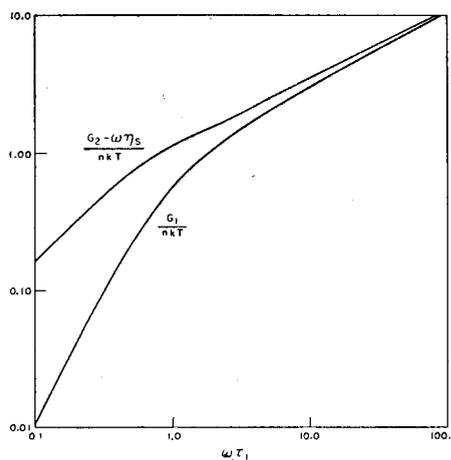


Fig. 2. Contribution of the polymer to the components of the complex rigidity relative to the contribution of a single relaxation mode to the instantaneous rigidity.

of intramolecular and intermolecular interferences on the motions of the segments of polymer chains.

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