

TEXTILE RESEARCH INSTITUTE
Princeton, New Jersey

Technical Report No. 11
to The Office of Naval Research
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A Molecular Theory of the Viscoelastic Behavior
of Noncross-linked Elastomers

by
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ABSTRACT

The purpose of this thesis is to develop a theory of the mechanical properties of noncross-linked polymers at temperatures above the glass transformation. The relationship between this theory and the dielectric dispersion of polar polymers is also discussed.

If the bond lengths and bond angles of the molecular chains are constant during extension of a polymer, the configuration of an entire molecule at any time t may be specified by the azimuth angles of the bonds in the chain, and by the two angular coordinates describing the rotation of the chain around its center of mass. The state of the material is described statistically by f , the relative number of molecules having each of the possible configurations.

For a noncross-linked polymer, the only intermolecular forces are viscous in nature, and the force on a single element (one skeletal atom together with its side groups) is proportional to the velocity of that element relative to the surrounding atoms. If the polymer is incompressible, and if the strain is everywhere the same, it follows that the molecular configurations during extension of the polymer may be described by Smoluchowski's diffusion equation:

$$\nabla \cdot \underline{D} \cdot [\nabla f + f \nabla V/kT] = \frac{\partial f}{\partial t},$$

where $\underline{D}$ is the diffusion tensor of a molecule, k is Boltzmann's constant, and T is the absolute temperature. The potential V under which the diffusion takes place is equal to the rate of extension multiplied by

a quadratic function of the positions of the elements relative to the center of mass of the molecule.

Once $\underline{D}$ and the rate of extension are known, the diffusion equation can be solved for f , the probability of each molecular configuration. From f it is possible to find the stress on the polymer. In other words, the diffusion equation leads to a general relationship between the stress and the extension.

The solution of the diffusion equation includes the theoretical dependence of the stress upon the temperature. The predicted temperature effects agree with the observed mechanical properties of high polymers such as polyisobutylene.

If it is assumed that the molecules in the unplasticized polymer move in the same way as in a dilute solution, the diffusion tensor is identical with the one given by Kirkwood and Fuoss in their treatment of the dielectric dispersion of polar polymers [J. G. Kirkwood and R. M. Fuoss, J. Chem. Phys. 9, 329 (1941)]. The stress relaxation calculated from this assumption decays too rapidly with time to fit the experimental properties of polyisobutylene. This discrepancy is believed to be due to the chain entanglements which occur in the unplasticized polymer. However, the diffusion tensor can be corrected arbitrarily so that it gives the proper time dependence of the stress relaxation and therefore includes the effect of the chain entanglements. A diffusion tensor is found which correctly describes the mechanical properties of polyisobutylene over nine decades of time. The corresponding theoretical dependence upon the molecular weight does not quite agree with experimental results.

In determining the response of a polar polymer to an electric field, Kirkwood and Fuoss use the diffusion tensor applicable to dilute solutions. It is possible to introduce into their calculations the new diffusion tensor obtained from the theory of extension. Except for the molecular weight dependence, the results of this correction agree reasonably well with the experimental dielectric dispersion of unplasticized polyvinyl chloride. It therefore seems possible to find a diffusion tensor correctly describing the time dependence of a polymer's response to both mechanical and electrical forces.

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I. INTRODUCTION

An elastomer may be defined as a cross-linked or noncross-linked linear high polymer in which the bonds of the molecular chains are free to rotate, or at least are free to assume easily a variety of positions. Contiguous molecules are also free to move relative to each other. Because the molecules lose much of their freedom of motion at temperatures below the brittle point, or glass transformation, it is necessary to specify the temperature range in which a polymer behaves as an elastomer. Examples of elastomers are polyisobutylene at room temperature and polymerized sulfur at higher temperatures. If not worked excessively, elastomers are amorphous. To obtain a crystalline x-ray pattern for polyisobutylene, for example, the polymer must be extended rapidly at least 1000% [1].

From the molecular properties of these materials, several things can be inferred about their response to mechanical stress. When no external forces are acting on the polymer molecules, they reach an equilibrium state in which the bonds are randomly distributed among their possible relative positions. On the average, each molecule is then coiled up, with the direct distance from one end of the molecule to the other proportional to the square root of the molecular weight [2]. External mechanical forces can extend a molecule to many times its equilibrium end-to-end length with only a slight change in the internal

-
1. C. S. Fuller, C. J. Frosch, and N. R. Pape, J. Am. Chem. Soc. **62**, 1905 (1940).
 2. L. R. G. Treloar, "Physics of Rubber Elasticity," Oxford, Oxford University Press, 1949, Chapter III.

energy. Consequently, elastomers are characterized by a small modulus and a very large extensibility.

The first successful application of the molecular description of elastomers was the theoretical treatment of the mechanical properties of cross-linked polymers in thermodynamic equilibrium [3]. If the molecules are cross-linked, as in vulcanized rubber, the chains form a network running throughout the material. When stretched, this network can support a force so long as the cross-links are not disrupted chemically. To compute the force necessary to sustain a given strain, the chain configurations consistent with that strain are counted. The entropy and the force are then computed by ordinary thermodynamic arguments. In this calculation, changes in the internal energy are neglected, a reasonable assumption in view of the fact that the average inter-atomic distance is affected very little by the strain. The dependence of the stress upon both the strain and the temperature, calculated in this way, agrees reasonably well with experiment [4].

Noncross-linked elastomers, on the other hand, cannot support any stress in equilibrium. The chains are free to slip past one another and to resume unstressed configurations. If the material is suddenly

3. From a large literature one might cite:

K. H. Meyer, G. von Susich, and E. Valko, Kolloid-Z **59**, 208 (1932),
 W. T. Busse, J. Phys. Chem. **36**, 2862 (1932),
 E. Karrer, Phys. Rev. **39**, 857 (1932),
 H. M. James, and E. Guth, J. Polymer Sci. **4**, 153 (1949),
 F. T. Wall, J. Chem. Phys. **11**, 527 (1943),
 P. J. Flory, and J. Rehner, Jr., J. Chem. Phys. **11**, 512 (1943),
 W. Kuhn, Kolloid-Z. **76**, 258 (1936), and
 L. R. G. Treloar, Trans. Faraday Soc. **40**, 59 (1944).

4. P. J. Flory, Chem. Revs. **35**, 51 (1944); and P. J. Flory, N. Rabjohn, and M. C. Shaffer, J. Polymer Sci. **4**, 225 (1949).

extended and then kept at a constant length, the stress decays very slowly to zero from its initial value. During a large part of this relaxation, the force is approximately a linear function of the logarithm of the time [5].

The effect of temperature on the stress relaxation is twofold. First, the force at small times is proportional to the absolute temperature, similar to the equilibrium forces for cross-linked polymers. Secondly, raising the temperature makes the relaxation more rapid. Reducing the molecular weight also increases the rate of relaxation, but does not alter the magnitude of the force at small times.

When an elastomer is polar, it not only has interesting mechanical properties but it also exhibits an anomalous dielectric behavior [6]. The dielectric dispersion of a polymer such as polyvinyl chloride depends on the frequency of the applied voltage, and has a broad, low maximum in the audio frequency range. Debye's single relaxation time does not explain the frequency dependence of the loss, and a distribution of relaxation times is necessary to describe the experimental results. The frequency of maximum loss varies with the temperature, indicating a temperature-time relationship similar to that observed for the mechanical properties.

A theoretical treatment of the dielectric dispersion has been given by Kirkwood and Fuoss [7]. In this theory, it is assumed that the

-
5. R. D. Andrews, N. Hofman-Bang, and A. V. Tobolsky, J. Polymer Sci. 3, 669 (1948).
 6. A summary of the dielectric relaxation of polymers is given by W. Kauzmann, Rev. Mod. Phys. 14, 12 (1942).
 7. J. G. Kirkwood, and R. M. Fuoss, J. Chem. Phys. 9, 329 (1941).

the bond lengths and bond angles of each polymer molecule are always constant, but that the azimuth angles of the bonds are continually rotating due to the thermal motion of the atoms. In the presence of an electric field, the azimuth angles tend to rotate so that the individual dipoles of the molecule are aligned as much as possible with the direction of the field. The only forces opposing this change in the molecular configuration are viscous drag forces on each of the polymer atoms. The solution of the diffusion equation describing this process indicates that a molecular chain moves in sections of various length, with each section acting as a single mechanical and electrical unit. One might say, roughly, that the distribution of possible section lengths for a single molecule produces the distribution of relaxation times. This theory predicts a broad maximum for the dielectric loss at low frequencies, but the calculated maximum is too large and too narrow to agree quantitatively with the experimental results for unplasticized polyvinyl chloride.

Kirkwood [8] has extended the diffusion theory to include a treatment of the nonequilibrium mechanical properties of cross-linked elastomers. He assumes that the stress on the material is carried entirely by the cross-links between the polymer chains. Each molecule tends to increase in length under the stress-dependent force across its tiepoints, with the motion of the molecule being retarded by the viscous forces on each of the polymer atoms. The results of this theory have not been compared with the experimental properties of elastomers.

8. J. G. Kirkwood, J. Chem. Phys. 14, 51 (1946).

In Kirkwood's theory, it is assumed that the viscous force on an atom in a given molecule is proportional to the velocity of that atom relative to the center of mass of the molecule. Actually, however, the viscous force depends on the motion of the atom relative to its immediate surroundings. That is to say, the force is proportional to the velocity of the atom minus the velocity of the material around the atom, where both motions may be measured relative to the center of mass of the molecule. The velocity of the material at any point is zero during the application of an electric field, but is not zero if the polymer body is being strained by a mechanical force. For extension, it may be shown readily that this velocity is proportional to the rate of extension of the polymer body. Consequently, there is a term in the viscous force which is not related directly to the stress on the polymer or to the motion of the molecule, but depends instead on the rate of extension. This term is neglected by Kirkwood although it can contribute to the intermolecular forces.

The importance of this term may be seen most clearly if we consider a noncross-linked polymer. In Kirkwood's theory, an external stress cannot be applied to a polymer molecule unless it is cross-linked to the rest of the material. This comes about because it is assumed that the stress is carried entirely by the cross-links. The predicted modulus of a noncross-linked elastomer is therefore zero, a result that does not agree with experiment.

In this thesis, the mechanical properties of an elastomer will be derived by a method which includes the effects of the viscous intermolecular forces. We shall begin by relating the rate of extension

of the polymer to the flow of the material around the center of mass of a given molecule. The way in which the flow affects the viscous forces on the molecule will then be derived. A diffusion equation will be found which describes the way in which the molecules change their configurations under these forces. Only noncross-linked polymers will be considered in order to emphasize the strain-dependent nature of the intermolecular forces.

Qualitatively, the diffusion equation indicates that the molecules move in the following way. If there are no external forces on the polymer, the thermal motion of the molecules tends to orient them randomly, and the distribution of bond directions is spherically symmetric. During extension of the polymer, the azimuth angles rotate so that the molecules tend to line up in the direction of the extension. If the elastomer is then kept at a constant length, the molecules slowly return by their thermal motion to a spherically symmetric distribution. This latter process is accompanied by the stress relaxation.

Once the configurations of the molecules are known, one can calculate the stress on the elastomer. Since the configurations are determined by the rate of strain, it is possible to find a general relationship between the stress on the elastomer and its resultant extension. This relationship will be expressed in terms of a distribution of mechanical relaxation times.

The theoretical stress relaxation obtained in the above manner has the correct temperature dependence, but decays too rapidly in time to agree with the experimental data for unplasticized polyisobutylene.

It is believed that the primary reason for this discrepancy is that the motion of a polymer molecule is altered by its entanglements with the neighboring chains. These entanglements retard the changes in the configurations of the molecule and effectively increase the resistance constant of each atom, where the resistance constant is the ratio of the viscous force on an atom to its velocity. In other words, the viscous force on an atom in an unplasticized polymer will be much greater than the corresponding force in a dilute polymer solution. Furthermore, the magnitude of the force will depend upon the position of the atom in its polymer chain. In order to introduce the effect of the entanglements into the theory, the resistance constants of the atoms will be made an arbitrary function of distance from the ends of the chain, contrasting with Kirkwood's assumption that the resistance constants are the same for all the atoms. A set of constants will be found which, when substituted into the diffusion equation, gives the correct dependence of the stress relaxation upon the time as well as upon the temperature. The dependence upon the molecular weight is not predicted correctly.

The treatment of the dielectric dispersion by Kirkwood and Fuoss is applicable only to dilute solutions of a polar polymer, because it does not include any interactions between the polymer molecules. However, the theory can be corrected for the chain entanglements by introducing the set of resistance constants which gives the correct mechanical properties of an unplasticized polymer. This correction will be carried out in the last section of this thesis. The resultant dielectric dispersion agrees quantitatively with the experimental properties of unplasticized polyvinyl chloride.

Except for the molecular weight dependence, it would therefore appear that the ad hoc set of resistance constants correctly describes the molecular diffusion within an unplasticized polymer at temperatures above its glass transformation.

II. THE MOLECULAR PROCESSES RESULTING FROM MECHANICAL EXTENSION

This section describes the effects of mechanical extension upon the positions and configurations of the molecules in a noncross-linked elastomer. By evaluating the intermolecular forces which result from extension, we can find the diffusion equation satisfied by the molecular configurations. It is then shown that solution of the diffusion equation leads to a relationship between the stress on the polymer and the resultant strain. This relationship includes the dependence of the stress and the strain upon the time.

A. The Macroscopic Flow During Extension

Consider a right circular cylinder of elastomer, of unit cross-section and unit length when unstressed. The dimensions of the cylinder are much larger than the dimensions of the molecules. Let the cylinder be extended parallel to its axis by a stress $s(t)$ applied to the ends of the cylinder. The stress is an arbitrary function of the time t . The macroscopic strain $\epsilon(t)$ is the relative increase in the length of the cylinder. It will be assumed that $\epsilon(t)$ is always much less than unity and that the area of the cylinder changes only slightly during extension. It will also be assumed that any heat generated by the application of the external force to the body is carried off rapidly enough so that the temperature T of the elastomer is constant.

Let us erect a coordinate system at the center of mass of any one of the molecules in the cylinder, with the z axis parallel to the axis of the cylinder. During extension of the polymer, the origin of this coordinate system moves with the center of mass of the molecule.

The usual cylindrical coordinates ρ , ϕ , and z will be used to measure position relative to the coordinate system.

Consider a volume ΔV which has dimensions small compared with the dimensions of the elastic body under consideration, but large compared with the size of a single atom. Also, let us define a time interval Δt which is small compared with the times involved in any experiment on the polymer body, but large compared with the time intervals necessary to describe any single atomic collision or interaction. Let $\underline{v}$ denote the average velocity of all the atoms inside ΔV during the time interval Δt . This velocity is measured relative to the coordinate system moving with the molecule. It will be assumed that ΔV and Δt exist such that $\underline{v}$ is a continuous and differentiable function of time and of position in the body.

If the strain inside the cylinder is everywhere the same, the velocity $\underline{v}$ is independent of the choice of molecule upon which the coordinate system is erected. From this fact, an expression may be found for $\underline{v}$ in terms of the rate of extension. By cylindrical symmetry, $\underline{v}$ will not have a component in the ϕ direction, nor will any of its components be a function of ϕ . Also, it may be shown readily that the z component of $\underline{v}$ is everywhere independent of ρ , and that the ρ component of $\underline{v}$ is independent of z . We can summarize these results by the vector equation^{*}

$$\nabla_3 \times \underline{v} = 0. \quad (1)$$

^{*} ∇_3 denotes the usual three-dimensional vector operator (see page 16).

A second property of $\underline{v}$ is obtained from conservation of the mass of the body. If the elastomer is incompressible, the density is independent of the time and the divergence of $\underline{v}$ is zero:

$$\nabla_3 \cdot \underline{v} = 0. \quad (2)$$

Finally, the boundary conditions upon $\underline{v}$ may be given. If $\epsilon(t)$ is much less than unity, the limit of $(\underline{v})_z$ as z becomes very large is

$$\lim_{z \rightarrow \infty} (\underline{v})_z = z \frac{d\epsilon}{dt}. \quad (3)$$

At the origin of the coordinate system, $\underline{v}$ is identically zero. Equations (1) and (2), together with these boundary conditions, uniquely define the velocity function. The z component of the velocity is given everywhere by

$$\underline{(\underline{v})_z} = z \frac{d\epsilon}{dt} \quad (4)$$

and the ρ component by

$$\underline{(\underline{v})_\rho} = -\frac{1}{2} \rho \frac{d\epsilon}{dt}. \quad (5)$$

From these equations, we may show readily that the trajectories of the material relative to the molecular coordinate system are

$$\rho^2 z = \text{constant}. \quad (6)$$

This set of trajectories implies that every small, right circular cylinder of material, with its axis parallel to the z axis, always moves inside the main cylinder so as to retain its cylindrical shape and constant volume. The flow pattern of the material is shown in Figure 1.

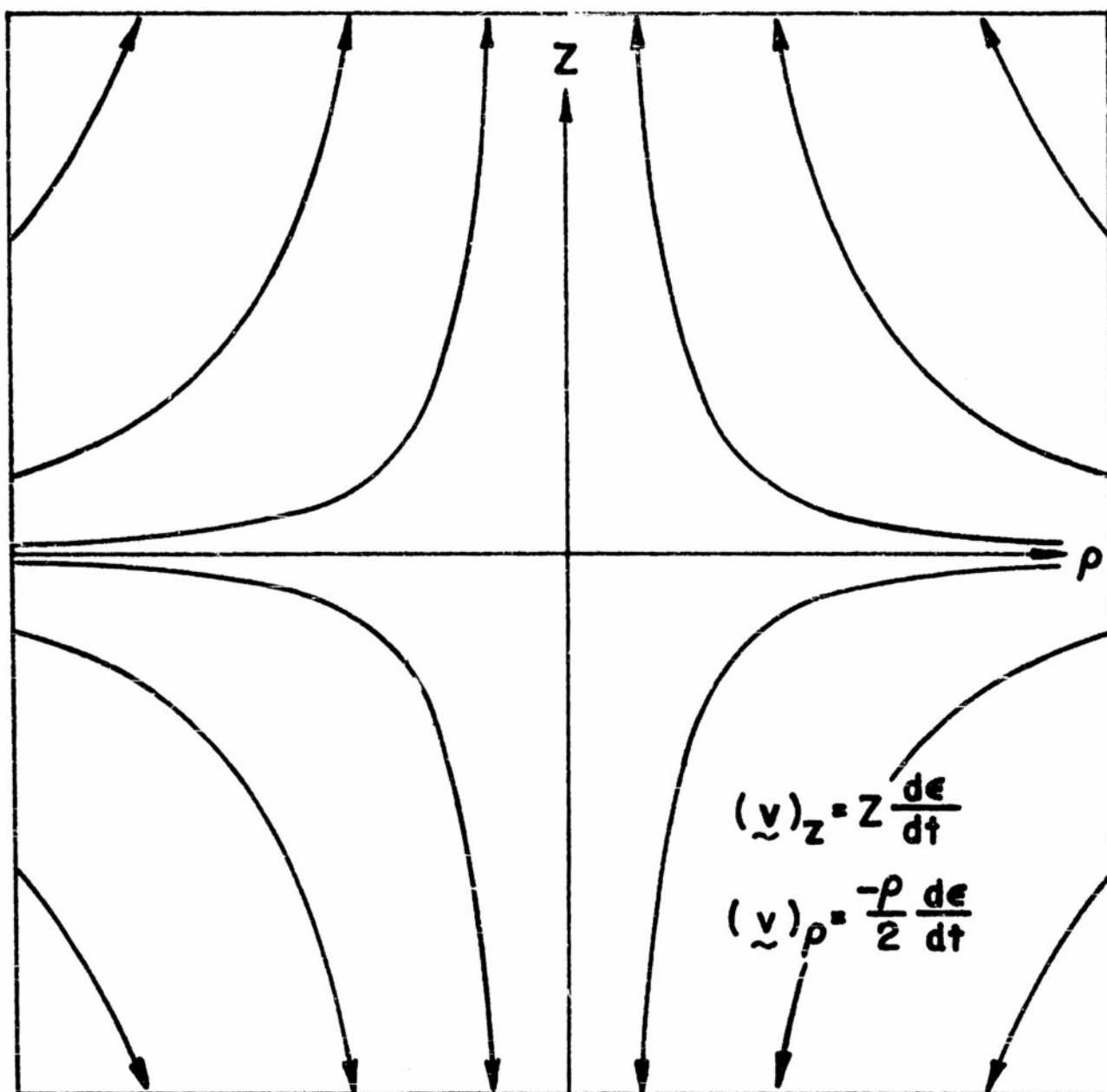


Fig. 1. Flow Pattern of an Incompressible Material in Extension

B. Description of the Molecular State

To define the state of the polymer at any time t , it is necessary to add to ψ a description of the configurations of the molecules. The instantaneous configuration of a molecule relative to a coordinate system erected at its center of mass can be specified by the direction of the center bond and by the azimuth angles along the polymer chain. If de/dt is small, the bond lengths and bond angles are constant during extension. The side groups of the molecule may be free to change position internally and to rotate around the bonds connecting them to the main chain, but these motions can be neglected if the side chains are relatively short.

The zenith and azimuth angles Θ and ϕ will be used to specify the direction of the center bond. If the molecular chain consists of $2n-1$ single bonds, the azimuth angles can be denoted by $\chi_2, \chi_3, \dots, \chi_{2n-1}$, numbered from one end of the chain. Exact definitions of Θ, ϕ and $\chi_2, \chi_3, \dots, \chi_{2n-1}$ are given in Appendix I. The configuration of an entire molecule is specified by its $\Theta, \phi, \chi_2, \dots, \chi_{2n-1}$.

Without loss in generality, it may be assumed that all of the molecules have the same structure and molecular weight, and are indistinguishable. Consequently, the state of the molecules at any time t may be specified by the number of molecules having each possible configuration, without specifying which molecules have which configurations. For this purpose, $f(\Theta, \phi, \chi_2, \dots, \chi_{2n-1})$ is defined such that $f \sin \Theta d\Theta d\phi d\chi_2 \dots d\chi_{2n-1}$ is the fraction of the molecules having configurations between $\Theta, \phi, \chi_2, \chi_3, \dots, \chi_{2n-1}$ and $\Theta + d\Theta, \phi + d\phi, \chi_2 + d\chi_2, \dots, \chi_{2n-1} + d\chi_{2n-1}$. The number of molecules is constant,

and the integral of ζ over all possible configurations is always unity:

$$\int \zeta dq = 1. \quad (7)$$

The configurations of the molecules may be described most conveniently in the $2n$ dimensional coordinate space in which $\Theta, \phi, \chi_2, \dots, \chi_{2n-1}$ are orthogonal coordinates. The differential volume element dq in this space is equal to $\sin\Theta d\Theta d\phi d\chi_2 \dots d\chi_{2n-1}$. If the configurations of all the molecules of the polymer body are plotted as points in this space, the configurational probability ζ is proportional to the density of the points.

