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A Molecular Theory of the Viscoelastic Behavior of an Amorphous Linear Polymer

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The kinetic theory of rubber elasticity is extended in two respects. First, the distribution of relative displacements of every chain atom is considered, not merely the distribution of relative chain-end displacements. Second, the rate of approach to elastic equilibrium, as well as the equilibrium itself, is considered. As a first approximation, it is predicted that a linear amorphous polymer will possess a distribution of elastic retardation times of the form $J(\tau)d\tau = (C \ln \tau - D)d \ln \tau$, where C and D are constants characteristic of the material.

INTRODUCTION

THE only well-established molecular theory relating to the plastoelastic properties of amorphous high polymers is the kinetic theory of long range elasticity.¹⁻³ This theory has proved valuable in understanding the magnitude and the temperature dependence of elastic moduli connected with configurational changes, and in the hands of Guth and James² has served as a quantitative tool in the study of a series of (cross-linked) elastomers. In the study of linear polymers, however, the kinetic theory has two serious shortcomings.

(1) The undue emphasis which the theory places on the separation of chain ends is acceptable only in the case of a cross-linked network, where mesh points take the place of chain ends. This emphasis corresponds to the assumption that a tensile stress acts upon a polymer molecule only through the chain ends—as though the chain ends were grasped by microscopic tweezers and pulled apart. This is justified in the case of a cross-linked polymer, since at elastic equilibrium the network bears the entire stress load, and the chains connecting the two mesh points are indeed pulled at the ends. It is never justified in the case of a linear polymer.

(2) In any case, the existing kinetic theory is purely an equilibrium treatment. It predicts an equilibrium elastic deformation in the presence of a stress, but does not yield any information concerning the transient conditions during the establishment of elastic equilibrium.

There is need for a molecular theory which eliminates these restrictions and predicts the viscoelastic spectrum of an amorphous linear polymer—i.e., the function $J(\tau)d\tau$, which gives the amount of elastic compliance* with retardation time τ in the range $d\tau$. The purpose of this paper is to lay down the general method which such a theory should follow, and to provide an explicit first approximation.

QUALITATIVE CONSIDERATIONS

The long chain molecules in an unstressed amorphous linear polymer are distributed among their possible configurations (shapes and orientations) according to the laws of statistics. Most molecules will be neither extended to maximum length nor tightly curled into balls, but will be in the statistically favored half-curled forms. Such a randomly kinked molecule will possess bends and convolutions of all sizes. There will be local kinks, of relatively short segments, bends and curls of intermediate size, and long range convolutions of the chain as a whole. When the sample is subjected to a tensile stress, this stress will act directly upon each unit of the chain, via its environment, not merely upon the chain ends. The stress tends to straighten out the molecule and orient it in the direction of the stress. A new equilibrium distribution of configurations will hold in the presence of the stress. In this new distribution, the local kinks, the intermediate curls, and the long range convolutions will all be somewhat straightened out and oriented. During the transient period when the new elastic equilibrium is being established, the local kinks will straighten out most quickly, the intermediate

¹ E. Guth and H. Mark, *Monats. F. Chem.* **65**, 93 (1934); *Naturwiss.* **25**, 353 (1937).

² E. Guth and H. M. James, *J. Chem. Phys.* **11**, 455 (1943); *Ind. Eng. Chem.* **33**, 1624 (1941).

³ F. T. Wall, *J. Chem. Phys.* **10**, 132 (1942); **10**, 485 (1942).

* The elastic compliance is the reciprocal of the modulus.

bends more slowly, and the long range convolutions most slowly of all. This results in a certain amount of elastic compliance which attains its equilibrium value quickly and other compliance which attains its equilibrium value slowly. Superimposed upon this retarded elastic response will be the irreversible flow which results from the slippage of entire chains past each other. This flow response can be separated out and will not be considered in this paper. In the limit, this behavior appears as a continuous distribution of elastic compliance over a wide range of retardation times.

The above qualitative remarks cannot be said to constitute a working theory, since they offer no computational framework for actually deducing the viscoelastic spectrum from molecular structure. In the following section, such a computational framework will be presented.

QUANTITATIVE CONSIDERATIONS

Consider a sample of a monodisperse linear polymer, made up of N molecules, each of which contains n chain atoms. In order to specify the position of each chain atom in the sample, $3nN$ coordinates are necessary. A point in $3nN$ -dimensional phase space expresses this information, and can be considered to represent a molecular configuration of the whole sample. The diffusional motion of the sample, including both the micro- and the macro-Brownian motion, can be represented by a diffusional motion of the point in phase space. Each point in phase space represents some definite macroscopic shape of the sample. In the absence of an external stress, the representative point wanders about through a region in phase space which corresponds to the "unstrained" shape of the sample. In the presence of a stress, the representative point wanders into new regions of phase space, which correspond to finite macroscopic strains. The whole problem of the plastoelastic behavior of such a material would be solved if we were able (1) to formulate and solve the equations of motion of the point in $3nN$ -dimensional phase space and (2) to compute the macroscopic strain from the values of the $3nN$ coordinates. The difficulties involved are obviously very great, if the $3nN$ Cartesian coordinates of the individual chain atoms are chosen as the reference coordinates. The question

arises—can a molecular configuration be described in terms of some set of parameters other than the Cartesian coordinates of the atoms, so chosen as to simplify the mathematical problem projected here?