The velocity of all the points in the volume element dq , when averaged over the time interval Δt , is denoted by $\underline{v}$. The components of $\underline{v}$ are $\dot{\Theta}, \dot{\phi} \sin\Theta, \dot{\chi}_2, \dot{\chi}_3, \dot{\chi}_4, \dots, \dot{\chi}_{2n-1}$. The velocity $\underline{v}$ at a particular point in the space gives the rate of change of the corresponding molecular configuration. Specification of $\underline{v}$ over the entire space describes the way in which all of the configurations are changing with time.

In summary, the state of an incompressible elastomer may be specified for our purpose by ζ , the probability of each configuration. The rate at which the state is changing may be specified by the velocities $\underline{v}$ and $\underline{u}$. By using this statistical description of the molecular state, we can find the response of an elastomer to mechanical and electrical forces.

C. The Diffusion Equation for the Molecular Configurations

Once the state of the elastomer is defined, it is possible to describe the intermolecular forces. Knowing these forces, we can

obtain the equation of motion of the molecules. Because the stress and strain are measured as averages over times at least as large as the interval Δt , the forces acting on a given molecule may also be averaged over Δt . Only that average force need be considered in finding an equation of motion.

If the side groups are small, the average motion of the groups on any single atom of the main molecular chain is the same as the average motion of the atom itself. Hence, the entire molecule including its side groups may be divided into $2n$ equal elements which may be treated as rigid bodies. Each element is at a constant bond length and bond angle from the next element along the chain, but is free to rotate around the azimuth angle of the bond. The forces on each element consist of the constraint forces required to keep the bond lengths and bond angles constant, plus the average external force due to the surrounding atoms. The constraint forces need not be considered if the molecular motion is described in the internal coordinate space of $\Theta, \phi, \chi_2, \dots, \chi_{2n-1}$.

The thermal motion of an element consists of jumps from one stable position to another, accompanied by rearrangement of the surrounding atoms. Let $\underline{v}_i$ denote the velocity of the i -th element in the chain (numbered from one end). This velocity is measured relative to the center of mass of the molecule, and is averaged over the time interval Δt . If the energy of thermal agitation is large compared with the energy required for a single jump, many such motions occur during Δt . To a good approximation, $\underline{v}_i$ is a continuous function of time. This approximation implies that $\underline{v}$ is also continuous.

From this description of the motion of the molecules, it may be postulated immediately that the average intermolecular force $\underline{F}_i$ on the i -th element is viscous in nature, and is proportional to the velocity of the element relative to its surroundings:

$$\underline{F}_i = \zeta_i(\underline{v} - \underline{v}_i), \quad (8)$$

where $\underline{v}$ is measured at the position of the element in question. The resistance constant ζ_i is assumed to be independent of the velocity and position of the element.

One part of $\underline{F}_i$ may be derived from a potential V_i , defined by

$$-\nabla_3 V_i = \zeta_i \underline{v}. \quad (9)$$

As in Equation (8), $\underline{v}$ is measured at the position of the i -th element. From Equations (4) and (5) we may show readily that

$$V_i = \frac{1}{4} \frac{d\epsilon}{dt} \zeta_i (\rho_i^2 - 2 z_i^2). \quad (10)$$

Introduction of V_i into Equation (8) gives

$$\underline{F}_i = -\nabla_3 V_i - \zeta_i \underline{v}_i. \quad (11)$$

For an unplastized polymer, there is no need to consider the hydrodynamic interactions between elements of the same molecule. The flow represented by $\underline{v}$ describes the motion of all the atoms near the i -th element, including those on the same chain. $\underline{F}_i$ therefore includes the forces between elements of the same molecule. This case is quite different from that of a dilute solution of a polymer, in which

the hydrodynamic interactions must be considered separately from the viscous forces due to the flow of the solvent [9].

All of the viscous forces acting on a molecule are equivalent to a generalized force $\underline{F}_f$ in the internal coordinate space of $\Theta, \phi, \chi_2, \chi_3, \dots, \chi_{2n-1}$. This force is given by

$$\underline{F}_f = -\nabla V_f - \underline{\rho} \cdot \underline{u}, \quad (12)$$

where $\underline{\rho}$ is the resistance tensor. The components of $\underline{\rho}$ may be found from the resistance constants by computing T_i , the torque around an angle χ_i produced by rotation around some other angle χ_j :

$$T_i = \sum_j \rho_{ij} \dot{\chi}_j. \quad (13)$$

The calculations for $\underline{\rho}$ are given in Appendix I. The potential V_f is the sum of all the individual potentials of the elements:

$$V_f = \frac{1}{4} \frac{d\varepsilon}{dt} \sum_i \zeta_i (\rho_i^2 - 2z_i^2). \quad (14)$$

It should be noted that the ∇ in Equation (12) (and in all succeeding equations) is the vector operator associated with the internal coordinate space, and consequently has $2n$ dimensions. The ∇_3 in Equations (9) and (11) is the usual three-dimensional quantity.

If the polymer body is in equilibrium and there are no external forces on the molecules, the angles $\Theta, \phi, \chi_2, \dots, \chi_{2n-1}$ are free to assume any possible set of values (assuming that the bond rotations are

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9. F. Bueche, J. Chem. Phys. **20**, 1959 (1952). The hydrodynamic interactions and their effects in polymer solutions are described by J. G. Kirkwood, and J. Riseman, J. Chem. Phys. **16**, 565 (1948); J. G. Kirkwood, Rec. Trav. Chim. **68**, 649 (1949); and J. G. Kirkwood, and P. L. Auer, J. Chem. Phys. **19**, 281 (1951).

entirely unrestricted). Owing to the thermal motion of the molecules, all possible configurations of the molecules are attained during a long interval of time. The configurational probability ϕ is equal to ϕ_0 , a constant in the internal coordinate space:

$$\phi = \phi_0 \equiv [\int dq]^{-1}. \quad (15)$$

Furthermore, ψ is identically zero.

If the body is not in equilibrium, ϕ is not equal to ϕ_0 . The thermal motion of the molecules tends to shift ϕ gradually back toward the equilibrium distribution, and ψ is not zero. The effective force (averaged over Δt) that is equivalent to this tendency to return to the equilibrium state is $-k_0 T \nabla \phi / \phi$, where k_0 is Boltzmann's constant. During this motion, ϕ must satisfy the equation of continuity:

$$\nabla \cdot (\phi \psi) = - \frac{\partial \phi}{\partial t}. \quad (16)$$

When there are no electric torques acting on the molecules, the sum of the thermodynamic force and the viscous force is equal to zero (assuming negligible inertia for the molecules):

$$\underline{F}_\phi - k_0 T \nabla \phi / \phi = 0. \quad (17)$$

Introduction of the diffusion tensor $\underline{D}$, defined as

$$\underline{D} \equiv k_0 T \underline{\rho}^{-1}, \quad (18)$$

and use of Equations (12), (16), and (17) lead finally to the diffusion equation:

$$\underline{\nabla} \cdot \underline{D} \cdot [\nabla \phi + \phi \nabla V_\phi / k_0 T] = \frac{\partial \phi}{\partial t}. \quad (19)$$

This equation can be solved for ϕ if the potential V_ϕ and the diffusion tensor $\underline{D}$ are known^{*}.

The diffusion equation may be written in the form of Equation (19) only when V_ϕ exists, that is, when the viscous forces are "conservative". The existence of a potential follows immediately from the fact that the curl of the velocity is zero (Equation 1). If the external stresses applied to the elastomer were shear forces, then the curl of the velocity would not be zero and a scalar potential would not exist. The solution of the diffusion equation for shear forces will not be studied in this thesis[#].

If an electric field instead of a mechanical stress is applied to the polymer, the only change in the diffusion equation is the replacement of V_ϕ by V_e , the electric potential of a molecule in the field. The same diffusion tensor is applicable in both cases. The diffusion equation is then identical with that used by Kirkwood and Fuoss to compute the dielectric response of a polar polymer [7]. In general, for the application of either an electric field, a mechanical extension, or both simultaneously, the equation of motion for ϕ may be written as

$$\nabla \cdot \underline{D} \cdot [\nabla \phi + \phi \nabla V / k_o T] = \frac{\partial \phi}{\partial t}, \quad (20)$$

^{*}This section is not meant to be a demonstration of the applicability of Smoluchowski's diffusion equation to elastomers at temperatures above the glass transformation. It is intended, rather, to show that the applicability of the diffusion equation is a reasonable assumption, and that the potential for noncross-linked molecules is then given by Equation (14). For a discussion of Smoluchowski's equation, see S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943).

[#]For a discussion of shear forces in solutions, see [9]. A somewhat different method of approach is given by P. Debye and A. M. Bueche, J. Chem. Phys. **16**, 573 (1948).

where the total potential is

$$V = V_e + V_f. \quad (21)$$

This potential applies only to noncross-linked polymers and does not include the forces on a molecule due to permanent cross-links. No study of such forces will be made here.

D. The Relationship between the Stress and the Strain

Returning to the problem of mechanical extension of a noncross-linked elastomer, we can derive a general expression for the mechanical energy required for extension. The rate at which energy is withdrawn from the surrounding atoms by each molecule is the sum of the scalar products of $\underline{F}_i$ and $\underline{v}^*$:^{*}

$$\left(\frac{\partial \mathcal{E}}{\partial t}\right)_{\text{molecule}} = \sum_i \underline{F}_i \cdot \underline{v}^*. \quad (22)$$

Replacing $\underline{v}$ by $(\underline{v} - \underline{v}_i) + \underline{v}_i$ and using Equation (8), we have

$$\left(\frac{\partial \mathcal{E}}{\partial t}\right)_{\text{molecule}} = \sum_i \underline{F}_i \cdot \left[\frac{1}{\epsilon_i} \underline{F}_i + \underline{v}_i \right]^*. \quad (23)$$

The corresponding equation in the internal coordinate space is

$$\left(\frac{\partial \mathcal{E}}{\partial t}\right)_{\text{molecule}} = \underline{F}_f \cdot [\underline{\rho}^{-1} \cdot \underline{F}_f + \underline{v}]^*. \quad (24)$$

From Equations (12), (17), and (18), we obtain

$$\left(\frac{\partial \mathcal{E}}{\partial t}\right)_{\text{molecule}} = - \frac{\nabla_f \cdot \underline{D} \cdot \nabla V_f^*}{f}. \quad (25)$$

^{*} $\underline{v}^*$, the complex conjugate of $\underline{v}$, is introduced to ensure that the energy is real.

If the total number of molecules per unit volume is n_0 , the number of molecules with configurations between $\Theta, \phi, \chi_2, \dots, \chi_{2n-1}$ and $\Theta + d\Theta, \phi + d\phi, \chi_2 + d\chi_2, \dots, \chi_{2n-1} + d\chi_{2n-1}$ is $n_0 f dq$, where dq is $\sin\Theta d\Theta d\phi d\chi_2 \dots d\chi_{2n-1}$. The total rate at which energy is introduced into the body is the rate at which energy is supplied to each molecule, multiplied by the number of molecules having the same configuration, and integrated over the internal coordinate space:

$$\frac{\partial \mathcal{E}}{\partial t} = -n_0 \int \nabla_f \cdot \underline{D} \cdot \nabla V_f^* dq. \quad (26)$$

Applying the divergence theorem and noting that the coordinate space has no boundaries (it is everywhere re-entrant as the angles $\Theta, \phi, \chi_2, \dots, \chi_{2n-1}$ change by π or 2π), we obtain

$$\frac{\partial \mathcal{E}}{\partial t} = n_0 \int V_f^* \nabla \cdot \underline{D} \cdot \nabla_f dq. \quad (27)$$

Thus the total rate at which energy is supplied to the elastomer may be calculated from the potential and the configurational probability. It is not necessary to determine explicitly any of the forces or velocities.

In order to interpret the rate of energy transfer in physical terms, Equation (26) may be considered in a slightly different form:

$$\frac{\partial \mathcal{E}}{\partial t} = -n_0 k_0 T \int \left(\frac{\nabla f}{f} \right) \cdot \underline{D} \cdot \left(\frac{f \nabla V_f^*}{k_0 T} \right) dq, \quad (28)$$

or

$$\frac{\partial \mathcal{E}}{\partial t} = n_0 k_0 T \int \ln f \nabla \cdot \underline{D} \cdot \left(\frac{f \nabla V_f^*}{k_0 T} \right) dq. \quad (29)$$

By substituting for $\nabla \cdot \underline{D} \cdot (\underline{f} \nabla V_f^* / k_o T)$ from the diffusion equation and applying the divergence theorem, it is possible to obtain:

$$\frac{\partial \mathcal{E}}{\partial t} = n_o k_o T \frac{\partial}{\partial t} \int \underline{f}^* \ln \underline{f} d\underline{q} + n_o k_o T \int \frac{\nabla \underline{f} \cdot \underline{D} \cdot \nabla \underline{f}^*}{\underline{f}} d\underline{q}. \quad (30)$$

If the entropy per unit volume were defined as

$$S = n_o k_o \int \underline{f}^* \ln \underline{f} d\underline{q}, \quad (31)$$

the first term in Equation (30) would be the time derivative of TS . It represents the rate at which energy is stored in the elastomer, and is dependent only upon the configurations of the molecules. Over a complete cycle of sinusoidal motion, this term does not contribute to the total energy loss. The second term in Equation (30) is a positive definite quantity that increases the energy supplied to the elastomer monotonically with the time. It represents the viscous loss due to the relative motions of the molecules, and is the rate at which energy is dissipated as heat.

It is now possible to find an expression for the stress $s(t)$. The rate at which energy is supplied to the body is equal to

$$\frac{\partial \mathcal{E}}{\partial t} = s(t) \frac{d\varepsilon}{dt}. \quad (32)$$

Equating this energy to the energy given in Equation (27), we obtain finally

$$s(t) = \frac{n_o}{\varepsilon(t)} \int \underline{f}^* \nabla \cdot \underline{D} \cdot \nabla \underline{f} d\underline{q}. \quad (33)$$

This equation completes a general description of the phenomena occurring during extension of a noncross-linked polymer. If the extension $\varepsilon(t)$ is given, the velocity $\dot{\varepsilon}$ describing the relative motions of

the molecules may be calculated from Equations (4) and (5). Equation (14) gives the potential $V_{\mathbf{f}}$ in terms of $d\epsilon/dt$. If the resistance tensor and its inverse are known, the diffusion equation may then be solved to find the internal configurations of the molecules. Substitution of $V_{\mathbf{f}}$ and $\mathbf{f}$ into Equation (33) gives the stress. In other words, it is possible to find the external stress that must be impressed on the cylindrical polymer body in order to produce a given extension.

The above set of equations is equivalent to a distribution of relaxation times defining the general relationship between $s(t)$ and $\epsilon(t)$. In Section IV, a method will be given for calculating the distribution of relaxation times once the resistance tensor is known.

III. QUALITATIVE DESCRIPTION OF THE MOLECULAR MOTION DURING EXTENSION

Before deriving a general solution for $s(t)$, it might be pertinent to discuss qualitatively the molecular motion resulting from various types of extension. If the material is initially in equilibrium, the molecules are randomly oriented and have equal probability of assuming all possible configurations. The molecules move from one configuration to another by random thermal motion, and there is no net gain or loss in the number of molecules having each configuration. This state corresponds to $\phi = \phi_0$ and $\psi = 0$.

Let us suppose that the material is now extended at a constant rate. The molecules move past one another in a continuous stream. Relative to the center of mass of any given molecule, the flow may be represented by the lines in Figure 1. The molecules move in from the sides and out toward the top and bottom of the figure. This motion tends to pull the randomly oriented molecules into alignment with the direction of extension. Each element along a molecule is subjected to a viscous force proportional to its velocity relative to the surrounding material. At first, when the extension is small, the elements are free to move nearly at the same velocity as the surrounding atoms, and the forces on the molecule are small. As the flow continues, the constant bond lengths and bond angles prevent the elements from following the flow lines, and the forces on the molecule increase. After very long times, a steady state of viscous flow is reached, in which the molecules on the average are not changing their configurations although they are still moving relative to each other. The external stress, an

average of the molecular forces through a cross-section of the material, has then risen to a constant maximum value. The probability of each configuration is again independent of the time, but is now given by

$$\nabla \zeta + \zeta \nabla V_{\zeta} / k_b T = 0, \quad (34)$$

or
$$\zeta = A e^{-V_{\zeta} / k_b T}, \quad (35)$$

where A is a normalizing constant. In other words, the configurations of the molecules are described by a Boltzmann distribution, and are in thermodynamic equilibrium even though the macroscopic dimensions of the elastomer are changing with time.

Let us assume that the extension is now suddenly stopped, and that the length of the cylindrical body is fixed. The flow of the molecules past one another is zero. Each molecular chain is free to diffuse back to the state $\zeta = \zeta_0$, assuming, of course, that no crystallization has occurred. The contracting molecules tend to drag the surrounding atoms back with them along the flow lines, and an external force is necessary to keep the material at constant extension. After a very long time, ζ again returns to ζ_0 , and all possible configurations are equally probable. The viscous forces are then reduced to zero. So far as the individual molecules are concerned, this state is precisely the same as the initial state even though the macroscopic dimensions of the material have changed permanently.

Let us consider finally what happens during an experiment in stress relaxation in which the elastomer is suddenly extended to a constant length. If the extension is rapid enough relative to the rate

of diffusion, the bonds are distorted and new degrees of freedom are introduced into the molecular configurations. In this state, f cannot be described solely in terms of $\Theta, \phi, \chi_2, \dots, \chi_{2n-1}$. After the extension is fixed, the bonds return quickly to their equilibrium length, and the stress simultaneously decreases from a large value to a more moderate one. At this moderate stress, the molecular configurations can again be expressed in the internal coordinate space of $\Theta, \phi, \chi_2, \dots, \chi_{2n-1}$, and the intermolecular forces are entirely viscous in nature. At still later times, the molecules slowly diffuse back to the equilibrium state. The force decays to zero during this process in the same way as it decays during the relaxation described first (constant length after slow elongation), and may be calculated from the solution of the diffusion equation.

It is apparent from this discussion that the diffusion theory of Section II correctly describes the stress relaxation only at fairly long times after extension. Unless changes in the bond lengths and bond angles are introduced, the theory cannot be used to describe the initial, rapid decay of the stress [10].

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10. A. V. Tobolsky, J. Am. Chem. Soc. **74**, 3786 (1952) points out that there are two distinct phenomena occurring during the stress relaxation.

IV. GENERAL SOLUTION OF THE DIFFUSION EQUATION

In order to find a general solution for $s(t)$ in terms of $\epsilon(t)$, let us assume that $\epsilon(t)$ is given by (the real part of)

$$\epsilon = \epsilon_0 e^{i\omega t}. \quad (36)$$

The (complex) amplitude ϵ_0 is independent of the time. From Equation (14), the potential is then^{*}

$$V = \frac{i\omega\epsilon_0}{4} \sum_i \zeta_i (\rho_i^2 - 2z_i^2) e^{i\omega t}. \quad (37)$$

The resistance constants ζ_i will all be equal to a constant ζ_0 in a solution so dilute that there are no interactions between the molecules. Whether ζ_i is equal to ζ_0 or not, V may be written as

$$V = V_0 e^{i\omega t}, \quad (38)$$

where
$$V_0 = \frac{i\omega\epsilon_0\zeta_0}{4} \sum_i \frac{\zeta_i}{\zeta_0} (\rho_i^2 - 2z_i^2). \quad (39)$$

For a potential of the above form, f may be expanded in a Fourier series in the time:

$$f = \sum_{n=0}^{\infty} f_n e^{in\omega t}, \quad (40)$$

where f_n is independent of the time but is a function of $\theta, \phi, \chi_2, \dots, \chi_{2n-1}$. If ϵ_0 is small, the potential of any possible configuration will be small compared with k_0T . From Equation (19), it follows that f_n is much smaller than f_{n-1} , and the higher terms

^{*}The subscript on the potential will be omitted hereafter.

in the Fourier series for f may be neglected:

$$f \cong f_0 + f_1 e^{i\omega t}. \quad (41)$$

Substitution of V and f into Equation (19) gives

$$\nabla \cdot \underline{D} \cdot \nabla f_0 = 0 \quad (42)$$

and

$$\nabla \cdot \underline{D} \cdot [\nabla f_1 + f_0 \nabla V_0 / k_0 T] = i\omega f_1. \quad (43)$$

If V were identically zero, f would reduce to f_0 . Consequently, f_0 must represent the state of equilibrium and be independent of $\Theta, \phi, \chi_2, \chi_3, \dots, \chi_{2n-1}$. When normalized,

$$f_0 = \left[\int dq \right]^{-1} = 1/2(2\pi)^{2n-1}, \quad (44)$$

and is identical with the f_0 introduced previously.

Let us now define the orthogonal eigenfunctions ψ_λ of the diffusion operator $\nabla \cdot \underline{D} \cdot \nabla$:

$$\underline{\nabla \cdot \underline{D} \cdot \nabla \psi_\lambda + \lambda \psi_\lambda = 0.} \quad (45)$$

The ψ_λ are a complete set of all the functions of $\Theta, \phi, \chi_2, \dots, \chi_{2n-1}$ satisfying Equation (45). Each eigenfunction ψ_λ has a corresponding eigenvalue λ . The eigenfunctions are to be normalized as well as orthogonal:

$$\int \psi_\lambda \psi_\mu^* dq = \delta_\lambda^\mu, \quad (46)$$

where ψ_μ^* is the complex conjugate of ψ_μ and δ_λ^μ is Kronecker's delta.

V_0 may be expanded in terms of the eigenfunctions:

$$V_0 = \frac{i\omega\epsilon_0\mathcal{E}_0}{4\sqrt{f_0}} \sum_{\lambda} d_{\lambda} \psi_{\lambda}. \quad (47)$$

From Equations (39) and (46), the expansion coefficients d_{λ} , which are independent of $\Theta, \phi, \chi_2, \dots, \chi_{2n-1}$ as well as the time, are given by

$$d_{\lambda} = \sqrt{f_0} \int \sum_i \frac{\xi_i}{\xi_0} (\rho_i^2 - 2z_i^2) \psi_{\lambda}^* dq. \quad (48)$$

The time dependent part of the configurational probability also may be expanded in terms of the ψ_{λ} :

$$f_t = \sum_{\lambda} b_{\lambda} \psi_{\lambda}. \quad (49)$$

Substituting the expansions of V and f_t into Equation (43), using Equation (45), and integrating over the internal coordinate space after multiplication by ψ_{λ}^* , we obtain

$$b_{\lambda} = -\frac{i\omega\epsilon_0\mathcal{E}_0\sqrt{f_0}}{4k_0T(1+i\omega/\lambda)} d_{\lambda}. \quad (50)$$

Finally, substituting b_{λ} into the expression for ξ , we have

$$f = f_0 - \frac{i\omega\epsilon_0\mathcal{E}_0\sqrt{f_0}}{4k_0T} \sum_{\lambda} \frac{d_{\lambda} \psi_{\lambda}}{(1+i\omega/\lambda)} e^{i\omega t}. \quad (51)$$

By Equations (45) and (51), $\nabla \cdot \underline{D} \cdot \nabla f$ is

$$\nabla \cdot \underline{D} \cdot \nabla f = \frac{i\omega\epsilon_0\mathcal{E}_0\sqrt{f_0}}{4k_0T} \sum_{\lambda} \frac{\lambda d_{\lambda} \psi_{\lambda}}{(1+i\omega/\lambda)} e^{i\omega t}. \quad (52)$$

The complex conjugate of the potential, by Equation (47), is

$$V^* = \frac{i\omega\epsilon_0\epsilon_0}{4\sqrt{f_0}} \sum_{\lambda} d_{\lambda}^* \psi_{\lambda}^* e^{i\omega t} \quad (53)$$

Introducing these last two expressions into Equation (33) together with $d\epsilon/dt$ from Equation (36) and using the orthonormality of the ψ_{λ} , we have

$$s(t) = \frac{in_0\omega\epsilon_0\epsilon_0}{16h_0T} \sum_{\lambda} \frac{\lambda d_{\lambda} d_{\lambda}^*}{(1+i\omega/\lambda)} e^{i\omega t} \quad (54)$$

This equation gives the amplitude and phase of the stress that must be applied to a cylinder of the elastomer in order to produce a sinusoidal extension of amplitude ϵ_0 .^{*}

To the approximation that the stress is a linear function of the strain, a convenient way to express the general experimental relationship between the stress and the extension is in terms of a distribution of relaxation times $E'(\gamma)$. $E'(\gamma)$ is defined by

$$s(t) = \int_{t'=-\infty}^t \int_{\gamma=0}^{\infty} e^{-(t-t')/\gamma} E'(\gamma) \frac{d\epsilon(t')}{dt'} dt' d\gamma. \quad (55)$$

^{*}When $\epsilon(t)$ is given by the real part of $\epsilon_0 e^{i\omega t}$, the succeeding equations for V , f , and $s(t)$ should also be prefaced on their right sides by the words "the real part of." Equation (33) for the stress should be written as the real part of V^* , multiplied by the real part of $\nabla \cdot \mathbf{D} \cdot \nabla f$, and divided by the real part of $d\epsilon/dt$. However, V is always in phase with $d\epsilon/dt$, and "the real part of" may be omitted in all the equations. It should also be noted that V^* is determined by changing the factor in V dependent upon the configuration of the molecule and does not involve a change in the complex dependence upon t .

The sinusoidal solution of the diffusion equation given by Equation (54) is sufficient to calculate the distribution of relaxation times. Let us define $\Omega(\lambda)$ as the sum of all the terms d_λ, d_λ^* having λ' less than λ :

$$\Omega(\lambda) \equiv \sum_{\lambda' \leq \lambda} d_{\lambda'} d_{\lambda'}^* \quad (56)$$

In practice it is nearly impossible to perform this summation exactly, and $\Omega(\lambda)$ must be approximated by a continuous function of λ . To this approximation, its derivative exists:

$$H(\lambda) \equiv \frac{d\Omega(\lambda)}{d\lambda} \quad (57)$$

By introducing $H(\lambda)$ into Equation (54), we may express $s(t)$ as an integral instead of a summation:

$$s(t) = \frac{i n_0 \omega \epsilon_0 \zeta_0^2}{16 k_0 T} \int_{\lambda=0}^{\infty} \frac{\lambda H(\lambda) d\lambda}{(1 + i\omega/\lambda)} e^{i\omega t} \quad (58)$$

Substituting a new variable

$$\tau \equiv \frac{1}{\lambda} \quad (59)$$

into this equation, we have

$$s(t) = \frac{i n_0 \omega \epsilon_0 \zeta_0^2}{16 k_0 T} \int_{\tau=0}^{\infty} \frac{H(\frac{1}{\tau}) d\tau}{\tau^3 (1 + i\omega\tau)} e^{i\omega t} \quad (60)$$

For sinusoidal motion, Equation (55) becomes

$$s(t) = i\omega \epsilon_0 \int_{\tau=0}^{\infty} \frac{\tau E'(\tau) d\tau}{(1 + i\omega\tau)} e^{i\omega t} \quad (61)$$

If Equations (60) and (61) are to give the same amplitude and phase for the stress, $E'(\tau)$ must be identical with

$$E'(\tau) = \frac{n_0 \zeta_0^2 H(\frac{1}{\tau})}{16 k_B T \tau^4} . \quad (62)$$

This equation completes the derivation of the general theoretical relationship between the stress and the strain. The method for finding $E'(\tau)$ from the diffusion tensor $\underline{D}$ may be summarized as follows: (1) the eigenfunctions ψ_λ of $\nabla \cdot \underline{D} \cdot \nabla$ are calculated from Equation (45); (2) from the ψ_λ , the expansion coefficients d_λ of the potential are obtained from Equation (48); (3) the function $\tilde{H}(\lambda)$ is calculated from the d_λ by Equations (56) and (57); and (4) $H(\lambda)$ is substituted into Equation (62) to find $E'(\tau)$. The solution for $E'(\tau)$ may then be substituted into Equation (55) to find the stress corresponding to any form of $\epsilon(t)$, whether sinusoidal or not.

V. SPECIFIC SOLUTION FOR THE STRESS RELAXATION

In this section, the distribution of relaxation times is computed from the diffusion tensor obtained originally by Kirkwood and Fuoss. The stress relaxation at constant extension is then calculated from $E'(\tau)$ and compared with published experimental results for polyisobutylene.

The first step in finding $E'(\tau)$ from the general derivation in Section IV is to evaluate $\mathcal{D}$, the diffusion tensor. $\mathcal{D}$ is defined as $k_B T \underline{\rho}^{-1}$, where $\underline{\rho}$ expresses the relationship between the viscous torques and the rates of change of the angular coordinates

$\theta, \phi, \chi_2, \dots, \chi_{2n-1}$:

$$\tau_i = \sum_j \rho_{ij} \dot{\psi}_j. \quad (63)$$

The resistance tensor $\underline{\rho}$ has been evaluated by Kirkwood and Fuoss^{*}; their derivation is reproduced in Appendix I. The tensor $\underline{\rho}$ is dependent upon the resistance constants ξ_i of the individual elements of the chain. It is assumed in Appendix I that all of the ξ_i are equal to ξ_0 , where ξ_0 (introduced and defined approximately on page 26) is the resistance constant of an element moving in a liquid composed of the unpolymerized elements. In other words, it is assumed that the viscous force on a polymer chain is the same whether or not the surrounding fluid is polymerized.

The resistance tensor $\underline{\rho}$ resulting from this assumption is a complicated, nondiagonal function of the angles defining the

^{*}See Appendix I of [7].

configuration of the chain. It is so complicated that exact evaluation of its inverse is impracticable. However, we can approximate ρ by noting that f_1 is much smaller than f_0 in Equation (41). In other words, the distribution of molecular configurations is very close to the equilibrium distribution f_0 . Thus, there should be only a small change in $E(r)$ if ρ is replaced by $\bar{\rho}$, its average over all possible configurations of the molecule. To this approximation, the diffusion tensor becomes

$$\bar{D} \equiv k_B T (\bar{\rho})^{-1} \quad (64)$$

Evaluation of $\bar{D}$ is quite simple because $\bar{\rho}$ is diagonal in the internal coordinate space. From Equations (130) and (131) in Appendix I, the nonzero components of $\bar{D}$ are

$$\bar{D}_{\phi\phi} = \bar{D}_{\phi\phi} = D_0/2 \quad (65)$$

$$\text{and} \quad \bar{D}_{ii} = D_0 \left[1 - \left| \frac{i-n}{n} \right| \right]^{-2} \quad (66)$$

$$\text{where} \quad D_0 = 3k_B T / \zeta_0 a^2 n^2, \quad (67)$$

a is the bond length and n is half the number of elements per molecule. (For substituted polyethylenes, n is equal to the number of monomers per molecule.)

From Equations (133) and (134), the corresponding eigenfunctions ψ_λ of the diffusion operator are

$$\psi_\lambda = \left[\frac{(2\ell+1)(\ell-|m_\phi|)!}{4\pi(\ell+|m_\phi|)!} \right]^{1/2} (2\pi)^{-n+1} P_\ell^{m_\phi}(\cos\theta) e^{im_\phi\phi} \prod_{i=2}^{2n-1} e^{im_i X_i} \quad (68)$$

and the eigenvalues are

$$\lambda = D_0 \left\{ \frac{1}{2} \ell(\ell+1) + \sum_{i=2}^{2n-1} \left[1 - \left| \frac{i-n}{n} \right| \right]^2 m_i^2 \right\}. \quad (69)$$

The $P_\ell^{m_0}$ are the associated Legendre polynomials. The total set of eigenfunctions includes the ψ_λ for all positive ℓ , all m_0 whose absolute values are less than or equal to ℓ , and all positive and negative m_i . The above results are those obtained by Kirkwood and Fuoss [7].

The next problem is to find the expansion coefficients d_λ of the potential. From Equation (48), the d_λ are equal to

$$d_\lambda = \sqrt{\epsilon_0} \int \sum_i (\rho_i^2 - 2\pi_i^2) \psi_\lambda^* dq \quad (70)$$

when $\xi_i = \xi_0$. We might note that the potential is a quadratic function of the position of the elements. This case contrasts with that for an electric field, where V is linearly dependent upon the positions of the polar side groups. Because the potential is quadratic, evaluation of the d_λ is quite laborious. A summary of the computations for the d_λ is given in Appendix II.

After the d_λ have been determined, the next step is to find

$$\Omega(\lambda) \equiv \sum_{\lambda' \leq \lambda} d_{\lambda'} d_{\lambda'}^*. \quad (71)$$

$\Omega(\lambda)$ is the sum of the squares of all $d_{\lambda'}$ whose corresponding eigenvalues are less than λ . It is nearly impossible to evaluate this summation exactly, but it can be approximated in the following way. Let us consider all the d_λ having some particular absolute value. These d_λ have corresponding eigenvalues (given by Equation (69))

that are all nearly equal. It is not too much in error, then, to assume that the d_λ having the same absolute value also have the same eigenvalue. To this approximation, $\Omega(\lambda)$ is given by

$$\Omega(\lambda) = \sum_{\bar{\lambda} \leq \lambda} N(\bar{\lambda}) d_{\bar{\lambda}} d_{\bar{\lambda}}^* \quad (72)$$

where $N(\bar{\lambda})$ is the number of d_λ having some particular absolute value. The corresponding average eigenvalue is $\bar{\lambda}$. This approximation to $\Omega(\lambda)$ is similar to one used by Kirkwood and Fuoss in their treatment of the dielectric dispersion.

$\Omega(\lambda)$ is evaluated in Appendix III. From Equations (187) and (189), we have

$$\Omega(\lambda) \cong \frac{16}{9} n^4 \alpha^4 (c+3)^{-4} \left\{ \frac{(c+3)^4 - 3^4}{4} - c - 16 - 6 \ln(c+1) + \frac{12}{(c+1)} + \frac{4}{(c+1)^2} \right\}, \quad (73)$$

where
$$c \equiv 3\lambda / 2nD_0. \quad (74)$$

Once $\Omega(\lambda)$ is known, $H(\lambda)$ and $E'(\tau)$ can be found from Equations (57) and (62). The distribution of relaxation times is^{*}

$$E'(\tau) = \frac{8N_0(k_0T)^2 c^4}{9\zeta_0 \alpha^2 (c+3)^5} \left\{ 142 + 3c + 24 \ln(c+1) - \frac{6(c+11)}{(c+1)} - \frac{4(3c+13)}{(c+1)^2} - \frac{8(c+3)}{(c+1)^3} \right\}. \quad (75)$$

When expressed in terms of τ , the variable c is

$$c = \tau_0 / \tau, \quad (76)$$

where
$$\tau_0 = \zeta_0 \alpha^2 n / 2k_0 T. \quad (77)$$

N_0 is half the total number of elements in a unit volume of the polymer, and is independent of the molecular weight. (For substituted polyethylenes,

^{*}Equations (75), (78), and (79) are correct only if $\tau_0/n \ll \tau \ll \tau_0 n$. If $\tau < \tau_0/n$ or $\tau > \tau_0 n$, $E'(\tau)$ is zero. Because n is very large, these limits can be neglected in the calculations for $s(t)$.

N_0 is the number of monomers per unit volume.) The time τ_0 is a function of both the temperature and the molecular weight.

The distribution of relaxation times is plotted versus τ/τ_0 in Figure 2, with logarithmic scales for both variables. The limiting value of $E'(\tau)$ for small τ is

$$E'(\tau) \cong \frac{8N_0(k_b T)^2}{3\zeta_0 a^2} \quad \tau \ll \tau_0 \quad (78)$$

As τ increases from zero, $E'(\tau)$ rises slowly to a maximum at $\tau \cong 0.1\tau_0$, and then drops off rapidly. When τ is large

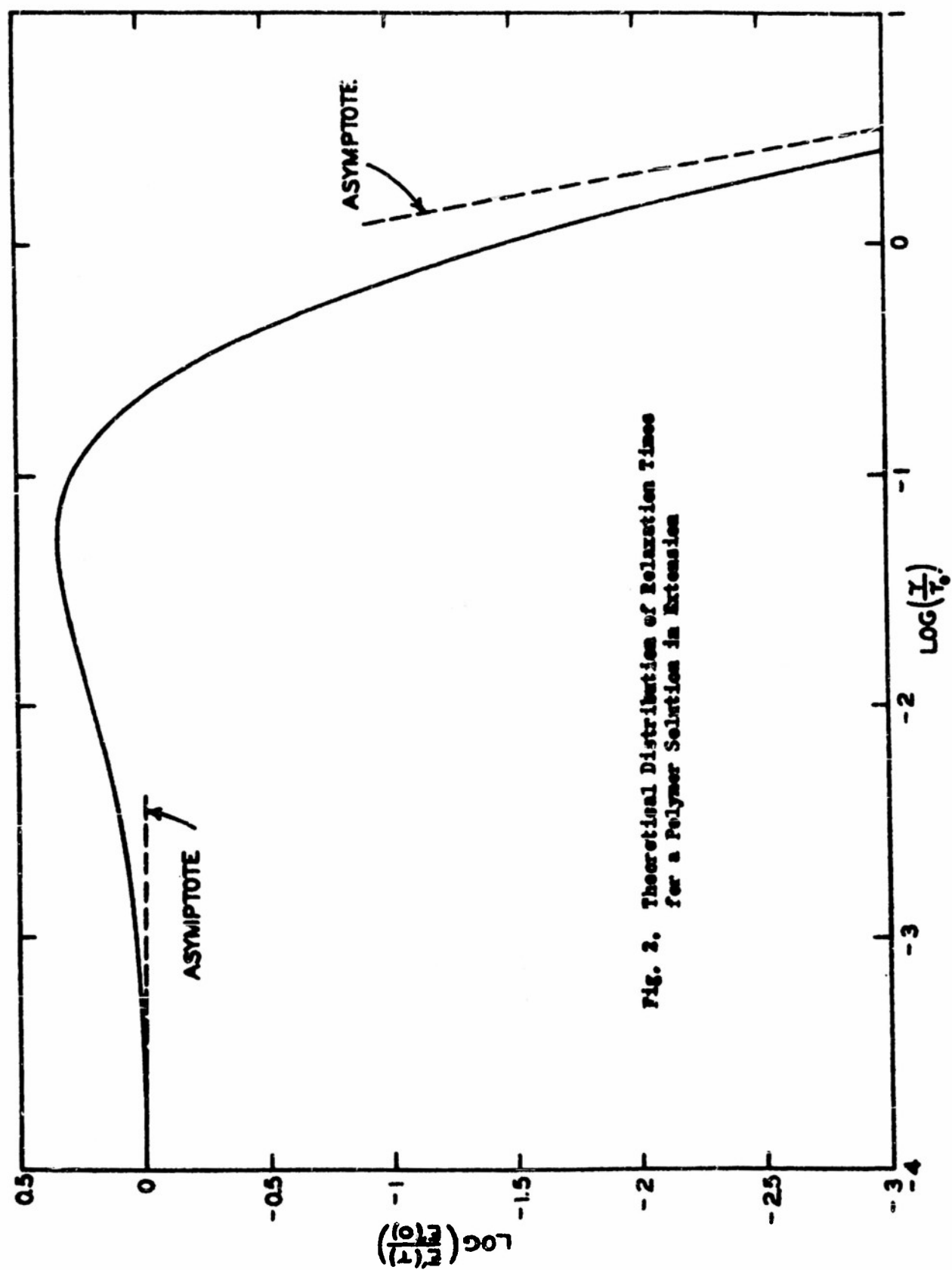
$$E'(\tau) \cong \frac{8N_0(k_b T)^2}{9\zeta_0 a^2} \left(\frac{\tau_0}{\tau}\right)^5 \quad \tau \gg \tau_0 \quad (79)$$

The next problem is to determine how closely the theoretical distribution describes the experimental properties of noncross-linked elastomers. We shall calculate the stress relaxation from $E'(\tau)$ and compare it with the relaxation of a typical elastomer. One of the most nearly complete experimental investigations [11] has been of polyisobutylene, and we shall compare the theoretical results with the data for this polymer.

From Equation (55), the stress relaxation $s(t)$ at constant extension ϵ is given by

$$s(t) \Big|_{\epsilon} = \epsilon \int_{\tau=0}^{\infty} e^{-t/\tau} E'(\tau) d\tau. \quad (80)$$

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11. R. S. Marvin, "Interim Report on the Cooperative Program on Dynamic Testing," National Bureau of Standards, 1951; and E. R. Fitzgerald, L. D. Grandine, Jr., and J. D. Ferry, J. Appl. Phys. **24**, 650 (1953).



The time t is measured from the instant of extension. To find $s(t)$ it is necessary to substitute $E(\tau)$ into this equation and integrate over τ for various values of t .

The calculations for $s(t)$ are described in Appendix IV, and $s(t)$ is plotted in Figure 3. In the figure, the stress is normalized to unit force at $t=0$ by dividing by

$$\frac{s(0)}{\epsilon} = \frac{7}{9} N_0 n k_0 T \epsilon. \quad (81)$$

No explicit equation for $s(t)$ can be given because the integration is performed graphically.

Also shown in Figure 3 is the composite experimental stress relaxation of an unfractionated polyisobutylene at 30°C [12]. The average molecular weight is 6,600,000. The curve has been normalized by dividing the original data by 10.4×10^6 dynes/cm²-unit extension. The time scale for the theoretical stress relaxation has been chosen so that the two curves coincide at a normalized stress of 0.50 ($\tau_0 = 10^{2.04}$ hours).

The experimental stress relaxation may be divided into two quite distinct regions. One region includes the slow relaxation of stresses less than 10^7 dynes/cm²-unit extension. This relaxation is due to the molecular diffusion treated in this thesis. The other region includes the stresses larger than 10^7 dynes/cm²-unit extension. These forces decay very rapidly at 30°C, and have almost entirely disappeared

12. The composite curve has been formed by superposition of the data plotted in Figure 2 of R. D. Andrews and A. V. Tobolsky, J. Polymer Sci. 7, 221 (1951).

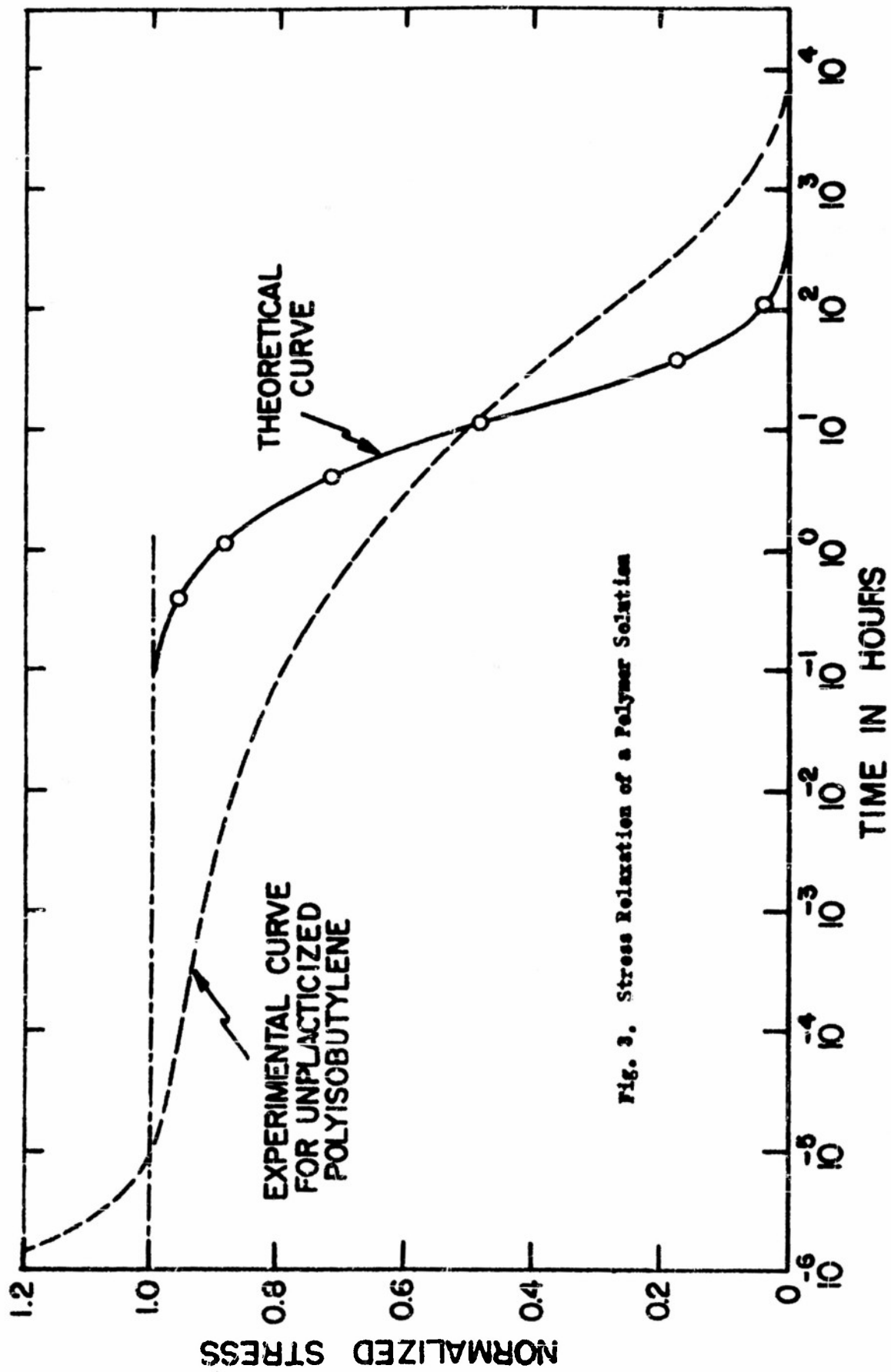


Fig. 3. Stress Relaxation of a Polymer Solution

10^{-5} hours after extension. For polyisobutylene, this relaxation is not experimentally observable unless the temperature is much lower than 30°C . No attempt has been made to include the more rapid relaxation in the theoretical discussion, and the calculated curve may be compared only with the relaxation at relatively large times. For this reason, the normalization factor has been chosen so that the stress due to diffusion is unity when t is equal to zero.