Such a transformation of coordinates is, of course, common practice in strictly dynamical problems. The vibration and rotation of polyatomic molecules, for example, are most effectively approached in terms of the normal coordinates of the molecule. In general, the normal coordinates are complicated functions of the atomic Cartesian coordinates of the molecule. This fact, however, is more than compensated for by the simplicity of the equations of motion when expressed in terms of the new coordinates. Our problem is one of diffusion, rather than vibration, but it may still be helpful to replace the $3n$ atomic Cartesian coordinates for a given molecule by a new set of $3n$ coordinates in terms of which the diffusional motion can be more simply expressed, and more simply connected with the macroscopic strain. It should not be surprising if the new coordinates are complicated functions of the old; indeed, it would be surprising if this were not true.

In the first place, since we intend to separate out flow (irreversible displacements of whole molecules relative to each other) and consider only configurational elastic deformation (change in the distribution of molecules among shapes and orientations), the molecular phase space for each individual molecule is to be preferred to the $3nN$ dimensional phase space for the sample as a whole. In order to make an intelligent choice of the $3n$ coordinates which are to replace the Cartesian coordinates of the chain atoms, let us consider how the macroscopic configurational strain is determined by the molecular configuration of the sample. Any definite molecular configuration of the whole sample means a definite set of values of all $3nN$ atomic Cartesian coordinates, and hence a definite distribution of values of the $3n$ coordinates defining the configuration of each individual molecule. This can be represented by a density distribution function about a reference point such as an end of the chain. This density distribution is the sum of the density distributions for the individual chain atoms. We already have, from the kinetic theory of high

elasticity, an expression for the (equilibrium unstressed) density distribution of the second chain end about the first.⁴

$${}^nW_0(x, y, z) = \frac{A}{n^{\frac{1}{2}}} \cdot \exp \left[-\frac{B}{n} (x^2 + y^2 + z^2) \right]. \quad (1)$$

The constant A is here chosen to normalize W_0 to unity. Using this expression for the equilibrium unstressed density distribution of the r th chain atom about the first, whether the r th atom is a chain end or not, we obtain for the total (equilibrium unstressed) density distribution about an end of the chain:

$${}^nD_0(x, y, z) = \sum_{r=1}^n \frac{A}{r^{\frac{1}{2}}} \cdot \exp \left[-\frac{B}{r} (x^2 + y^2 + z^2) \right]. \quad (2)$$

This density distribution is spherically symmetrical and corresponds to the unstrained state. A linear high polymer which possesses configurational strain will have a different distribution among molecular shapes, and hence a different density distribution function which will not be spherically symmetrical, but rather ellipsoidally symmetrical, at least for small strains.

According to Wall,⁵ a tensile stress S in the x direction changes the equilibrium distribution of chain end separations from the form (1) to a form which can be rewritten as follows (for small stresses):

$${}^nW_S(x, y, z) = \frac{A}{n^{\frac{1}{2}}} \cdot \exp \left\{ -\frac{B}{n} \left[\frac{x^2}{(1+an)^2} + (1+an)(y^2 + z^2) \right] \right\}, \quad (3)$$

where

$$a = S/3\rho kT.$$

We now assume that in the presence of the stress the equilibrium distribution of the r th chain atom, whether it is a chain end or not, about the first, is given by the analogous expression (4).

This specific assumption is admittedly not justified in any rigorous fashion, but is introduced as a reasonable first approximation. A rigorous justification may be possible.

$${}^rW_S(x, y, z) = \frac{A}{r^{\frac{1}{2}}} \cdot \exp \left\{ -\frac{B}{r} \left[\frac{x^2}{(1+ar)^2} + (1+ar)(y^2 + z^2) \right] \right\}. \quad (4)$$

It follows that the total equilibrium density distribution function in the stressed state, including the distribution of each successive chain atom about the first, is given by the equation:

$${}^nD_S(x, y, z) = \sum_{r=1}^n \frac{A}{r^{\frac{1}{2}}} \cdot \exp \left\{ -\frac{B}{r} \left[\frac{x^2}{(1+ar)^2} + (1+ar)(y^2 + z^2) \right] \right\}. \quad (5)$$

We now assume that the macroscopic strain is connected with the smeared-out molecular shape by the following equation:

$$1 + \gamma_{xx} = \frac{L}{L_0} = \frac{\int_0^\infty \int_0^\infty \int_0^\infty x \cdot {}^nD_S(x, y, z) dx dy dz}{\int_0^\infty \int_0^\infty \int_0^\infty x \cdot {}^nD_0(x, y, z) dx dy dz}. \quad (6)$$

This compares the mean extension-in- x of a molecule in the strained state to that in the unstrained state. It is an extension of the ordinary kinetic theory approximation which compares the mean x separation of the chain ends with that in the unstrained state. (In the rest of the discussion, other subscripts will appear. In order to avoid multiple subscripts, it will be assumed that γ always refers to an x tensile strain, γ_{xx} .) Using the assumed density distribution (5) for the stressed state, it is possible to evaluate the integrals in (6) explicitly.