It is apparent from the figure that the stress decays much more slowly than is predicted theoretically. This result implies that the relaxation times given by Equation (75) are not distributed in τ as widely as would be necessary to describe the experimental data for polyisobutylene.

The theoretical and experimental stress relaxations also do not agree in their dependence upon the molecular weight. Experimentally, the time scale of the relaxation is proportional to $M^{3.3}$ [12,13]. The magnitude of the force is not dependent upon M . In other words, a plot of $s(t)$ versus $t/M^{3.3}$ is independent of the molecular weight. From Equations (77) and (81), it may be seen that the calculated results are quite different: both the force and the time scale are proportional to the first power of M . A plot of the calculated $s(t)/M$ versus t/M is independent of the molecular weight.

We are more successful in comparing the predicted and experimental dependence on temperature. The only parameter affecting $E'(\tau)$

13. T. G. Fox, Jr., and P. J. Flory, J. Am. Chem. Soc. 70, 2384 (1948).

that can depend upon T (other than the temperature itself) is the resistance constant ζ_0 . Whether or not the elements along the polymer chain are spheres, ζ_0 is proportional to η_0 , the viscosity of the liquid composed of unpolymerized elements^{*}. For nearly all unpolymerized liquids, the viscosity is exponentially dependent upon $1/T$, and η_0 presumably varies in the same way here:

$$\zeta_0 \propto \eta_0 \propto e^{A/RT}. \quad (82)$$

If this temperature dependence is substituted into Equation (77), we see that

$$\tau_0 \propto T^{-1} e^{A/RT}. \quad (83)$$

Also, from Equation (81) for $s(0)$, the calculated stress is directly proportional to the absolute temperature and independent of ζ_0 . The proportionality of $s(0)$ to T and of τ_0 to $e^{A/RT}$ correspond to the temperature dependence observed experimentally for polyisobutylene [11,12].

It is possible to find the dependence of the stress upon the temperature without calculating $s(t)$ explicitly. $\Omega(\lambda)$ consists of a partial sum of the expansion coefficients $d_\lambda d_\lambda^*$ of the potential. Change of the temperature will alter the relaxation time $1/\lambda$ of each expansion coefficient but will not change its magnitude. This effect implies that Ω is equal to some function of $\lambda \tau_0$ and not just λ alone:

$$\Omega = \Omega(\lambda \tau_0). \quad (84)$$

^{*}For a discussion of the relationship between the viscosity and the resistance constants, see [6,8].

From Equations (57), (62), (80), and (84), we obtain

$$s(t) \Big|_E \propto T \int_0^{\infty} e^{-(t/\tau_0)\beta'} G(\beta) d\beta, \quad (85)$$

where the variable β denotes τ/τ_0 , and

$$G(\beta) \equiv \beta^{-4} \frac{d\Omega(\beta)}{d\beta}. \quad (86)$$

From Equations (83) and (85), it follows that a plot of $s(t)/T$ versus $tT_0^{-A/\hat{R}T}$ is independent of the temperature. The stress at $t=0$ is therefore proportional to T , and the time scale of the relaxation depends exponentially upon $1/T$. This temperature dependence satisfies the usual reduction method [14] for relating the mechanical properties of elastomers at different temperatures, and agrees with the experimental results for polyisobutylene.

From the above discussion, it may be seen that the dependence of $s(t)$ upon the temperature is not related to the specific form of the diffusion tensor. On the other hand, the dependence of $s(t)$ upon the time and the molecular weight does vary with Q . It would therefore appear that the general solution for $\xi(\tau)$ in Section IV may be correct, but that the approximations in this section to find Q are in error.

An important source of error is the assumption that the resistance tensor of a molecule is the same whether or not the surrounding

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14. R. S. Marvin, E. R. Fitzgerald, and J. D. Ferry, J. Appl. Phys. **21**, 197 (1950); and J. D. Ferry, E. R. Fitzgerald, M. F. Johnson, and L. D. Grandine, Jr., J. Appl. Phys. **22**, 717 (1951); see also F. Schwarzl, and A. J. Staverman, J. Appl. Phys. **23**, 838 (1952).

fluid is polymerized. Furthermore, the approximation of $\bar{Q}$ to Q may be inaccurate enough to change $E'(\tau)$ appreciably. Both of these approximations tend to make $E'(\tau)$ too narrow a function of τ . From this point of view, the theoretical stress relaxation in Figure 3 may be considered as an upper limit upon the rate at which the relaxation can proceed.

It might be pointed out that the theoretical distribution of relaxation times should agree much better with the extension properties of a dilute solution of a polymer. In a solution, the fluid surrounding each polymer molecule is unpolymerized and ζ_i is equal to ζ_0 .

VI. CORRECTION OF THE MECHANICAL PROPERTIES FOR CHAIN ENTANGLEMENTS

From the previous section it may be concluded that the calculated stress relaxation does not agree with the experimental results for a typical elastomer, and that the primary reasons for this discrepancy are the approximations used to find the diffusion tensor. To obtain a more precise $E'(\gamma)$, it is necessary to evaluate the effects of polymerization of the surrounding molecules upon the resistance tensor ρ of a polymer chain.

Let us examine qualitatively the interactions of the chains by considering a rotation around some azimuth angle χ_j . If all the other angles along the same chain are fixed, one part of the molecule (on that side of the j -th bond containing the center of the chain) remains stationary. The other and smaller half rotates around the bond as a rigid, irregular rod. If the surrounding molecules are small (as in a dilute polymer solution), the forces on the chain can be calculated from the resistance constant ζ_0 of each element. Evaluation of these forces leads directly to the diffusion tensor used in the previous section.

In the unplasticized polymer, however, the molecules are entangled with each other. The part of the chain rotating around the j -th bond carries with it a large number of surrounding elements, and the resistance to the rotation is much larger than the corresponding force in the unpolymerized fluid. If the effective resistance constant ζ_j of each element includes the viscous forces on all the chains wound around that element, ζ_j is much larger than ζ_0 . Furthermore, if

$i \leq n$, the number of chains caught on the i -th element is larger than the number caught on the $(i-1)$ th element. This comes about because the chains are free to slip off the end of the rotating molecule. As a result, the effective ζ_i are larger near the center of the chain than they are at the ends.

We might summarize this discussion by suggesting that the diffusion tensor may be calculated in the same way as in Appendix I, but with ζ_i introduced as a function of i .

We shall not attempt to determine the effect of the chain entanglements quantitatively. Instead, we shall assume some ad hoc dependence of ζ_i upon i and calculate the corresponding stress relaxation. The purpose of this procedure is to find a simple set of resistance constants correctly describing the mechanical properties of elastomers. Once the proper ζ_i are determined, they should be applicable to the solution of the diffusion equation for all types of external forces, whether mechanical or not.

Let us assume that ζ_i is given by

$$\zeta_i = \begin{cases} \zeta_0 A i^p & i \leq n \\ \zeta_0 A (2n+1-i)^p, & i \geq n+1 \end{cases} \quad (87)$$

where A and p are constants independent of the temperature. These diffusion constants are symmetric around the center of the chain, increase rapidly toward its center, and are a multiple A of ζ_0 at the ends of the molecule. From Equation (14) it is apparent that the potential as well as the diffusion tensor is modified by this assumption.

The new $\bar{D}$, d_λ , and $\Omega(\lambda)$ are calculated in Appendix V.

If the function $K(c)$ is defined by

$$K(c) \equiv (c+3)^{-\left(\frac{2p+4}{p+1}\right)} \int_1^{1+c} (x+2)^{\left(\frac{p+3}{p+1}\right)} \left[1 - x^{-\left(\frac{2p+3}{p+1}\right)}\right] dx, \quad (88)$$

$\Omega(\lambda)$ may be expressed as

$$\Omega(\lambda) = \frac{16 n^{2p+4} a^4 A^2}{3(p+1)^3 (2p+3)} K(c), \quad (89)$$

where c is equal to τ'_0/τ and

$$\tau'_0 = \xi_0 A a^2 n^{p+1} / (p+2) k_0 T. \quad (90)$$

The corresponding distribution of relaxation times is*

$$E'(\tau) = \frac{N_0 (p+2)^3 (k_0 T)^2 c^4}{3(p+1)^3 (2p+3) \xi_0 A a^2 n^p} \frac{dK(c)}{dc}. \quad (91)$$

If τ is very small compared with τ'_0 ,

$$E'(\tau) \cong \frac{N_0 (p+2)^3 (k_0 T)^2}{3(p+1)^3 \xi_0 A a^2 n^p} \left(\frac{\tau}{\tau'_0}\right)^{-\left(\frac{p}{p+1}\right)} \quad \tau \ll \tau'_0 \quad (92)$$

If τ is much larger than τ'_0 ,

$$E'(\tau) \cong \frac{N_0 (p+2)^3 (k_0 T)^2}{9(p+1)^4 \xi_0 A a^2 n^p} \left(\frac{\tau}{\tau'_0}\right)^{-5} \quad \tau \gg \tau'_0 \quad (93)$$

*Equations (91), (92), and (93) are correct only if $\tau'_0/n^{p+1} \ll \tau \ll \tau'_0 n$. When $\tau < \tau'_0/n^{p+1}$ or $\tau > \tau'_0 n$, $E'(\tau)$ is zero. These limits can be neglected in the calculations for $s(t)$.

From Equation (80), the stress relaxation is

$$s(t)\Big|_{\epsilon} = \frac{(\rho+2)^2 N_0 n k_0 T \epsilon}{3(\rho+1)^3 (2\rho+3)} \int_{c=0}^{\infty} e^{-(\frac{t}{\tau_0'})^c} c^2 \frac{d h(c)}{dc} dc. \quad (94)$$

Two important results may be obtained directly from these equations. In the first place, the temperature dependence of the stress relaxation is the same as in the previous section. The stress at small times is proportional to the absolute temperature, and the time scale is dependent exponentially upon $1/T$. Secondly, τ_0' is dependent upon the molecular weight raised to the $\rho+1$ power, provided that A and p are independent of M . The form of this dependence corresponds quite well to the experimental relationship that the time scale of the relaxation is proportional to $M^{3.3}$.

The stress relaxation of polyisobutylene may be fitted quite accurately by setting p equal to five. The calculations for $E(\tau)$ and $s(t)$ when p is five are described in Appendix VI. From Equation (220),

$$E(\tau) \cong \frac{0.04072 N_0 (k_0 T)^2 c^4}{\xi_0 a^2 n^5 A (c+3)^{10/3}} \left\{ 7.287 + (c+1)^{1/6} \left[\frac{7}{3} \left(6 - \frac{320}{(c+1)} - \frac{0.36}{(c+1)^2} \right) - \left(\frac{c+3}{c+1} \right)^{7/3} \right] \right\}. \quad (95)$$

This distribution of relaxation times is plotted against the logarithm of τ/τ_0' in Figure 4. The corresponding stress relaxation is plotted in Figure 5, with the force at $t=0$ normalized to unity by dividing by

$$s(0)\Big|_{\epsilon} = 0.348 N_0 n k_0 T \epsilon. \quad (96)$$

Also shown in this figure is the experimental stress relaxation plotted in Figure 4 (polyisobutylene for $M = 6,600,000$ and $T = 30^\circ\text{C}$) [12].

The experimental curve is again normalized by dividing by

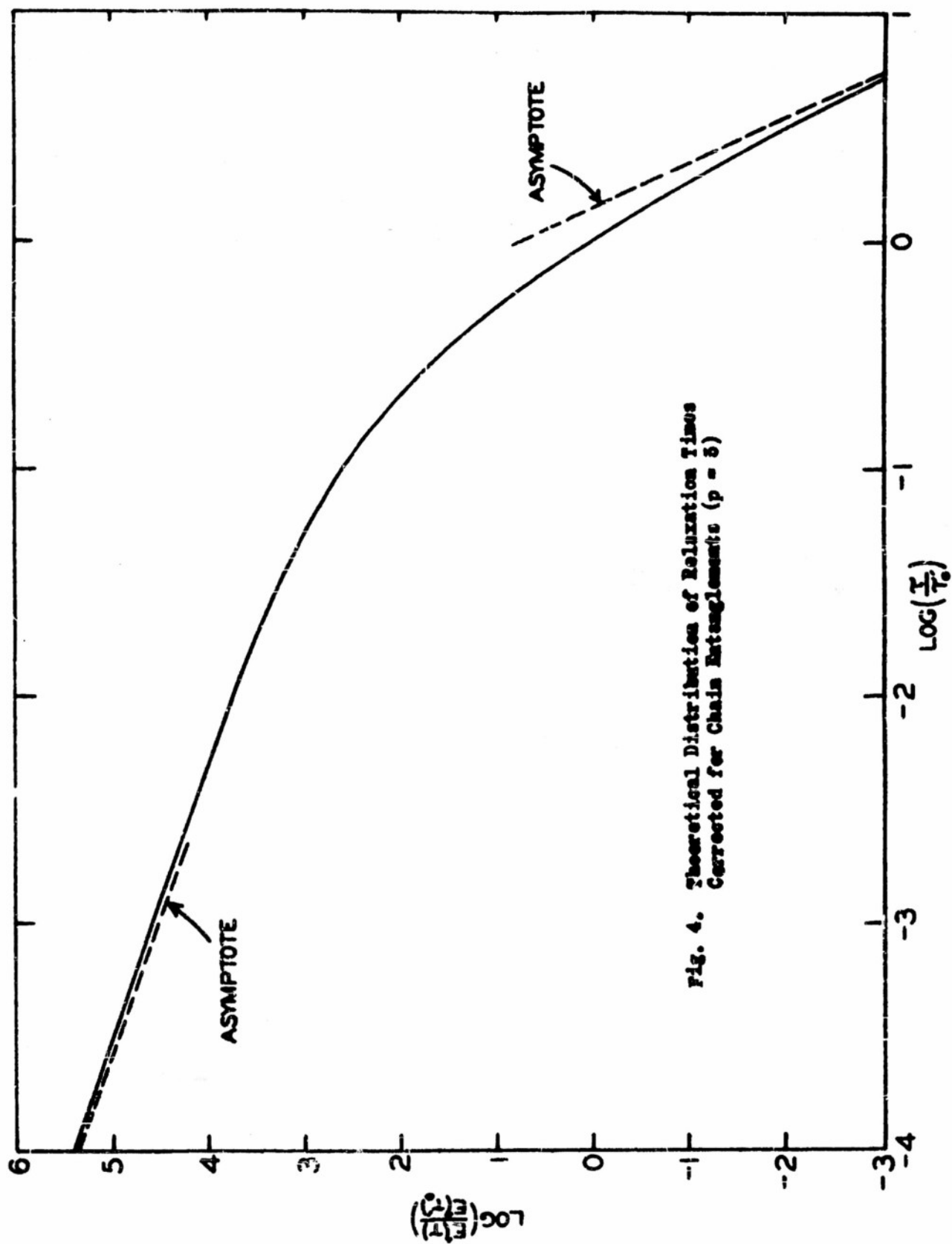


Fig. 4. Theoretical Distribution of Relaxation Times
Corrected for Chain Entanglements ($p = 5$)

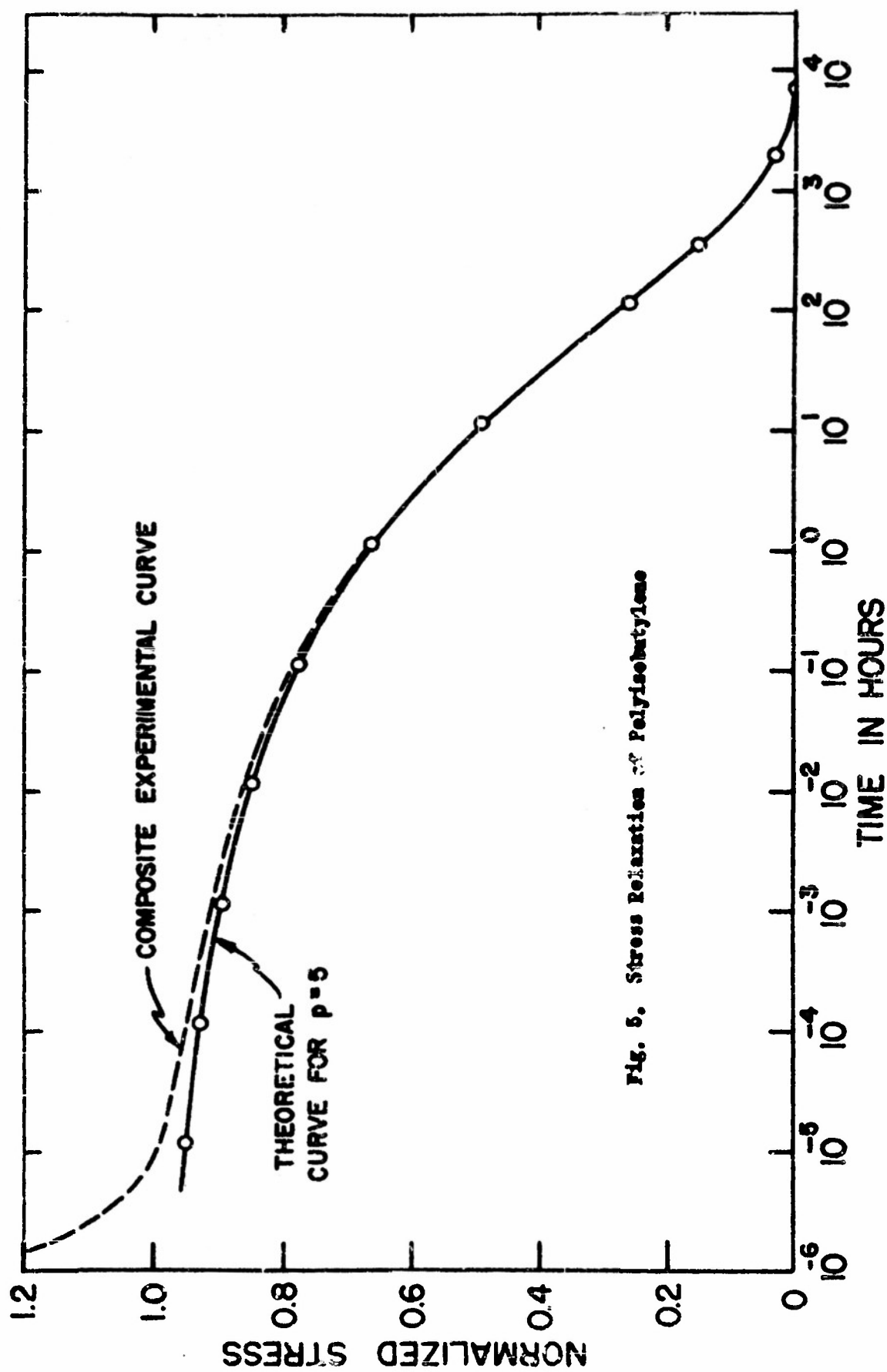


Fig. 5. Stress Relaxation of Polyisobutylene

10.4×10^6 dynes/cm²-unit extension; τ'_0 is chosen so that the curves coincide at a normalized stress of 0.50 ($\tau'_0 = 10^{4.07}$ hours).

The theoretical curve agrees with the composite experimental curve to within 0.05 over nine decades of time. Only at very small times after extension do the two curves disagree. At these times, the relaxation is not produced by diffusion of the azimuth angles of the molecules. It may be concluded that a set of diffusion constants given by the rule

$$\underline{e_i = \begin{cases} \xi_i A_i^5 & i \leq n \\ \xi_i A(2n+1-i)^5 & i \geq n+1 \end{cases}} \quad (97)$$

predicts a stress relaxation in excellent agreement with the properties of polyisobutylene. The temperature dependence is also correctly described by this law.

The molecular weight dependence predicted by these e_i does not quite agree with the experimental results. In the first place, the calculated τ'_0 is proportional to the sixth power of M , rather than the 3.3 power observed experimentally. This disagreement is not totally unexpected, however. We have selected a value of p which corrects the time dependence not only for the effect of the chain entanglements but also for the substitution of $\bar{D}$ for D . The latter approximation changes the time dependence of $s(t)$ without altering the dependence upon the molecular weight. Consequently, a p of five overcorrects for M^* . If A were independent of M , we might conclude that about

*The introduction of p also corrects for the approximation to $\Omega(\lambda)$ in Equation (72), and for the distribution of molecular weights in the unfractionated polymer. Both of these factors change the shape of $s(t)$ without altering the effect of M , and therefore tend to make the predicted dependence of τ'_0 upon M too large.

half of p corrects for the effects of chain entanglements, while the other half corrects for the approximation to $\bar{Q}$. A more accurate solution of the diffusion equation than is given here should lower the dependence of τ_0' upon M , and agree more closely with the experimental results.

The calculated stress relaxation depends in a second way upon the molecular weight. The magnitude of $s(0)$ from Equation (96) is proportional to $\bar{M}$, whereas experimentally it does not vary with M . One might suspect that $s(0)$ is independent of M for an unplasticized polymer because the chain entanglements act as temporary cross-links between the molecules. In other words, the rapid motion of one part of a chain may be entirely divorced from the rapid motion of another part of the same chain. The stress at small times would then be independent of the total length of the molecule. Only over relatively long periods of time would the motions of the various parts of a chain be related. During such motion, the sole effect of the entanglements would be to change the resistance constants of the elements. Since the stress relaxation is primarily a slow phenomenon, the treatment given here may be essentially correct with regard to the shape of the relaxation, even though it is not correct as a calculation for $s(0)$.

It might be pointed out again that the use of $E'(\tau)$ is not restricted to a calculation of the stress relaxation. Equation (55) gives $s(t)$ corresponding to almost any $\epsilon(t)$ whatsoever. For example, we may use $E'(\tau)$ to compute the stress required for a constant rate of extension. The only limitation upon Equation (55) is that $d\epsilon/dt$

must not be too large. In general, the published data for polyisobutylene are internally consistent, and the $E'(\gamma)$ which gives the proper stress relaxation also will predict the correct response to other types of motion.

VII. CORRECTION OF THE DIELECTRIC DISPERSION FOR CHAIN ENTANGLEMENTS

The diffusion equation for ϕ (Equation 20) can give the response of an elastomer to forces other than those accompanying mechanical extension. The only restriction upon the equation is that the molecular motion must consist of diffusion in the angles $\theta, \phi, \chi_2, \chi_3, \dots, \chi_{2n-1}$. The diffusion equation is applicable to the dielectric dispersion of polar polymers, for example, if the potential is changed to

$$V = \mu \cdot E_e e^{i\omega t} \quad (98)$$

E_e is the amplitude of the local electric field of frequency $\omega/2\pi$ and μ is the total dipole moment of the polymer molecule.

The diffusion equation for this potential has been solved by Kirkwood and Fuoss for a polymer in which the dipoles are attached rigidly to the atoms making up the molecular chain. Polyvinyl chloride is an example of such a polymer. Their calculation is intended to apply to a solution dilute enough so that all chain-to-chain entanglements may be neglected. Consequently, they use the diffusion tensor derived upon the assumption that all the resistance constants are equal. The substitution of $\bar{D}$ for D and the approximation to $\Omega(\lambda)$ given by Equation (72) are also employed in their calculation.

The results of Kirkwood and Fuoss may be expressed as a distribution of electrical relaxation times $G(\tau)$. For a perfectly fractionated polymer, this distribution is given by

$$G(\tau) = \frac{\tau_0}{(\tau + \tau_0)^2} \quad (99)$$

The reduced dielectric dispersion $H(\omega)$ at frequency $\omega/2\pi$ is the imaginary part of

$$-Q(\omega) = -\int_{\tau=0}^{\infty} \frac{G(\tau) d\tau}{(1+i\omega\tau)}. \quad (100)$$

By substituting $G(\tau)$ into this integral, they obtain

$$H(\omega) = \frac{x}{(1+x^2)^2} \left[(x^2-1)\ln x - x^2 + \pi x - 1 \right]. \quad (101)$$

The variable x is equal to $\omega\tau_0$, where τ_0 is the relaxation time defined by Equation (77).

$H(\omega)$, divided by its maximum value at $x = 1$, is plotted against the frequency in Figure 6. Also plotted in this figure is the audio frequency dispersion of unplasticized polyvinyl chloride [15]. The data were taken at about 100°C . The frequency scale of the theoretical curve has been chosen so that $H_{\max}$ coincides with the maximum of the experimental curve ($\tau_0 = 10^{-2.99}$ seconds).

The experimental dispersion exhibits a very broad maximum not fitted by the theoretical curve. We may conclude here, precisely as for the stress relaxation, that the calculated distribution of relaxation times is not broad enough to correspond to the experimental data.

It is not surprising that the results of Kirkwood and Fuoss disagree with the experimental dispersion of an unplasticized polymer, because their theory applies only to a dilute solution of a polymer.

15. The composite experimental curve has been formed by superposition of the data plotted in Figure 4 of R. M. Fuoss, J. Am. Chem. Soc. **63**, 369 (1941).

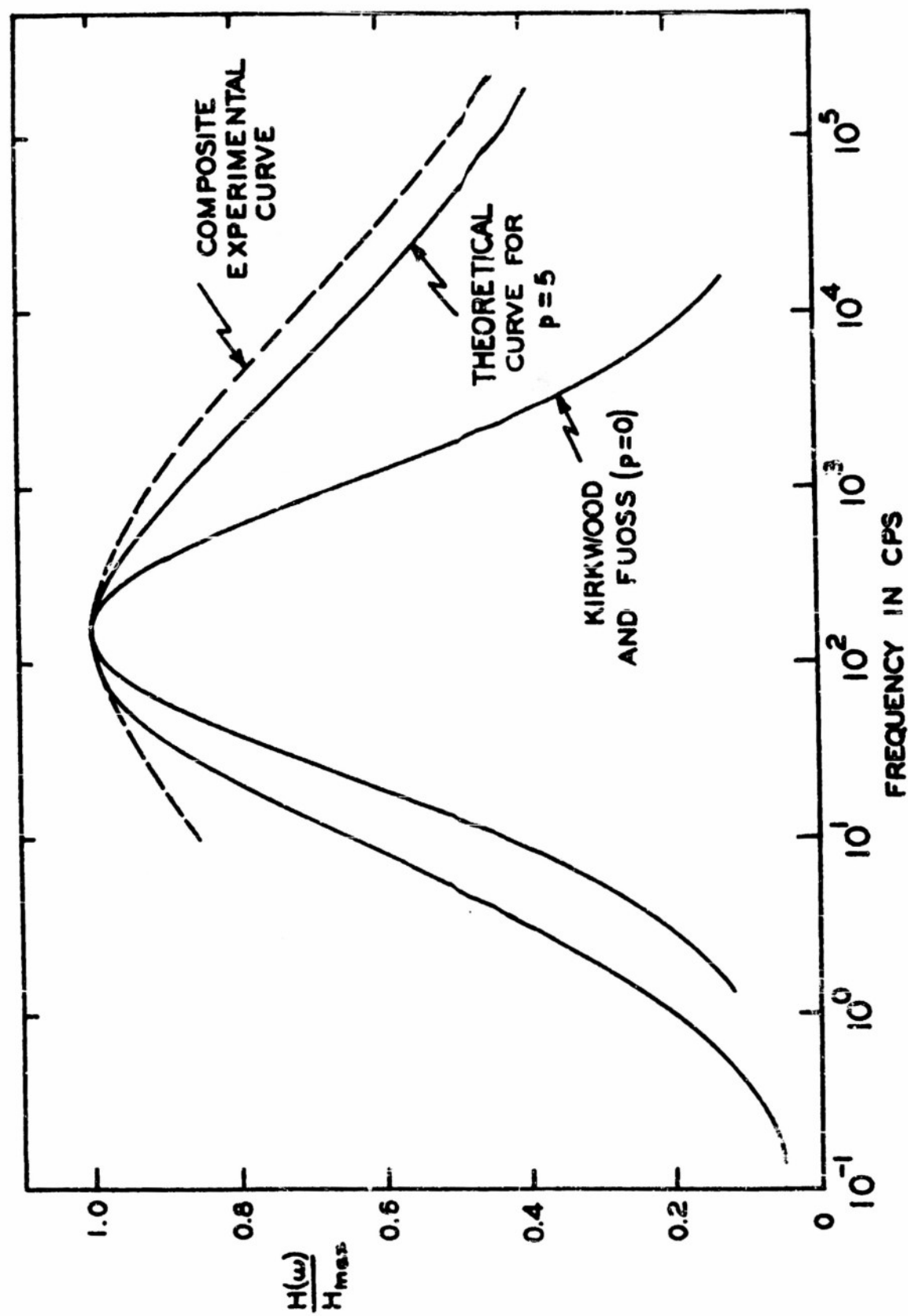


Fig. 6. Dielectric Dispersion of Polyvinyl Chloride

From Section VI, however, we have available a set of resistance constants, $\epsilon_i = \epsilon_o A_i^5$, that describes the effect of the molecular entanglements during mechanical extension of an unplasticized polymer. Since the same entanglements occur during the application of an electric field, introduction of these resistance constants into the Kirkwood and Fuoss theory should give the correct dielectric dispersion.

The solution of the diffusion equation for an electric field has been recalculated using the modified resistance constants. A summary of the computations is given in Appendix VII. The new distribution of electrical relaxation times is^{*}

$$G(\tau) = \frac{\tau_o'}{6\tau^{5/6}(\tau + \tau_o')^{7/6}}, \quad (102)$$

where τ_o' is given by Equation (90). $H(\omega)$, divided by $H_{\max}$, is plotted in Figure 6 against the frequency, with τ_o' set equal to $10^{-1.99}$ seconds so that $H_{\max}$ coincides with the maximum of the experimental curve. The corrected dielectric dispersion is much closer to the experimental result than is the uncorrected curve.

It might be pointed out that the dispersion for p equal to five is not symmetric about its maximum. This suggests that the Kirkwood and Fuoss theory has not been corrected properly for frequencies less than $2\pi/\tau_o'$. The stress relaxation at corresponding times is too small to measure accurately, and the correction is not applicable in

^{*}Equation (99) is correct only if $\tau_o/n \ll \tau \ll \tau_o n$. Equation (102) is correct only if $\tau_o'/n^{p+1} \ll \tau \ll \tau_o' n$. These limits may be neglected in the calculations for $H(\omega)$.

this region. Over the three decades of frequency larger than $2\pi/\tau_0'$ the theoretical curve is never more than 0.08 below the experimental $H(\omega)$. This precision is as good as can be expected because the value of p was determined from the mechanical properties of a different polymer. A more accurate check on the theory would be the calculation of the dielectric dispersion from the stress relaxation of polyvinyl chloride itself. With this reservation, the modified theory is an accurate representation of the electrical properties of polyvinyl chloride.

One way of summarizing the dependence of $H(\omega)$ upon frequency is to give its maximum value, because H_{max} decreases as the width of the dispersion increases. For polyvinyl chloride, H_{max} is about 0.10 at 100°C. In the Kirkwood and Fuoss theory, H_{max} is 0.285 (for a fractionated polymer). When the correction for the chain entanglements is introduced into the theoretical derivation, H_{max} is reduced to 0.143, a value almost as low as the experimental figure.

The predicted temperature dependence of $H(\omega)$ also agrees with the experimental results. For both of the theories and for polyvinyl chloride, the frequency of maximum dispersion is dependent exponentially upon $1/T$. The shape and magnitude of $H(\omega)$ are independent of T . Actually, for polyvinyl chloride there is a slight change in H_{max} as the temperature is raised, but this effect may be due to other types of dispersion occurring primarily at higher frequencies.

From Equation (90) we can show readily that the calculated frequency of the maximum dispersion is proportional to $(1/M)^{p+1}$.

Consequently, the frequency of H_{max} is proportional to $(1/M)^p$ when p is five, while it is proportional to $1/M$ for the Kirkwood and Fuoss theory. The only experimental data on the variation of $H(\omega)$ with M are for polyvinyl chloride plasticized with 20% diphenyl [16]. For this material, the frequency of maximum dispersion seems to vary with $1/M$, agreeing with the Kirkwood and Fuoss theory. The predicted variation corresponding to a p of five certainly does not fit the experimental data. It might be pointed out, however, that the plasticization of polyvinyl chloride increases H_{max} from 0.10 to about 0.17 and radically decreases the width of the dispersion. The value of p necessary to describe the frequency dependence of $H(\omega)$ would be quite a bit less than five. It therefore appears that the predicted frequency of H_{max} for the plasticized polymer would vary as a power of $1/M$ less than six but more than one. There is some indication from the experiments of Fuoss that this may be the case. Until data are available for an unplasticized polymer, however, it is necessary to conclude that the theoretical molecular weight dependence for a p of five does not agree with the available experimental results.

In summary, the resistance constants which give the proper time dependence of the mechanical properties of polyisobutylene may also be used in the diffusion theory of dielectric dispersion. The corrected dispersion agrees in its frequency and temperature dependence with experimental results for polyvinyl chloride, but does not give the proper dependence upon the molecular weight.

16. R. M. Fuoss, J. Am. Chem. Soc. 63, 2401 (1941).

VIII. SUMMARY

If an incompressible noncross-linked polymer is extended in such a way that all parts of the material are strained equally, the velocity $\mathbf{v}$ of the molecules relative to each other may be expressed in terms of the rate of extension $d\epsilon/dt$ (Equations (4) and (5)). The configurations of the molecules at any instant may be specified for our purpose by ϕ , the probability of each configuration. If the temperature is above the polymer's glass transformation, the bond lengths and bond angles are constant during extension. Then the only variables on which ϕ depends are the two directional angles of the center bond of the molecule and the azimuth angles along the chain.

If the molecules are not cross-linked, the intermolecular forces during extension are viscous in nature. The force on a single element (one skeletal atom together with its side groups) is proportional to the velocity of that element relative to the surrounding material. In other words, the force is equal to $\xi_i(\mathbf{v} - \mathbf{v}_i)$, where ξ_i is the resistance constant of the i -th element along the chain; $\mathbf{v}_i$ is the velocity of the element relative to the center of mass of the molecule. By substituting these forces into the equation of continuity for ϕ , the diffusion equation is obtained:

$$\nabla \cdot \mathbf{D} \cdot [\nabla \phi + \phi \nabla V / k_B T] = \frac{\partial \phi}{\partial t}. \quad (20)$$

The diffusion tensor $\mathbf{D}$ may be calculated from the ξ_i by the method of Kirkwood and Fuoss (Appendix I). If rotation of the bonds around their azimuth angles is completely unrestricted, the potential V is

equal to

$$V = \frac{1}{4} \frac{d\epsilon}{dt} \sum_i \xi_i (\rho_i^2 - 2 \bar{z}_i^2), \quad (14)$$

where ρ_i and z_i are the cylindrical coordinates of the i -th element relative to the center of mass of the molecule. We may conclude that the molecules change their configurations by diffusion under a potential proportional to the rate of extension $d\epsilon/dt$. For a given extension, the diffusion equation can be solved for the probability of each molecular configuration.

The rate at which energy is supplied to the polymer may be calculated from the potential and the probability of each configuration (Equation (27)). Since this energy is also equal to the product of the external stress and the rate of extension, it is possible to calculate the stress required for a given extension of the polymer. A linear relationship between the stress and the strain, in terms of a distribution of relaxation times $E'(\tau)$, may be obtained from a single solution of the diffusion equation. The general method for finding $E'(\tau)$ is summarized on page 31.

Without solving explicitly for the distribution of relaxation times, it is possible to derive the dependence of the stress $s(t)$ upon the temperature. For relaxation at constant extension, a plot of the calculated $s(t)/T$ versus $tT e^{-A/RT}$ is independent of the temperature. This dependence agrees with the experimental behavior of high polymers such as polyisobutylene.

To find $s(t)$ explicitly, it is necessary to determine the diffusion tensor D and solve for $E'(\tau)$. To get a first approximation

to $\underline{D}$, it may be assumed that the resistance constants ξ_i are all equal. This approximation is equivalent to assuming that the motion of the polymer molecule is the same whether or not the surrounding material is polymerized. The $s(t)$ calculated from these ξ_i decays too rapidly in time to fit the experimental stress relaxation of polyisobutylene (see Figure 3). Moreover, the predicted dependence of $s(t)$ upon the molecular weight fails to agree with the experimental results.

These disagreements are not surprising because the calculated $E'(\gamma)$ applies only to a dilute solution of a polymer. In order to determine the mechanical properties of an unplasticized polymer, it is necessary to take into account the chain-to-chain entanglements. We make the ad hoc assumption that ξ_i may be set equal to $\xi_0 A i^p$, where A and p are constants. When p is five, the shape of the theoretical stress relaxation agrees quite well with the relaxation of polyisobutylene. Over nine decades of time the maximum error is five percent (see Figure 5). Thus, it is possible to find a diffusion tensor which gives the correct time dependence of the mechanical properties of the polymer. The dependence of $s(t)$ upon the molecular weight is not correctly described even after the resistance constants have been changed.

The diffusion tensor which gives the proper stress relaxation of a polymer may also be used to find its response to other types of forces. The only restriction upon the applicability of $\underline{D}$ is that the force must result primarily in rotations of the azimuth angles of the molecules. One force of this type is an electric field of audio frequency. Kirkwood and Fuoss have calculated the dielectric dispersion

of polar polymers by techniques from which the above methods have been derived. However, they use the diffusion tensor applicable to dilute solutions. It is possible to carry through their computations with the new diffusion tensor descriptive of an unplasticized polymer. The results may be expressed as a distribution of (electrical) relaxation times given by Equation (102).

The corresponding dielectric dispersion is plotted in Figure 6 against the frequency, together with published experimental results for polyvinyl chloride. The agreement between the theory and the data is quite satisfactory. It is believed that the agreement would be even better if the diffusion tensor were derived from the stress relaxation of polyvinyl chloride itself, rather than polyisobutylene. The predicted temperature dependence of the dispersion also agrees with observation. The theoretical variation with the molecular weight does not agree with what experimental data are available in the literature.

It may be concluded that the ad hoc set of resistance constants correctly describes the time-dependent properties of a noncross-linked polymer at temperatures above its glass transformation, except for the dependence on the molecular weight.

APPENDIX I

DERIVATION OF THE DIFFUSION TENSOR

The resistance tensor for a polymer molecule has been obtained by Kirkwood and Fuoss [7]. Their derivation is reproduced here.

The Cartesian coordinates erected at the center of mass of the molecule are the unit vectors $\underline{e}_1$, $\underline{e}_2$ and $\underline{e}_3$, with $\underline{e}_3$ in the direction of extension. The elements of the chain are numbered from 1 to $2n$; $\underline{a}_k$ denotes the unit vector in the direction of the bond from element $k-1$ to element k . If the chain is very long, it may be assumed that the center of mass of the chain is always at its average position, the midpoint of the center bond. Then the vector $\underline{r}_k$, which denotes the position of element k relative to the center of mass, is equal to

$$\underline{r}_k = \begin{cases} a \left[\frac{1}{2} \underline{a}_{n+1} + \sum_{j=n+2}^k \underline{a}_j \right] & k \geq n+1 \\ -a \left[\frac{1}{2} \underline{a}_{n+1} + \sum_{j=k+1}^n \underline{a}_j \right], & k \leq n \end{cases} \quad (103)$$

where a is the bond length. The angle Θ is the angle between $\underline{e}_3$ and $\underline{a}_{n+1}$, while ϕ is the angle between the plane containing $\underline{e}_3$ and $\underline{a}_{n+1}$ and the plane containing $\underline{e}_2$ and $\underline{e}_1$. This definition of ϕ may be written as

$$\phi \equiv (\underline{a}_{n+1}, \underline{e}_3)(\underline{e}_3, \underline{e}_1). \quad (104)$$

In the same notation, the azimuth angles χ_2 to χ_{2n-1} are defined by

$$\chi_{n+1} \equiv (a_{n+2}, a_{n+1})(a_{n+1}, e_3) \quad (105)$$

$$\chi_n \equiv (a_n, a_{n+1})(a_{n+1}, e_3) \quad (106)$$

$$\chi_k \equiv \begin{cases} (a_{k+1}, a_k)(a_k, a_{k-1}) & 2n-1 \geq k \geq n+2 \\ (a_k, a_{k+1})(a_{k+1}, a_{k+2}) & n-1 \geq k \geq 2 \end{cases} \quad (107)$$

The supplement of the bond angle, η , is the angle between any pair of consecutive vectors a_k and a_{k+1} . In carbon chains, η is approximately 71° . For the purpose of simplifying the following calculations, however, η will be set equal to 90° . It is believed that no serious errors are introduced by this difference.

The velocity of the element k relative to the center of gravity is

$$v_k = \Omega_0 \times r_k + \sum_{j=n+1}^{k-1} \Omega_j \times (r_k - r_j), \quad k \geq n+1 \quad (108)$$

where $\Omega_j = a_j \dot{\chi}_j$ (109)

and $\Omega_0 = -(\sin\phi) \dot{\Theta} e_1 + (\cos\phi) \dot{\Theta} e_2 + (\sin\Theta) \dot{\phi} e_3$ (110)

If the molecule is moved through a quiescent fluid, the force on the element k is $\zeta_k v_k$, and the torque at the position of another element i is $\zeta_k (r_k - r_i) \times v_k$. The total vector torque acting at the position of element i due to the forces on all the elements is

$$\tau_i = \sum_{k=i+1}^{2n} \zeta_k (r_k - r_i) \times v_k - \sum_{k=n+1}^i \zeta_k (r_k - r_i) \times v_k, \quad i \geq n+1 \quad (111)$$

The component of τ_i in the direction of a_i is the scalar torque T_i associated with the angle χ_i . Substituting Equation (108) into

Equation (111) and rearranging after dotting with q_i , we have, for $i \geq n+1$,

$$T_i = \underline{T}_i \cdot q_i = \sum_{j=2}^{2n-1} \rho_{ij} \dot{\chi}_j + \rho_{i0} \Omega_0, \quad (112)$$

where

$$\rho_{ij} = \begin{cases} \sum_{k=j+1}^{2n} \zeta_k q_i \cdot \underline{y}_{ijk} \cdot q_j & j \geq i \\ \sum_{k=i+1}^{2n} \zeta_k q_i \cdot \underline{y}_{ijk} \cdot q_j - \sum_{k=j+1}^{i-1} \zeta_k q_i \cdot \underline{y}_{ijk} \cdot q_j & n+1 \leq j \leq i-1 \\ 0 & j \leq n \end{cases} \quad (113)$$

and

$$\rho_{i0} = \sum_{k=i+1}^{2n} \zeta_k q_i \cdot \underline{y}_{i0k} - \sum_{k=n+1}^{i-1} \zeta_k q_i \cdot \underline{y}_{i0k}. \quad (114)$$

The dyadics $\underline{y}_{ijk}$ are defined as

$$\underline{y}_{ijk} \equiv (r_k - r_j)(r_k - r_i) \underline{I} - (r_k - r_j)(r_k - r_i), \quad (115)$$

where $\underline{I}_{ij} \equiv \delta_i^j$. The dyadic $\underline{y}_{i0k}$ denotes $\underline{y}_{ijk}$ with r_j identically zero. A corresponding result may be obtained for the lower half of the chain. The torque $\underline{T}_0$ associated with the angles Θ and ϕ is the total torque on the molecule referred to the center of mass:

$$\underline{T}_0 = \rho_{00} \cdot \Omega_0 + \sum_{j=2}^{2n-1} \rho_{0j} \dot{\chi}_j, \quad (116)$$

where

$$\rho_{0j} = \begin{cases} \sum_{k=j+1}^{2n} \zeta_k \underline{y}_{0jk} \cdot q_j & j \geq n+1 \\ - \sum_{k=1}^{j-1} \zeta_k \underline{y}_{0jk} \cdot q_j & j \leq n \end{cases} \quad (117)$$

and

$$\rho_{00} = \sum_{k=1}^{2n} \zeta_k (r_k \cdot r_k \underline{I} - r_k r_k). \quad (118)$$

The dyadic γ_{cjk} denotes γ_{ijk} with r_i identically zero. All the terms of the resistance tensor ρ are given by Equations (113), (114), (117), and (118).

It is prohibitively difficult to find the inverse of ρ and thereby to obtain $D = k_b T \rho^{-1}$. However, the diffusion tensor may be approximated by $k_b T (\bar{\rho})^{-1}$, where $\bar{\rho}$ is the average of the resistance tensor over all possible configurations of the molecule. Substituting Equation (103) into the definition of γ_{ijk} , we may show that

$$\overline{a_i \cdot \gamma_{ijk} \cdot a_j} = \begin{cases} \delta_i^j a^2 \sum_{q=i+1}^k [1 - \overline{(a_i \cdot a_q)^2}] & k \geq i+1 \\ 0 & k \leq i \end{cases} \quad (119)$$

The value of $\overline{(a_i \cdot a_q)^2}$ is 1, 0, 1/2, 1/4, 3/8, 5/16, ... for q equal to $i, i+1, i+2, \dots$, and approaches 1/3 as $q-i$ becomes large. Without much error in $\bar{\rho}$, $\overline{(a_i \cdot a_q)^2}$ may be set equal to 1/3 for all q . Using Equation (113), we then have

$$\bar{\rho}_{ij} = \begin{cases} \frac{2}{3} a^2 \delta_i^j \sum_{k=i+1}^{2n} \zeta_k (k-i) & i \geq n+1 \\ \frac{2}{3} a^2 \delta_i^j \sum_{k=1}^{i-1} \zeta_k (i-k) & i \leq n \end{cases} \quad (120)$$

The value of $\bar{\rho}_{00}$ is given by

$$\bar{\rho}_{00} = \frac{2}{3} \sum_{k=1}^{2n} \zeta_k \overline{r_k \cdot r_k} \underline{I}. \quad (121)$$

Using Equation (103), and neglecting the term $\frac{1}{2} a_{n+1}$, we have

$$\sum_{k=1}^{2n} \zeta_k \overline{r_k \cdot r_k} \cong 2a^2 \sum_{k=1}^n \sum_{q=k+1}^n \sum_{r=k+1}^n \zeta_k \overline{a_q \cdot a_r}, \quad (122)$$

so long as

$$\zeta_k = \zeta_{2n+1-k}. \quad (123)$$

From the fact that $\overline{a_q \cdot a_r} = \delta_q^r$,

$$\overline{P}_{oo} = \frac{4}{3} a^2 \sum_{k=1}^{n-1} \xi_k (n-k) \underline{I}. \quad (124)$$

Also, it may be shown that

$$\overline{P}_{io} = \overline{P}_{oi} = 0. \quad (125)$$

The components of the diagonal diffusion tensor are readily found from the average resistance tensor, and are

$$\overline{D}_{\theta\theta} = \overline{D}_{\phi\phi} = D_o n^2 / 4 q(n) \quad (126)$$

and

$$\overline{D}_{ij} = D_o n^2 \delta_i^j / 2 q(i), \quad (127)$$

where

$$D_o \equiv 3 k_o T / \xi_o a^2 n^2, \quad (128)$$

and

$$q(i) \equiv \begin{cases} \sum_{k=i+1}^{2n} (k-i) \xi_k / \xi_o & i \geq n+1 \\ \sum_{k=1}^{i-1} (i-k) \xi_k / \xi_o & i \leq n \end{cases} \quad (129)$$

If it is assumed that ξ_k is equal to ξ_o , $q(i)$ is approximately $[n - |i-n|]^2 / 2$. The nonzero terms of the diffusion tensor are then

$$\overline{D}_{\theta\theta} = \overline{D}_{\phi\phi} = D_o / 2 \quad (130)$$

and

$$\overline{D}_{ii} = D_o [1 - |i-n|]^2. \quad (131)$$

The diffusion operator is equal to

$$\nabla \cdot \overline{D} \cdot \nabla = D_o \left\{ \frac{1}{2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] + \sum_{i=2}^{2n-1} \left[1 - \left| \frac{i-n}{n} \right| \right]^{-2} \frac{\partial^2}{\partial \chi_i^2} \right\} \quad (132)$$

and the eigenvalues and normalized eigenfunctions of this operator are

$$\lambda = D_0 \left\{ \frac{1}{2} \ell(\ell+1) + \sum_{i=2}^{2n-1} \left[1 - \left| \frac{i-n}{n} \right| \right]^{-2} m_i^2 \right\} \quad (133)$$

$$\psi_\lambda = \left[\frac{(2\ell+1)(\ell-1m_0)!}{4\pi(\ell+1m_0)!} \right]^{1/2} (2\pi)^{-n+1} P_\ell^{m_0}(\cos \theta) e^{im_0\phi} \prod_{i=2}^{2n-1} e^{im_i\chi_i}, \quad (134)$$

where $P_\ell^{m_0}(\cos \theta)$ are the associated Legendre polynomials.

APPENDIX II

EVALUATION OF $d_\lambda d_\lambda^*$

From Equation (70), d_λ is equal to

$$d_\lambda = \sqrt{f_0} \int \sum_i (\rho_i^2 - 2z_i^2) \psi_\lambda^* dq \quad (135)$$

when $\xi_i = \xi_0$. Using Equation (103) of Appendix I and neglecting

$\frac{1}{2} a_{n+1}$, we find that

$$\sum_{i=1}^{2n} r_i \cdot r_i \cong 2\alpha^2 \sum_{j=2}^n \sum_{k=j}^n (j-1) a_j \cdot a_k + 2\alpha^2 \sum_{j=n+2}^{2n} \sum_{k=n+2}^j (2n+1-j) a_j \cdot a_k \quad (136)$$

$$\text{and } \sum_{i=1}^{2n} z_i^2 \cong 2\alpha^2 \sum_{j=2}^n \sum_{k=j}^n (j-1) (\mathbf{e}_3 \cdot \mathbf{a}_j) (\mathbf{e}_3 \cdot \mathbf{a}_k) + 2\alpha^2 \sum_{j=n+2}^{2n} \sum_{k=n+2}^j (2n+1-j) (\mathbf{e}_3 \cdot \mathbf{a}_j) (\mathbf{e}_3 \cdot \mathbf{a}_k). \quad (137)$$

From $\rho_i^2 - 2z_i^2 = r_i^2 - 3z_i^2$, it follows that

$$d_\lambda = 2\alpha^2 \sum_{j=2}^n \sum_{k=j}^n (j-1) P_{jk}^{(\lambda)} + \sum_{j=n+2}^{2n} \sum_{k=n+2}^j (2n+1-j) P_{jk}^{(\lambda)}, \quad (138)$$

$$\text{where } P_{jk}^{(\lambda)} = \sqrt{f_0} \int [\mathbf{a}_j \cdot \mathbf{a}_k - 3(\mathbf{e}_3 \cdot \mathbf{a}_j)(\mathbf{e}_3 \cdot \mathbf{a}_k)] \psi_\lambda^* dq. \quad (139)$$

In order to find $P_{jk}^{(\lambda)}$, it is necessary to express $\mathbf{a}_j$ in terms of the angles $\theta, \phi, \chi_2, \dots, \chi_{2n-1}$. From the geometry of the molecular chain, it may be determined that

$$\mathbf{a}_j = \begin{cases} \hat{\Delta}(\theta, \phi) \cdot \hat{\Delta}(\eta, \chi_{n+1}) \cdot \hat{\Delta}(\eta, \chi_{n+2}) \cdot \dots \cdot \hat{\Delta}(\eta, \chi_{j-1}) \cdot \mathbf{e}_3 & j \geq n+1 \\ \hat{\Delta}(\theta, \phi) \cdot \hat{\Delta}(\eta, \chi_n) \cdot \hat{\Delta}(\eta, \chi_{n-1}) \cdot \dots \cdot \hat{\Delta}(\eta, \chi_j) \cdot \mathbf{e}_3 & j \leq n \end{cases} \quad (140)$$

where $\hat{\Lambda}(\theta, \phi) \equiv \begin{pmatrix} \cos \theta \cos \phi & -\sin \phi & \sin \theta \cos \phi \\ \cos \theta \sin \phi & \cos \phi & \sin \theta \sin \phi \\ -\sin \theta & 0 & \cos \theta \end{pmatrix}$. (141)

It will be assumed that η , the supplement of the skeletal bond angle, is equal to 90° .

For $j \geq n+1$, substitution of Equation (140) into Equation (139) gives

$$P_{jk}^{(\lambda)} = \sqrt{f_0} \int U \{ \mu^{(0)} : \mu^{(n+1)} : \mu^{(n+2)} : \dots : \mu^{(k-1)} : \nu^{(k)} : \nu^{(k+1)} : \dots : \nu^{(j-1)} : K \} \psi_\lambda^* dq, \quad (142)$$

where K is the dyadic $e_3 e_3$, and the fourth-order tensors $\mu^{(0)}$, $\mu^{(q)}$, and $\nu^{(q)}$ are defined by

$$\mu_{\alpha\beta\gamma\delta}^{(0)} \equiv \hat{\Lambda}(\theta, \phi)_{\alpha\beta} \hat{\Lambda}(\theta, \phi)_{\gamma\delta}, \quad (143)$$

$$\mu_{\alpha\beta\gamma\delta}^{(q)} \equiv \hat{\Lambda}(\eta, \chi_q)_{\alpha\beta} \hat{\Lambda}(\eta, \chi_q)_{\gamma\delta}, \quad (144)$$

and $\nu_{\alpha\beta\gamma\delta}^{(q)} \equiv \hat{\Lambda}(\eta, \chi_q)_{\alpha\beta} \mathbb{I}_{\gamma\delta}$. (145)

The scalar function U of any dyadic Π denotes

$$U(\Pi) \equiv \Pi_{11} + \Pi_{22} - 2\Pi_{33}. \quad (146)$$

The double dot product is defined as

$$[\mu^{(q)} : \mu^{(r)}]_{\alpha\beta\gamma\delta} \equiv \sum_{\epsilon, \zeta} \mu_{\alpha\epsilon\gamma\zeta}^{(q)} \mu_{\epsilon\beta\delta\zeta}^{(r)}, \quad (147)$$

and $[\mu^{(q)} : \Pi]_{\alpha\beta} \equiv \sum_{\epsilon, \zeta} \mu_{\alpha\epsilon\beta\zeta}^{(q)} \Pi_{\epsilon\zeta}$. (148)

Substituting for ψ_λ^* from Equation (134) of Appendix I, we obtain

$$P_{jk}^{(\lambda)} = U(\mu^{(0)} : \mu^{(n+1)} : \mu^{(n+2)} : \dots : \mu^{(k-1)} : \nu^{(k)} : \nu^{(k+1)} : \dots : \nu^{(j-1)} : K) \times \prod_{q=2}^n \delta_{m_q}^0 \prod_{q=j}^{2n-1} \delta_{r_q}^0, \quad (149)$$

where
$$\underline{U}(\underline{\mu}^{(0)}) = \frac{1}{\sqrt{4\pi}} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \underline{U}(\underline{\mu}^{(0)}) Y_{\ell}^{m_0}(\theta, \phi) \sin\theta d\theta d\phi, \quad (150)$$

$$\underline{M}^{(q)} = \frac{1}{2\pi} \int_0^{2\pi} \underline{\mu}^{(q)} e^{-im_q \chi_q} d\chi_q, \quad (151)$$

$$\underline{N}^{(q)} = \frac{1}{2\pi} \int_0^{2\pi} \underline{\nu}^{(q)} e^{-im_q \chi_q} d\chi_q, \quad (152)$$

$$[\underline{U}(\underline{\mu}^{(0)})]_{\alpha\beta} = \underline{\mu}_{1\alpha 1\beta}^{(0)} + \underline{\mu}_{2\alpha 2\beta}^{(0)} - 2\underline{\mu}_{3\alpha 3\beta}^{(0)}, \quad (153)$$

$$Y_{\ell}^{m_0}(\theta, \phi) = \left[\frac{(2\ell+1)(\ell-|m_0|)!}{4\pi(\ell+|m_0|)!} \right]^{1/2} P_{\ell}^{m_0}(\cos\theta) e^{im_0\phi}. \quad (154)$$

and

As the first step toward finding $P_{jk}^{(\lambda)}$, it is possible to evaluate the product

$$\underline{L} \equiv \underline{N}^{(k)} : \underline{N}^{(k+1)} : \dots : \underline{N}^{(j-1)} : \underline{K}. \quad (155)$$

Integration over χ_q gives

$$\underline{N}^{(q)} = \left[\delta_{m_q}^0 \underline{\Lambda}_0 + \frac{1}{2} \delta_{m_q}^1 \underline{\Lambda}_+ + \frac{1}{2} \delta_{m_q}^{-1} \underline{\Lambda}_- \right] \underline{I}, \quad (156)$$

where $\underline{\Lambda}_0 = -\underline{e}_1 \underline{e}_1$ and

$$\underline{\Lambda}_{\pm} = \underline{e}_2 \underline{e}_2 + \underline{e}_1 \underline{e}_3 \pm \underline{e}_2 \underline{e}_3 / \sqrt{1} \mp \underline{e}_1 \underline{e}_2 / \sqrt{1}. \quad (157)$$

By substitution into Equation (155) and contraction of the dot products, we find that^{*}

$$\begin{aligned} \underline{L} = & (-1)^{j-k-\sigma-1} \left(\frac{1}{2} \right)^{\sigma} (1)_{j-1}' \prod_{q=k+1}^{j-2} \left[(1)_q - (1)_{q-1}' (0)_q (1)_{q+1}' \right] \\ & \times \left[(1)_k' \underline{e}_1 \underline{e}_3 - (1)_k \underline{e}_2 \underline{e}_3 + (0)_k (1)_{k+1}' \underline{e}_3 \underline{e}_3 \right], \end{aligned} \quad (158)$$

^{*}Equations (158), (164), (165), (171), and (233) may be proved by induction.

where $(0)_q$, $(1)_q$ and $(1)'_q$ denote $\delta_{m_q}^0$, $(\delta_{m_q}^1 + \delta_{m_q}^{-1})$, and $(\delta_{m_q}^1 - \delta_{m_q}^{-1})/\sqrt{-1}$, respectively. Later in this appendix, $(2)_q$ and $(2)'_q$ will also appear; they denote $(\delta_{m_q}^2 + \delta_{m_q}^{-2})$ and $(\delta_{m_q}^2 - \delta_{m_q}^{-2})/\sqrt{-1}$, respectively. The quantity σ , defined as

$$\sigma \equiv \sum_{q=k}^{j-1} (1)_q, \quad (159)$$

is the number of m_q that are ± 1 for $q \geq k$. $\underline{L}$ is zero unless all the m_q are 0 or ± 1 ; $m_{j+1} = \pm 1$, and no consecutive m_q and m_{q+1} are zero simultaneously. If $\underline{L}$ is not zero, its absolute value depends only upon σ .

The next step in evaluating $P_{jk}^{(\lambda)}$ is to find $\underline{M}^{(q)}$ and its double dot products. From Equations (144) and (151), we may show that $\underline{M}^{(q)}$ is the sum of $\underline{M}_s^{(q)}$ and $\underline{M}_a^{(q)}$, where $\underline{M}_s^{(q)}$ is symmetric under transposition of the first and third indices and under transposition of the second and fourth indices, whereas $\underline{M}_a^{(q)}$ is antisymmetric under either transposition. From the nature of the $\underline{U}$ function, it is possible to show that only the symmetric parts of $\underline{M}^{(q)}$ and $\underline{L}$ contribute to $P_{jk}^{(\lambda)}$:

$$P_{jk}^{(\lambda)} = \underline{U}(\underline{M}^{(0)} : \underline{M}_s^{(n+1)} : \underline{M}_s^{(n+2)} : \dots : \underline{M}_s^{(k-1)} : \underline{L} : \prod_{q=2}^n (0)_q \prod_{q=j}^{2n-1} (0)_q. \quad (160)$$

The value of $\underline{M}^{(q)}$ obtained from integration of Equation (151) is

$$\begin{aligned} \underline{M}^{(q)} = & \left[\underline{\Lambda}_0 \underline{\Lambda}_0 + \frac{1}{4} \underline{\Lambda}_+ \underline{\Lambda}_- + \frac{1}{4} \underline{\Lambda}_- \underline{\Lambda}_+ \right] \delta_{m_q}^0 + \frac{1}{2} \left[\underline{\Lambda}_+ \underline{\Lambda}_0 + \underline{\Lambda}_0 \underline{\Lambda}_+ \right] \delta_{m_q}^1 \\ & + \frac{1}{2} \left[\underline{\Lambda}_- \underline{\Lambda}_0 + \underline{\Lambda}_0 \underline{\Lambda}_- \right] \delta_{m_q}^{-1} + \frac{1}{4} \underline{\Lambda}_+ \underline{\Lambda}_+ \delta_{m_q}^2 + \frac{1}{4} \underline{\Lambda}_- \underline{\Lambda}_- \delta_{m_q}^{-2}. \end{aligned} \quad (161)$$

Rearrangement of the terms and subtraction of the antisymmetric part

give $M_s^{(q)}$, which may be expressed as^{*}

$$[M_s^{(q)}]_{\alpha\beta\gamma\delta} = A_{\alpha\gamma}^{(q)} B_{\beta\delta}^{(q)} + (C_{\alpha\gamma} D_{\beta\delta} + E_{\alpha\gamma} F_{\beta\delta}) (u)_{\beta}, \quad (162)$$

where

$$A^{(q)} = \frac{1}{2} \begin{pmatrix} (2)_q & (2)'_q & (1)_q \\ (2)'_q & -(2)_q & (1)'_q \\ (1)_q & (1)'_q & 0 \end{pmatrix}, \quad B^{(q)} = \frac{1}{2} \begin{pmatrix} 0 & (1)'_q & -(1)_q \\ (1)'_q & -(2)_q & -(2)'_q \\ -(1)_q & -(2)'_q & (2)_q \end{pmatrix}, \quad (163)$$

$C = (e_1 e_1 + e_2 e_2)/2$, $D = e_2 e_1 + e_3 e_3$, $E = e_3 e_2$, and $F = e_1 e_3$. $M_s^{(q)}$ is zero unless $m_q = 0, \pm 1$, or ± 2 . Also, it may be seen immediately that $M_s^{(q)}: M_s^{(q')}$ is zero if either $m_q = 0$ and $m_{q'} = \pm 1$, or vice versa. Hence, the total product $M_s^{(q_1)}: \dots: M_s^{(q_{r-1})}$ (except perhaps near its ends) may be divided into a set of scalar products of the form

$$B^{(q)}: M_s^{(q_1)}: M_s^{(q_2)}: \dots: M_s^{(q_r)}: A^{(q_{r+1})}, \quad \text{where } |m_q| = |m_{q_{r+1}}| = 2,$$

and all m_q in between (there being r of them) have the same absolute value 0, 1, or 2. Each of these scalar products may be contracted separately, to give:

$$\begin{aligned} & B^{(q)}: M_s^{(q_1)}: \dots: M_s^{(q_r)}: A^{(q_{r+1})} = \\ & = \begin{cases} -\frac{3}{4} \left(-\frac{1}{2}\right)^r (2)_q (0)_{q_1} (0)_{q_2} \dots (0)_{q_r} (2)_{q_{r+1}} & m_q = 0, r \geq 1 \\ \frac{1}{2} \left(-\frac{1}{2}\right)^r (2)'_q (1)'_{q_1} (1)_{q_2} \dots (1)_{q_{r-1}} (1)'_{q_r} (2)'_{q_{r+1}} & |m_q| = 1, r \geq 1 \\ 4 \left(\frac{1}{4}\right)^{r+2} (2)_q (2)_{q_1} \dots (2)_{q_{r+1}} & |m_q| = 2, r \geq 0 \end{cases} \quad (164) \end{aligned}$$

The connection between the M_s and L_s can be expressed as the product of L_s with the M_s back to $B^{(k-r-1)}$, where $k-r-1$ is

^{*}Note that the indices in the right side of Equation (162) have been transposed from their order in Equation (144).

the largest integer such that $|m_{k-r-1}| = 2$. The nonzero values of this product are

$$\begin{aligned} & \underline{B}^{(k-r-1)} : \underline{M}_s^{(k-r)} : \underline{M}_s^{(k-r+1)} : \dots : \underline{M}_s^{(k-1)} : \underline{L}_s = \\ & = \begin{cases} \frac{\mathcal{W}}{2} \left(-\frac{1}{2}\right)^r (2)_{k-r-1} (0)_{k-r} (0)_{k-r+1} \dots (0)_k (1)_{k+1}' & m_k = 0, r \geq 0 \\ -\frac{\mathcal{W}}{2} \left(-\frac{1}{2}\right)^r (2)'_{k-r-1} (1)'_{k-r} (1)_{k-r+1} (1)_{k-r+2} \dots (1)_{k-1} (1)'_k & |m_k| = 1, r \geq 0 \end{cases} \quad (165) \end{aligned}$$

Where $\mathcal{W}$, from Equation (158), is

$$\mathcal{W} = (-1)^{j+k-\sigma-1} \left(\frac{1}{2}\right)_{j-1}' \prod_{q=k+1}^{j-2} [(1)_q - (1)'_{q-1} (0)_q (1)'_{q+1}]. \quad (166)$$

From the definition of $\underline{\mu}^{(a)}$ in Equation (143), it follows that

$$\underline{U}(\underline{\mu}^{(a)}) = \frac{3}{2} \begin{pmatrix} \cos 2\theta - \frac{1}{3} & 0 & \sin 2\theta \\ 0 & 1 & 0 \\ \sin 2\theta & 0 & -\cos 2\theta - \frac{1}{3} \end{pmatrix}. \quad (167)$$

Substituting $\underline{U}(\underline{\mu}^{(a)})$ into Equation (150), we find that

$$\underline{U}(\underline{M}^{(a)}) = \delta_m^0 \left[\delta_\ell^0 \underline{G} + \frac{2}{\sqrt{5}} \delta_\ell^2 \underline{H} + \frac{3}{2} \sum_{\text{odd } \alpha} a_\alpha \sqrt{\frac{1}{2\alpha+1}} \delta_\ell^\alpha \underline{J} \right], \quad (168)$$

where $\underline{G} = -e_1 e_1 + e_2 e_2$, $\underline{H} = e_1 e_1 - e_3 e_3$, $\underline{J} = e_1 e_3 + e_3 e_1$.

The numbers a_α are the expansion coefficients of $\sin 2\theta$ in terms of the Legendre polynomials of $\cos \theta$ [17]:

$$\sin 2\theta = \sum_{\text{odd } \alpha} a_\alpha P_\alpha(\cos \theta), \quad (169)$$

17. W. E. Byerly, "Fourier Series and Spherical, Cylindrical, and Ellipsoidal Harmonics," Ginn, 1893, p. 183.

with $\alpha_1 = 3\pi/8$, and

$$a_{\alpha+2} = \frac{(\alpha-2)(\alpha+2)(2\alpha+5)}{(\alpha+1)(\alpha+5)(2\alpha+1)} a_\alpha. \quad (170)$$

The connection between $U(M^{(n)})$ and the M_j can be expressed as the product of $U(M^{(n)})$ with the M_j up to $A^{(n+r+1)}$, where $n+r+1$ is the smallest integer such that $|m_{n+r+1}| = 2$. The only values of this product which are not zero are

$$U(M^{(n)}) : M_5^{(n+1)} : \dots : M_i^{(n+r)} : A^{(n+r+1)} =$$

$$= \begin{cases} -(2)_{n+1} \delta_{m_0}^0 & \ell=0, r=0 \\ \frac{3}{\sqrt{5}} \left(-\frac{1}{2}\right)^r (0)_{n+1} (0)_{n+2} \dots (0)_{n+r} (2)_{n+r+1} \delta_{m_0}^0 & \ell=2, r \geq 1 \\ \frac{2}{\sqrt{5}} (2)_{n+1} \delta_{m_0}^0 & \ell=2, r=0 \\ -\left(-\frac{1}{2}\right)^r \frac{1}{\sqrt{2\ell+1}} (1)_{n+1} (1)_{n+2} \dots (1)_{n+r-1} (1)_{n+r}' (2)_{n+r+1}' \delta_{m_0}^0 & \text{odd } \ell, r \geq 1 \end{cases} \quad (171)$$

The above connection formula completes the determination of $P_{jk}^{(\lambda)}$. For a given ψ_λ , $P_{jk}^{(\lambda)}$ may be evaluated by substituting ℓ , m_0 , and the m_q into Equations (164), (165), (166), and (171). It may be seen from these equations that $P_{jk}^{(\lambda)}$ is zero unless, for $j \geq k \geq n+1$,

- 1) $m_0 = 0$
- 2) $m_q = 0$ for $q \leq n$
- 3) $\delta_\ell^0 (2)_{n+1} + \delta_\ell^2 (0)_{n+1} + \delta_\ell^2 (2)_{n+1} + \delta_\ell^{\text{odd}} (1)_{n+1} = 1$
- 4) $|m_q| = 0, 1, \text{ or } 2$ for $n+1 \leq q \leq k-1$
- 5) $(1)_q (0)_{q+1} + (0)_q (1)_{q+1} = 0$ for $n+1 \leq q \leq k-2$
- 6) $(0)_{k-1} (0)_k + (1)_{k-1} (1)_k + (2)_{k-1} (0)_k + (2)_{k-1} (1)_k = 1$
- 7) $|m_q| = 0 \text{ or } 1$ for $k \leq q \leq j-2$
- 8) $(0)_q (0)_{q+1} = 0$ for $k \leq q \leq j-3$
- 9) $|m_{j-1}| = 1$
- 10) $m_j = 0$ for $q \geq j$.

Corresponding selection rules occur when $j \leq k \leq n$.

After $P_{jk}^{(\lambda)}$ has been determined, d_λ may be found from Equation (138). From selection rules 9) and 10) above, it is apparent that there is at most one nonzero term in the sum over j , corresponding to the largest j for which $|m_j| = 1$. The other selection rules permit more than one nonzero term in the sum over k only if there exists a q such that $|m_{q+1}| = |m_{q+2}| = \dots = |m_{q+r}| = 1$, $|m_{q+r+1}| = 0$, and q is the largest integer for which $|m_q| = 2$. For this case, there are r nonzero terms in d_λ . It may be shown that the cross product terms in $d_\lambda d_\lambda^*$ ($P_{jk}^{(\lambda)} P_{jk'}^{*(\lambda)}$ with $k \neq k'$) contribute nothing to $\Omega(\lambda)$. Furthermore, all of the squared terms $P_{jk}^{(\lambda)} P_{jk}^{*(\lambda)}$ are equal under these circumstances, so that we obtain the correct $\Omega(\lambda)$ if we use

$$d_\lambda d_\lambda^* = 4r a^4 (2n+1-j)^2 P_{jk}^{(\lambda)} P_{jk}^{*(\lambda)}. \quad (172)$$

The factor r is present only if there exists a q satisfying the criterion above. Since r changes $\Omega(\lambda)$ very slightly, it will be neglected in the later calculations.

From the equations for $P_{jk}^{(\lambda)}$, it may be seen that $d_\lambda d_\lambda^*$ does not depend explicitly upon the exact values of the nonzero m_q , but rather upon certain functions describing their number and relative positions. In order to express $d_\lambda d_\lambda^*$ succinctly, let us denote by μ the number of m_q between m_{n+1} and m_{k-1} that are equal to zero:

$$\mu \equiv \sum_{q=n+1}^{k-1} (0)_{\frac{q}{2}}. \quad (173)$$

Similarly, ν and ξ denote the number of ± 1 's and ± 2 's respectively:

$$\nu \equiv \sum_{q=n+1}^{k-1} (1)_{q_0}, \quad \text{and} \quad \xi \equiv \sum_{q=n+1}^{k-1} (2)_{q_0}. \quad (174)$$

Also, let α , β , and γ denote respectively the number of sets of 0's, ± 1 's, and ± 2 's between m_{n+1} and m_{k-1} , where a set of 0's, for example, is an uninterrupted string of one or more m_q having the value zero:

$$\alpha \equiv \sum_{q=n+1}^{k-1} [(0)_{q_0} - (0)_{q_0}(0)_{q+1}] + (0)_{k-1} \quad (175)$$

$$\beta \equiv \sum_{q=n+1}^{k-1} [(1)_{q_0} - (1)_{q_0}(1)_{q+1}] + (1)_{k-1} \quad (176)$$

$$\gamma \equiv \sum_{q=n+1}^{k-1} [(2)_{q_0} - (2)_{q_0}(2)_{q+1}]. \quad (177)$$

Finally, let σ be defined by Equation (159) above. Then $d_\lambda d_\lambda^*$ depends only upon α , β , γ , μ , ν , ξ , σ , and j , and upon ℓ , $|m_{n+1}|$, $|m_{k-1}|$, and $|m_k|$. As an example, let us choose $\ell = m_{k-1} = 0$. If $d_\lambda d_\lambda^*$ is not zero, it is necessary that $|m_{n+1}| = 2$, $m_k = 0$, and $|m_{k+1}| = 1$. Also, $m_0 = 0$, and $|m_{j-1}| = 1$. For this case, Equations (164), (165), (166), (171), and (172) give

$$d_\lambda d_\lambda^* = \frac{16}{9} a^{4(2n+1-j)} \left(\frac{3}{4}\right)^{2\alpha} \left(\frac{1}{2}\right)^{2\beta} (4)^{2\gamma} \left(\frac{1}{2}\right)^{2\mu} \left(\frac{1}{2}\right)^{2\nu} \left(\frac{1}{2}\right)^{2\xi} \left(\frac{1}{2}\right)^{2\sigma}, \quad (178)$$

where j is the largest integer such that $m_j \neq 0$. Values of ℓ , $|m_{n+1}|$, $|m_{k-1}|$, and $|m_k|$ other than those chosen above give the same dependence of $d_\lambda d_\lambda^*$ upon α , β , γ , μ , ν , ξ , σ , and j , but with a multiplicative constant different from 16/9.

APPENDIX III

EVALUATION OF $\Omega(\lambda)$

From Equation (72), $\Omega(\lambda)$ is approximately

$$\Omega(\lambda) = \sum_{\bar{\lambda} \in \Lambda} N(\bar{\lambda}) d_{\bar{\lambda}} d_{\bar{\lambda}}^*, \quad (179)$$

where $N(\bar{\lambda})$ is the number of d_{λ} having some particular absolute value, and $\bar{\lambda}$ is the average eigenvalue of these d_{λ} . From Appendix II, the absolute value of d_{λ} depends only upon ℓ , $|m_{n+1}|$, $|m_{k-1}|$, and $|m_k|$, and upon $\alpha, \beta, \gamma, \mu, \nu, \xi, \sigma$, and j . Hence, $N(\bar{\lambda})$ is the total number of nonzero d_{λ} that may be obtained by rearrangement of the m_q while keeping $\ell, |m_{n+1}|, \dots, j$ constant. The calculation is simplified somewhat by introducing the variable s in place of j ; s is equal to the total number of m_q from m_n up to m_{j-1} , inclusive:

$$s \equiv j - n - \mu - \nu - \xi - 1. \quad (180)$$

The dependent variable w will be used to denote $\mu + \nu + \xi$.

As an example of the method for finding $\Omega(\lambda)$, let us assume that $\ell = m_{n+1} = 0$, and thus that $|m_{n+1}| = 2$, $m_k = 0$, and $|m_{k+1}| = 1$.

Evaluation of $N(\bar{\lambda})$ may be facilitated by the following theorem:

there are

$$\binom{A-1}{B-1}$$

possible ways of placing A indistinguishable objects into B distinguishable sets with at least one object in each set [18]. Between m_{n+1} and m_{k-1}

18. E. Ising, Zeits. f. Physik. 31, 253 (1925), Footnote 1.

there are thus

$$2^{\nu+\xi} \binom{\mu-1}{\alpha-1} \binom{\nu-1}{\beta-1} \binom{\xi-1}{\gamma-1}$$

arrangements of the m_q into their sets. The factor $2^{\nu+\xi}$ is the number of possible arrangements of the plus and minus signs of the m_q .

It is also possible to show that there are

$$\binom{\gamma-1}{\alpha-1}$$

different ways of arranging the order of the sets, keeping $|m_{n+1}| = 2$, $m_{k-1} = 0$, and with alternate sets formed of ± 2 's. Finally, there are

$$2^{\sigma} \binom{\sigma-1}{s-\sigma-1}$$

arrangements of the ± 1 's and 0's between m_k and m_{j-1} , keeping $(0)_q(0)_{q+1} = 0$, $m_k = 0$, and $|m_{j-1}| = 1$. Combining these results, we have

$$N(\bar{\lambda}) = 2^{\nu+\xi+\sigma+1} \binom{\mu-1}{\alpha-1} \binom{\nu-1}{\beta-1} \binom{\xi-1}{\gamma-1} \binom{\gamma-1}{\alpha-1} \binom{\sigma-1}{s-\sigma-1}. \quad (181)$$

The additional power of two appears when both sides of the molecular chain are included in $N(\bar{\lambda})$.

From Equation (133) in Appendix I, the value of $\bar{\lambda}$ is

$$\bar{\lambda} = D_0 \sum_{q=2}^{2n-1} \left[1 - \left| \frac{q-n}{n} \right| \right]^{-2} \frac{1}{m_q^2} \quad (182)$$

when $\ell = 0$. Changing the summation to an integral:

$$\bar{\lambda} \cong D_0 \left[\frac{(\nu+4\xi)}{w} \int_{q-n=0}^w \frac{d(q-n)}{(1 - \frac{q-n}{n})^2} + \frac{\sigma}{s} \int_{q-n=w}^{w+s} \frac{d(q-n)}{(1 - \frac{q-n}{n})^2} \right], \quad (183)$$

or

$$\bar{\lambda} = \frac{n D_0 [\sigma n + (4\xi + \nu)(n - w - s)]}{(n-w)(n-w-s)}. \quad (184)$$

From Equation (178) in Appendix II and the above results, it follows that the contribution to $\Omega(\lambda)$ for $\lambda = m_{k-1} = 0$ is

$$[\Omega(\lambda)]_{\lambda=0} = \sum_{\substack{\sigma, s, \mu, \nu, \\ \xi, \alpha, \gamma}} \frac{32}{9} a^4 (n-w-s)^2 \left(\frac{3}{2}\right)^{2\alpha} \left(\frac{1}{2}\right)^{2\mu+\nu+3\xi+\sigma-2\gamma} \times \binom{\mu-1}{\alpha-1} \binom{\nu-1}{\beta-1} \binom{\xi-1}{\gamma-1} \binom{\gamma-1}{\alpha-1} \binom{\sigma-1}{s-\sigma-1}, \quad (185)$$

where $\beta = \gamma - \alpha$. When the sum is taken in the order $\sigma, s, \mu, \nu, \xi, \alpha, \gamma$, and γ , the limits are approximately $s/2 \leq \sigma \leq s$, $0 \leq s \leq n-w$, $\alpha \leq \mu \leq n-\nu-\xi$, $\beta \leq \nu \leq n-\xi-\alpha$, $\gamma \leq \xi \leq n-\gamma$, $0 \leq \alpha \leq \gamma$, $0 \leq \gamma \leq n/2$, and $\sigma n + (4\xi + \nu)(n-w-s) \leq \lambda(n-w)(n-w-s)/nD_0$.

If the molecule is very long ($n \gg 1$), the summation may be evaluated quite accurately by replacing the binomial coefficients with their asymptotic expansions for large numbers [19]. As an example, the first sum is

$$\sum_{\sigma} \left(\frac{1}{2}\right)^{\sigma} \binom{\sigma-1}{s-\sigma-1},$$

with limits $s/2 \leq \sigma \leq s$ and $\sigma \leq (n-w-s)\{[\lambda(n-w)/nD_0] - (4\xi + \nu)\}/n$. By expansion of the binomial term for σ near $2s/3$, the sum may be replaced by

$$\int \frac{1}{\sqrt{2\pi\sigma}} \exp\left[-\frac{(2s-3\sigma)^2}{2\sigma}\right] d\sigma.$$

This integral is approximately $1/3$, provided that

$$s \leq \frac{3(n-w)\left[\frac{\lambda}{nD_0}(n-w) - (4\xi + \nu)\right]}{2n\left\{1 + \frac{3}{2n}\left[\frac{\lambda}{nD_0}(n-w) - (4\xi + \nu)\right]\right\}}. \quad (186)$$

19. H. Jeffreys, "Theory of Probability," Oxford, Oxford University Press, 1939, p. 50.

If s is greater than this quantity, the integral is approximately zero. In this way, Equation (185) may be evaluated by a sevenfold integration. The result of the integration is the partial contribution to $\Omega(\lambda)$ for $\ell = m_{k-1} = 0$:

$$[\Omega(\lambda)]_{\ell=0, m_{k-1}=0} = \frac{8}{135} a^4 n^4 (c+3)^4 \left\{ \frac{(c+3)^4 - 3^4}{4} - c - 14 - 6 \ln(c+1) + \frac{12}{(c+1)} + \frac{4}{(c+1)^2} \right\}, \quad (187)$$

$$\text{where} \quad c \equiv 3\lambda/2\pi D_0. \quad (188)$$

To obtain the total value of $\Omega(\lambda)$, it is necessary to find $\bar{\lambda}$, $N(\bar{\lambda})$, and $d_{\bar{\lambda}} d_{\bar{\lambda}}^*$ for all values of ℓ , $|m_{k+1}|$, $|m_k|$, and $|m_k|$ which give nonzero $d_{\bar{\lambda}} d_{\bar{\lambda}}^*$. Change of these variables alters $d_{\bar{\lambda}} d_{\bar{\lambda}}^*$ by a multiplicative constant (see Appendix II), alters β slightly in terms of γ and α , and affects the term $\binom{\gamma-1}{\alpha-1}$ in $N(\bar{\lambda})$. Furthermore, the value of $\bar{\lambda}$ is dependent upon ℓ , but this effect can be neglected. When all the partial contributions to $\Omega(\lambda)$ are totalled, the final result is thirty times the partial sum given above:

$$\Omega(\lambda) = 30 [\Omega(\lambda)]_{\ell=0, m_{k-1}=0}. \quad (189)$$

From Equations (187) and (189), we can show that

$$\Omega(\infty) = \frac{4}{9} n^4 a^4. \quad (190)$$

$\Omega(\infty)$ may also be obtained from Equation (48):

$$\Omega(\infty) = \overline{\left[\sum_i (\rho_i^2 - 2z_i^2) \right]^2}, \quad (191)$$

that is, $\Omega(\infty)$ is the average over all possible configurations of the square of the sum over i of $(\rho_i^2 - 2z_i^2)$. By using Equations (136) and (137), it may be shown that Equation (191) leads to the same value for $\Omega(\infty)$ as is given above. This agreement serves as an excellent check on the magnitude of $\Omega(\lambda)$.

APPENDIX IV

CALCULATION OF THE STRESS RELAXATION

From Equation (80), the force at constant extension is

$$s(t) \Big|_{\epsilon} = \epsilon \int_0^{\infty} e^{-t/\tau} E'(\tau) d\tau. \quad (192)$$

If the function $Z(c)$ is defined by

$$Z(c) \equiv \frac{c^4}{(c+3)^2} \left\{ 142 + 3c + 24 \ln(c+1) - \frac{6(c+11)}{(c+1)} - \frac{4(3c+13)}{(c+1)^2} - \frac{8(c+3)}{(c+1)^3} \right\}, \quad (193)$$

Equation (75) may be written as

$$E'(\tau) = \frac{8N_0(k_b T)^2}{9a^2 \zeta_0} Z(c), \quad (194)$$

where $c = \tau_0/\tau$ and $\tau_0 = a^2 n \zeta_0 / 2k_b T$. Substitution of $E'(\tau)$ into Equation (192) gives

$$s(t) \Big|_{\epsilon} = \frac{4}{9} N_0 n k_b T \epsilon \int_0^{\infty} Z(c) e^{-(t/\tau_0)c} d\left(\frac{1}{c}\right). \quad (195)$$

The integrand has been evaluated numerically as a function of $1/c$ and integrated graphically. The results are given in the following table.

Table I

Theoretical Stress Relaxation for $\zeta_i = \zeta_0$.

t/τ_0	$\int_0^{\infty} Z(c) e^{-(\frac{t}{\tau_0})c} d\left(\frac{1}{c}\right)$	$s(t)/s(0)$
0	1.753	1.000
0.0035	1.676	0.956
0.01	1.553	0.886
0.035	1.257	0.717
0.1	0.846	0.483
0.35	0.310	0.177
1.0	0.070	0.040

The normalized stress $s(t)/s(0)$ is obtained by dividing the integral by 1.753.

The graphical integration may be checked by finding the exact value of the integral when $t=0$. By ordinary analytic methods, it may be shown that

$$\int_0^{\infty} \frac{Z(r)dr}{r^2} = \frac{7}{4}, \quad (196)$$

agreeing with the value obtained by graphical integration to within 0.2%. The stress at $t=0$ is thus

$$s(0) \Big|_{\epsilon} = \frac{7}{9} N_a n k_o T \epsilon. \quad (197)$$

$s(t)/s(0)$ is plotted versus the logarithm of t/τ_o in Figure 3, with τ_o equal to $10^{2.04}$ hours.

APPENDIX V

EVALUATION OF $\Omega(\lambda)$ FOR $\xi_i = \xi_0 A i^p$

It is the purpose of this appendix to calculate the diffusion tensor, the expansion coefficients of the potential, and $\Omega(\lambda)$ that result from the assumption:

$$\xi_i = \begin{cases} \xi_0 A i^p & i \leq n \\ \xi_0 A (2n+1-i)^p & i \geq n+1 \end{cases} \quad (198)$$

The derivation of the average diffusion tensor is carried out in Appendix I in a way somewhat more general than was first given by Kirkwood and Fuoss, and its results are directly applicable here. From Equations (126), (127), (128), and (129), the only nonzero terms in $\bar{D}$ are

$$\bar{D}_{\theta\theta} = \bar{D}_{\phi\phi} = \frac{(p+1)(p+2)D_0}{4An^p} \quad (199)$$

and

$$\bar{D}_{ii} = \frac{(p+1)(p+2)D_0}{2An^p \left[1 - \left|\frac{i-n}{n}\right|\right]^{p+2}}, \quad (200)$$

where, as before,

$$D_0 = 3k_B T / \xi_0 a^2 n^2. \quad (201)$$

The normalized eigenfunctions remain the same as in Equation (134), but the eigenvalues are now

$$\lambda = \frac{(p+1)(p+2)D_0}{2An^p} \left\{ \frac{1}{2} \ell(\ell+1) + \sum_{i=2}^{2n-1} \left[1 - \left| \frac{i-n}{n} \right| \right]^{-(p+2)} m_i^2 \right\}. \quad (202)$$

The expansion coefficients of the potential are

$$d_\lambda = \sqrt{f_0} \int \sum_{i=1}^{2n} \frac{\xi_i}{\xi_0} (\rho_i^2 - 2z_i^2) \psi_\lambda^* dq. \quad (203)$$

Using Equation (103) of Appendix I and neglecting $\frac{1}{2}a_{n+1}$, we find that

$$\sum_{i=1}^{2n} \frac{e_i}{\xi_i} z_i z_i \cong 2a^2 \sum_{j=2}^n \sum_{k=j}^n b(j) a_j \cdot a_k + 2a^2 \sum_{j=n+2}^{2n} \sum_{k=n+2}^j b(j) a_j \cdot a_k \quad (204)$$

and

$$\sum_{i=1}^{2n} \frac{e_i}{\xi_i} z_i^2 \cong 2a^2 \sum_{j=2}^n \sum_{k=j}^n b(j) (e_j \cdot a_j) (e_j \cdot a_k) + 2a^2 \sum_{j=n+2}^{2n} \sum_{k=n+2}^j b(j) (e_j \cdot a_j) (e_j \cdot a_k), \quad (205)$$

where

$$b(j) \equiv \begin{cases} \sum_{i=1}^{j-1} \frac{e_i}{\xi_i} & j \leq n \\ \sum_{i=j+1}^{2n} \frac{e_i}{\xi_i} & j \geq n+1 \end{cases} \quad (206)$$

By evaluating $b(j)$ and using $\rho_i^2 - 2z_i^2 = r_i^2 - 3z_i^2$ we find that

$$d_\lambda = \frac{2a^2 A}{(p+1)} \left[\sum_{j=2}^n \sum_{k=j}^n (j-1)^{p-1} \rho_{jk}^{(\lambda)} + \sum_{j=n+2}^{2n} \sum_{k=n+2}^j (2n+1-j)^{p-1} \rho_{jk}^{(\lambda)} \right]. \quad (207)$$

$\rho_{jk}^{(\lambda)}$ is unaltered by change of the diffusion coefficients and may be found from the formulas in Appendix II. For the example given previously, ($\ell = m_{k-1} = 0$), substitution of $\rho_{jk}^{(\lambda)}$ into Equation (207) gives, for $j \geq n+1$,

$$d_\lambda d_\lambda^* = \frac{16a^4 A^2}{9(p+1)^2} (2n+1-j)^{2p+2} \left(\frac{3}{4}\right)^{2\alpha} \left(\frac{1}{2}\right)^{2\beta} (4)^{2\gamma} \left(\frac{1}{2}\right)^{2\mu} \left(\frac{1}{2}\right)^{2\delta} \left(\frac{1}{4}\right)^{2\xi} \left(\frac{1}{2}\right)^{2\sigma} \quad (208)$$

It is now possible to find $\Omega(\lambda)$. $N(\bar{\lambda})$ has the same value as in Equation (151), but $\bar{\lambda}$ is

$$\bar{\lambda} = \frac{(p+1)(p+2) D_0}{2 A n^p} \sum_{q=2}^{2n-1} \left[1 - \left| \frac{q-n}{n} \right| \right]^{- (p+2)} \frac{1}{n^q} \quad (209)$$

when $\ell = 0$. Using an integral as an approximation to this summation,

we have

$$\bar{\lambda} = \frac{(p+2) n^2 D_0}{2 A} \left\{ \left(\frac{4\xi+2}{w} \right) \left[\frac{1}{(n-w)^{p+1}} - \frac{1}{n^{p+1}} \right] + \frac{\pi}{2} \left[\frac{1}{(n-w-\pi)^{p+1}} - \frac{1}{(n-w+\pi)^{p+1}} \right] \right\}. \quad (210)$$

From Equations (179), (181), and (208), the contribution to $\Omega(\lambda)$ when $\ell = m_{k-1} = 0$ is

$$[\Omega(\lambda)]_{\ell=0} = \sum_{\substack{\sigma, s, \mu, \nu, \\ m_{k-1}=0 \\ \xi, \alpha, \gamma}} \frac{32A^2 a^4}{9(\rho+1)^2} (n-w-s)^{2\rho+2} \left(\frac{3}{2}\right)^{2\sigma} \left(\frac{1}{2}\right)^{2\mu+\nu+3\xi+\sigma-2\gamma} \\ \times \binom{\mu-1}{\alpha-1} \binom{\nu-1}{\beta-1} \binom{\xi-1}{\gamma-1} \binom{\gamma-1}{\alpha-1} \binom{\sigma-1}{s-\sigma-1}. \quad (211)$$

The limits on this sum are the same as are given in Appendix III, except that the last one (derived from $\bar{\lambda} \leq \lambda$) is now

$$\left(\frac{n-w}{n-w-s}\right)^{\rho+1} \leq 1 + \frac{s(n-w)^{\rho+1}}{\sigma} \left\{ \frac{2A\lambda}{(\rho+2)n^2 D_0} - \left(\frac{4\xi+\nu}{w}\right) \left[\frac{1}{(n-w)^{\rho+1}} - \frac{1}{n^{\rho+1}} \right] \right\}. \quad (212)$$

By asymptotic expansion of the binomial terms for large values of the variables, the sum may be transformed into a sevenfold integral and evaluated by the procedures exemplified in Appendix III. Six integrations yield

$$[\Omega(\lambda)]_{\ell=0} = \frac{8A^2 a^4 n^{(2\rho+4)}}{45(\rho+1)^3(2\rho+3)} h(c) \quad (213)$$

where

$$h(c) = (c+3)^{-\left(\frac{2\rho+4}{\rho+1}\right)} \int_0^{1+c} \frac{\left(\frac{\rho+3}{\rho+1}\right)}{(x+2)^{\left(\frac{\rho+3}{\rho+1}\right)}} \left[1 - x^{-\left(\frac{2\rho+3}{\rho+1}\right)} \right] dx, \quad (214)$$

with

$$c = \frac{3n^{\rho+1}A}{(\rho+2)D_0}\lambda = \gamma'_0\lambda. \quad (215)$$

The seventh integral is not generally expressible in closed form.

As before, the total value of $\Omega(\lambda)$ is the sum of the contributions for various ℓ , $|m_{n+1}|$, $|m_{k-1}|$, and $|m_k|$. The relative magnitudes of the contributions are unaltered by change of the resistance constants, and $\Omega(\lambda)$ is thirty times the partial sum above.

From Equations (213) and (214) we may show that

$$\Omega(\infty) = \frac{8A^2 a^4 n^{2p+4}}{3(p+1)^2(p+2)(2p+3)} \quad (216)$$

As in Appendix III, it is also possible to find $\Omega(\infty)$ from Equation (48):

$$\Omega(\infty) = \overline{\left[\sum_i \frac{\xi_i}{\xi_0} (\rho_i^2 - 2z_i^2) \right]^2} \quad (217)$$

By using Equations (136) and (137) we find that this average leads to the same value for $\Omega(\infty)$ as is obtained above, indicating that the magnitude of $\Omega(\lambda)$ is correct.

APPENDIX VI

CALCULATION OF THE CORRECTED STRESS RELAXATION

When p is equal to five, $\bar{g}(c)$ in Equation (214) becomes

$$\bar{g}(c) = (c+3)^{-\frac{7}{3}} \int_1^{1+c} (x+2)^{\frac{4}{3}} (1-x^{-\frac{13}{6}}) dx. \quad (218)$$

We could find a solution in closed form for this integral, but it would be quite involved. Instead, we shall use the approximation that

$$\int_1^{1+c} (x+2)^{\frac{4}{3}} x^{-\frac{13}{6}} dx \cong (c+1)^{\frac{1}{6}} \left[6 - \frac{3.20}{(c+1)} - \frac{0.36}{(c+1)^2} \right] - 2.440. \quad (219)$$

From Equation (91), $E(\tau)$ is then equal to

$$E(\tau) = \frac{0.04072 N_0 (k_B T)^2 c^4}{\zeta_0 a^2 n^2 A (c+3)^{10/3}} \left\{ 7.287 + (c+1)^{\frac{1}{6}} \left[\frac{7}{3} \left(6 - \frac{3.20}{(c+1)} - \frac{0.36}{(c+1)^2} \right) - \left(\frac{c+3}{c+1} \right)^{\frac{7}{3}} \right] \right\}. \quad (220)$$

From Equation (94), the stress at constant extension is

$$s(t) \Big|_c = 0.005817 N_0 n k_B T c \int_0^{\infty - \frac{t}{\tau_c}} \frac{e^{-\frac{t}{\tau_c} c^2}}{(c+3)^{10/3}} \left\{ 7.287 + (c+1)^{\frac{1}{6}} \left[\frac{7}{3} \left(6 - \frac{3.20}{(c+1)} - \frac{0.36}{(c+1)^2} \right) - \left(\frac{c+3}{c+1} \right)^{\frac{7}{3}} \right] \right\} dc. \quad (221)$$

This integral has been evaluated graphically. The amount of graphical integration may be reduced considerably by analytic approximations to the tail of the integral from c_0 to ∞ , where c_0 is any number much greater than unity. Also, when t/τ_c' is much smaller than unity, $s(t) - s(0)$ may be determined analytically. Values of the integral for various t/τ_c' are given in the table below.

The graphical integration may be checked by computing the exact value of $s(0)$. For arbitrary p ,

$$s(0)\bigg|_{\epsilon} = \frac{(p+2)^2 N_0 n k_0 T \epsilon}{3(p+1)^3 (2p+3)} \int_0^{\infty} c^2 \frac{d h(c)}{dc} dc. \quad (222)$$

By ordinary methods, we find that

$$\int_0^{\infty} c^2 \frac{d h(c)}{dc} dc = \frac{(p+1)^3 (2p+1)}{2(p+2)(p+3)}. \quad (223)$$

For $p=5$, the integral is 59.79, agreeing with the value obtained by graphical integration to within 0.2%. It follows that

$$s(0)\bigg|_{\epsilon} = \frac{(p+2)(2p+1)}{6(p+3)(2p+3)} N_0 n k_0 T \epsilon. \quad (224)$$

For $p=5$, $s(t)/s(0)$ is plotted versus the logarithm of t/τ_0' in Figure 5, with τ_0' set equal to $10^{4.07}$ hours.

Table II

Theoretical Stress Relaxation for $\zeta_i = \zeta_0 A i^5$

t/τ_0'	$\int_0^\infty e^{-(\frac{t}{\tau_0'})c} c^2 \frac{d\zeta}{dc} dc$	$s(t)/s(0)$
0	59.86	1.000
10^{-9}	57.05	.953
10^{-8}	55.71	.931
10^{-7}	53.72	.897
10^{-6}	50.68	.850
10^{-5}	46.51	.777
10^{-4}	39.56	.661
10^{-3}	29.40	.491
10^{-2}	15.73	.263
0.017	12.62	.211
0.03	9.30	.155
0.06	5.77	.0964
0.1	3.74	.0625
0.17	2.14	.0358
0.3	1.07	.0179
0.6	0.35	.0059
1.0	0.12	.0021

APPENDIX VII

CALCULATION OF THE CORRECTED DIELECTRIC DISPERSION

The general solution of the diffusion equation for a polymer molecule in an electric field was given originally by Kirkwood and Fuoss [7]. Their solution is as follows. Let $\mathbf{e}_3$ be the unit vector in the direction of the electric field. Let μ_λ denote the expansion coefficients of $\boldsymbol{\mu} \cdot \mathbf{e}_3$, where $\boldsymbol{\mu}$ is the dipole moment of the molecule:

$$\boldsymbol{\mu} \cdot \mathbf{e}_3 = \frac{1}{\sqrt{f_0}} \sum_{\lambda} \mu_{\lambda} \psi_{\lambda}. \quad (225)$$

ψ_{λ} and λ , as before, are the set of eigenfunctions and eigenvalues of the diffusion operator $\nabla \cdot \mathbf{D} \cdot \nabla$. Let $\Omega(\lambda)$ be the sum of $\mu_{\lambda} \mu_{\lambda}^*$ for all $\lambda' \leq \lambda$, normalized so that $\Omega(\infty) = 1$:

$$\Omega(\lambda) = \frac{1}{(\boldsymbol{\mu} \cdot \mathbf{e}_3)^2} \sum_{\lambda' \leq \lambda} \mu_{\lambda'} \mu_{\lambda'}^*. \quad (226)$$

The normalization constant $\frac{1}{(\boldsymbol{\mu} \cdot \mathbf{e}_3)^2}$ is the average over all possible configurations of the square of $\boldsymbol{\mu} \cdot \mathbf{e}_3$. The reduced polarization of the polymer is

$$Q(\omega) = \int_0^{\infty} \frac{G(\tau) d\tau}{(1 + i\omega\tau)}, \quad (227)$$

where

$$G(\tau) = \left[\lambda^2 \frac{d\Omega}{d\lambda} \right]_{\lambda=1/\tau}. \quad (228)$$

Kirkwood and Fuoss calculate $Q(\omega)$ upon the assumption that $\epsilon_i = \epsilon_0$. Consequently, their result is applicable only to a dilute solution of the polymer. It is the purpose of this appendix to solve

for $Q(\omega)$ when $\zeta_i = \zeta_0 A i^p$. When p is five, this result should give the polarization of an unplasticized polymer. It will be assumed that the polymer is polyvinyl chloride.

In polyvinyl chloride, the individual dipole moments are associated with the C-Cl bonds. Let μ_{cl} be the scalar moment of each of these dipoles and b_k the unit vector in the direction of the C-Cl bond attached to the k -th carbon atom. Then

$$\mu = \mu_{cl} \sum_{\text{even } k} b_k \quad (229)$$

and

$$\mu_\lambda = \mu_{cl} \sum_{\text{even } k} \beta_\lambda^{(k)}, \quad (230)$$

where

$$\beta_\lambda^{(k)} = \sqrt{f_0} \int (b_k \cdot e_3) \psi_\lambda^* dq. \quad (231)$$

Using the geometry of the chain, we may show that^{*}

$$b_k \cdot e_3 = e_3 \cdot \Delta(\theta, \phi) \cdot \Delta(\eta, \chi_{n+1}) \cdot \Delta(\eta, \chi_{n+2}) \cdots \Delta(\eta, \chi_{k-1}) \cdot \Delta(\eta, \chi_k \pm \frac{2\pi}{3}) \cdot e_3, \quad (232)$$

if $k \geq n+1$. The matrix $\Delta(\theta, \phi)$ is defined by Equation (141). The integral for $\beta_\lambda^{(k)}$ may be evaluated in much the same manner as $\rho_{jk}^{(\lambda)}$ is found in Appendix II. For $k \geq n+1$, we find that

$$\begin{aligned} \beta_\lambda^{(k)} = & (-1)^{k-n-\sigma-1/2} \left(\frac{1}{2}\right)^\sigma (\gamma_\mp \delta_{m_k}^1 - \gamma_\pm \delta_{m_k}^{-1}) \prod_{q=n+2}^{k-1} [(1)_{q-1}' (1)_{q-1}'' (0)_q (1)_{q+1}'] \\ & \times \left[\frac{1}{\sqrt{3}} \delta_2^1 (0)_{n+1} (1)_{n+2}' - \sum_{\text{even } \alpha} \alpha' \sqrt{\frac{1}{2\alpha+1}} \delta_2^\alpha (1)_{n+1}' \right] \delta_{m_0}^\sigma \prod_{q=2}^n (0)_q \prod_{q=k+1}^{2n-1} (0)_q, \end{aligned} \quad (233)$$

^{*}The order of the dyadics in Equation (232) is the reverse of the order given by Kirkwood and Fuoss, which appears to be erroneous.

where $\gamma_{\pm}$ is $(1 \pm \sqrt{-3})/2$, and $(0)_q$, $(1)_q$, and $(1)'_q$ are defined in Appendix II^{*}. The numbers a'_α are the expansion coefficients of $\sin \theta$ in Legendre polynomials of $\cos \theta$ [17]:

$$\sin \theta = \sum_{\text{even } \alpha} a'_\alpha P_\alpha(\cos \theta), \quad (234)$$

with $a'_0 = \pi/4$ and

$$a'_{\alpha+2} = \frac{(\alpha-1)(\alpha+1)(2\alpha+5)}{(\alpha+2)(\alpha+4)(2\alpha+1)} a'_\alpha. \quad (235)$$

The quantity σ is equal to the number of m_q that are ± 1 :

$$\sigma = \sum_{q=2}^{2n-1} (1)_q. \quad (236)$$

From the form of $\beta_\lambda^{(k)}$ for $k \geq n+1$, it may be seen that μ_λ is zero unless there exists a k such that

- 1) $m_0 = 0$
- 2) $m_q = 0$ for $q \leq n$
- 3) $\delta'_\ell(0)_{n+1} + \delta_\ell^{\text{even}}(1)_{n+1} = 1$
- 4) $|m_q| = 0$ or 1 for $n+2 \leq q \leq k-1$
- 5) $(0)_q(0)_{q+1} = 0$ for $n+1 \leq q \leq k-2$
- 6) $|m_k| = 1$
- 7) $m_q = 0$ for $q \geq k+1$.

Corresponding selection rules occur if $k \leq n$. From 6) and 7), we may show that there is at most one nonzero $\beta_\lambda^{(k)}$ in the sum for μ_λ . It follows that

$$\mu_\lambda \mu_\lambda^* = \left(\frac{1}{2}\right)^{2\sigma} \left[\frac{1}{3} \delta'_\ell(0)_{n+1} + \sum_{\text{even } \alpha} \frac{(a'_\alpha)^2}{(2\alpha+1)} \delta_\ell^\sigma(1)_{n+1} \right] \mu_{cl}^2. \quad (237)$$

^{*}The positions of γ_+ and γ_- in Equation (233) are determined by the $\pm$ sign in Equation (232). Since $\beta_\lambda^{(k)} \beta_\lambda^{*(k)}$ does not depend upon the choice of sign, all the optical isomers of polyvinyl chloride have the same dielectric properties.

The next step is to evaluate $\Omega(\lambda)$. The same approximation can be used here as is employed in Appendix III:

$$\Omega(\lambda) \cong \frac{1}{(\mu \cdot e_3)^2} \sum_{\bar{\lambda} \leq \lambda} N(\bar{\lambda}) \mu_{\bar{\lambda}} \mu_{\bar{\lambda}}^* \quad (238)$$

$N(\bar{\lambda})$ is the number of nonzero μ_{λ} that may be obtained by rearrangement of the m_q while keeping ℓ , k , and σ constant; $\bar{\lambda}$ is the average eigenvalue of these μ_{λ} . For convenience, k will be replaced by the variable s , where s denotes the number of m_q between m_{n+1} and m_{k-1} inclusive:

$$s \equiv k - n. \quad (239)$$

As an example, let us assume that $\ell = 1$ and consequently that $m_{n+1} = 0$. From the theorem in Appendix III, it may be shown that

$$N(\bar{\lambda}) = 2^{\sigma+1} \binom{\sigma+1}{s-\sigma+1}. \quad (240)$$

The additional power of two appears when both sides of the chain are included in $N(\bar{\lambda})$. From Equation (209) in Appendix V, we have

$$\bar{\lambda} \cong \frac{(p+1)(p+2) D_0}{2 A n^p} \sum_{q=2}^{2n-1} \left[1 - \left| \frac{q-n}{n} \right| \right]^{-(p+2)} \frac{1}{m_q^2}. \quad (241)$$

The sum may be approximated by an integral, to give

$$\bar{\lambda} \cong \frac{(p+2) D_0 n^2 \sigma}{2 A s} \left[\frac{1}{(n-s)^{p+1}} - \frac{1}{n^{p+1}} \right]. \quad (242)$$

In addition, $\overline{(\mu \cdot e_3)^2}$ is equal to $n \mu_{\alpha}^2 / 3$ ^{*}. Combining Equations (237),

^{*} $\overline{(\mu \cdot e_3)^2} = \mu_{\alpha}^2 \sum_{j,k} (\bar{e}_3 \cdot b_k)(\bar{e}_3 \cdot b_j) = \mu_{\alpha}^2 \sum_j (\bar{e}_3 \cdot b_j)^2 = n \mu_{\alpha}^2 / 3.$

(238), and (240), we find that the contribution to $\Omega(\lambda)$ for $\ell=1$ is

$$[\Omega(\lambda)]_{\ell=1} = \frac{2}{n} \sum_{s, \sigma} \left(\frac{1}{2}\right)^{\sigma} \binom{\sigma-1}{s-\sigma-1}. \quad (243)$$

The limits on this sum are $0 \leq s \leq n$, $s/2 \leq \sigma \leq s$, s even, and

$$\sigma \leq \frac{2\lambda A s}{(p+2)D_0 n^2} \left[\frac{1}{(n-s)^{p+1}} - \frac{1}{n^{p+1}} \right]^{-1}. \quad (244)$$

If we introduce the asymptotic expansion of the binomial coefficient, the sum may be replaced by an integral

$$[\Omega(\lambda)]_{\ell=1} \approx \frac{1}{n} \int_{s=0}^n \int_{\sigma=s/2}^s \frac{1}{\sqrt{2\pi\sigma}} \exp\left[-\frac{(2s-3\sigma)^2}{2\sigma}\right] d\sigma ds, \quad (245)$$

with Equation (244) still to be added as a limit. The integral over σ is approximately $1/3$ if the limits include $2s/3$, and zero if they do not. Hence

$$[\Omega(\lambda)]_{\ell=1} = \frac{1}{n} \int_0^{s_0} \frac{ds}{3}, \quad (246)$$

with

$$\frac{2}{3} = \frac{2\lambda A}{(p+2)D_0 n^2} \left[\frac{1}{(n-s_0)^{p+1}} - \frac{1}{n^{p+1}} \right]^{-1}. \quad (247)$$

The second integration gives

$$[\Omega(\lambda)]_{\ell=1} = \frac{1}{3} \left[1 - (1 + \lambda \gamma'_0)^{-\frac{1}{p+1}} \right]. \quad (248)$$

As in Equation (90),

$$\gamma'_0 = \zeta_0 A a^2 n^{p+1} / (p+2) k_B T. \quad (249)$$

In order to find the total value of $\Omega(\lambda)$, it is necessary to add up the contributions for each value of ℓ . The dependence of $\bar{\lambda}$

upon ℓ can be neglected, and $\Omega(\lambda) = 3[\Omega(\lambda)]_{\ell=1}$:

$$\Omega(\lambda) = 1 - (1 + \lambda \tau'_0)^{-\frac{1}{p+1}}. \quad (250)$$

From Equations (227) and (228) it is readily found that

$$G(\tau) = \frac{\tau'_0}{(p+1) \tau^{\frac{p}{p+1}} (\tau + \tau'_0)^{\frac{p+2}{p+1}}} \quad (251)$$

and

$$Q(\omega) = \frac{\tau'_0}{(p+1)} \int_0^\infty \frac{d\tau}{\tau^{\frac{p}{p+1}} (\tau + \tau'_0)^{\frac{p+2}{p+1}} (1 + i\omega\tau)}. \quad (252)$$

By a change in variables, Equation (252) becomes

$$(i\omega\tau'_0 - 1)Q(\omega) = i\omega\tau'_0 \int_1^\infty \frac{r^{p-1} dr}{r^{p+1} + i\omega\tau'_0 - 1} - 1. \quad (253)$$

For arbitrary p , it is impossible to find $Q(\omega)$ in closed form. For $p=5$, however, the integration can be performed. We obtain

$$(i\omega\tau'_0 - 1)Q(\omega) = \frac{i\omega\tau'_0}{6y} \ln \left[\frac{(1+y)(1+y_+y)^{\frac{1}{6}}(1+y_-y)^{\frac{5}{6}}}{(1-y)(1-y_+y)^{\frac{1}{6}}(1-y_-y)^{\frac{5}{6}}} \right] - 1. \quad (254)$$

y is defined by

$$y = (1 - i\omega\tau'_0)^{\frac{1}{6}}. \quad (255)$$

As above, $y_{\pm}$ is $(1 \pm \sqrt{3})/2$. $Q(\omega)$ is given in the table below for various values of ω . $J(\omega)$ is the real part of $Q(\omega)$, while $-H(\omega)$ is the imaginary:

$$Q(\omega) = J(\omega) - iH(\omega). \quad (256)$$

The maximum value of $H(\omega)$ is about 0.143 at $\omega\tau_0' \cong 10$. $H(\omega)/H_{\max}$ is plotted in Figure 6, with τ_0' set equal to $10^{-1.99}$ seconds.

Table III

Theoretical Reduced Polarization for $\xi_i = \xi_{\infty} A i^5$

$\omega\tau_0'$	$J(\omega)$	$H(\omega)$	$H(\omega)/H_{\max}$
.01	.997	.0073	.051
.05	.988	.0236	.165
.2	.959	.0570	.398
.5	.923	.0837	.584
.7	.904	.0949	.662
1	.880	.1063	.742
2	.825	.1254	.875
5	.740	.1404	.980
7	.707	.1427	.996
10	.673	.1433	1.000
20	.606	.1399	.976
50	.525	.1290	.900
100	.468	.1193	.832
200	.418	.1085	.758
500	.359	.0947	.661
2,000	.285	.0759	.530
10,000	.218	.0583	.407

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