$$1 + \gamma = \frac{\int_0^\infty \int_0^\infty \int_0^\infty x \cdot \sum_{r=1}^n \frac{A}{r^{\frac{1}{2}}} \cdot \exp \left\{ -\frac{B}{r} \left[\frac{x^2}{(1+ar)^2} + (1+ar)(y^2 + z^2) \right] \right\} dx dy dz}{\int_0^\infty \int_0^\infty \int_0^\infty x \cdot \sum_{r=1}^n \frac{A}{r^{\frac{1}{2}}} \cdot \exp \left\{ -\frac{B}{r} [x^2 + y^2 + z^2] \right\} dx dy dz}, \quad (7)$$

⁴ Cf. citations in reference 1-3.

⁵ Cf. citations in reference 3.

$$1 + \gamma = \frac{\sum_{r=1}^n (r^{\frac{1}{2}} + ar^{\frac{1}{2}})}{\sum_{r=1}^n r^{\frac{1}{2}}}. \quad (8)$$

As an approximation we replace these two sums by integrals.

$$1 + \gamma = \frac{\int_1^n (r^{\frac{1}{2}} + ar^{\frac{1}{2}}) dr}{\int_1^n r^{\frac{1}{2}} dr}, \quad (9)$$

$$1 + \gamma = \frac{\int_0^\infty \int_0^\infty \int_0^\infty x \cdot \exp \left\{ -\frac{B}{n} \left[\frac{x^2}{(1+an)^2} + (1+an)(y^2+z^2) \right] \right\} dx dy dz}{\int_0^\infty \int_0^\infty \int_0^\infty x \cdot \exp \left\{ -\frac{B}{n} (x^2+y^2+z^2) \right\} dx dy dz}, \quad (13)$$

$$1 + \gamma = 1 + \frac{nS}{3\rho kT}, \quad (14)$$

$$\gamma = \frac{nS}{3\rho kT}. \quad (15)$$

The extended analysis thus yields no significantly new information concerning the equilibrium value of the *total* configurational elastic strain. The value of the new treatment lies in the fact that we can now resolve the total configurational strain into a series of terms $\gamma_1, \gamma_2, \gamma_3, \dots$, which indicate the strain contributions of chain sections of different lengths. This analysis follows.

First, for illustration, we will divide γ into a part γ_1 which is due to the uncurling and orientation of chain segments which are shorter than the length m , and a part γ_2 which is due to the uncurling and orientation of longer chain segments.

Consider the various segments, containing m chain atoms, as though they were complete molecules. There will be a certain density distribution ${}^mD(x, y, z)$ which will represent the average, or smeared-out, extension in space of these segments, in exactly the fashion that ${}^nD(x, y, z)$ represents the whole molecule.

$$1 + \gamma = 1 + \frac{3a}{5} \cdot \frac{(n^{5/2} - 1)}{(n^{3/2} - 1)}. \quad (10)$$

For large n , this reduces to:

$$1 + \gamma = 1 + \frac{3a}{5} \cdot n = 1 + \frac{nS}{5\rho kT}, \quad (11)$$

$$\gamma = \frac{nS}{5\rho kT}. \quad (12)$$

Except for the numerical factor, this result agrees with that obtained by the ordinary kinetic theory, where only the distribution of chain ends is considered. Considering only the ends, we would have obtained:

$${}^mD_s(x, y, z) = \sum_{r=1}^m \frac{A}{r^{\frac{1}{2}}} \times \exp \left\{ -\frac{B}{r} \left[\frac{x^2}{(1+ar)^2} + (1+ar)(y^2+z^2) \right] \right\}. \quad (16)$$

The elastic strain which results from the uncurling and orientation of short segments (containing less than m atoms) may be designated by γ_1 , and the strain which results from the uncurling and orientation of long segments by γ_2 .

$$\gamma_1 = \frac{\int \int \int x^m D_s(x, y, z) dx dy dz}{\int \int \int x^m D_0(x, y, z) dx dy dz} - 1, \quad (17)$$

$$\gamma_2 = \frac{\int \int \int x^n D_s(x, y, z) dx dy dz}{\int \int \int x^n D_0(x, y, z) dx dy dz} - \frac{\int \int \int x^m D_s(x, y, z) dx dy dz}{\int \int \int x^m D_0(x, y, z) dx dy dz}, \quad (18)$$

$$\gamma = \gamma_1 + \gamma_2 = \frac{\iiint x^n D_S(x, y, z) dx dy dz}{\iiint x^n D_0(x, y, z) dx dy dz} - 1. \quad (19)$$

By a generalization of this procedure, the total strain γ can be resolved into $(n-1)$ components, $\gamma_2, \gamma_3, \gamma_4, \dots, \gamma_n$, where each contribution arises from the shape changes of molecular segments of a given size.

$$\gamma_j = \frac{\iiint x^j D_S(x, y, z) dx dy dz}{\iiint x^j D_0(x, y, z) dx dy dz} - \frac{\iiint x^{j-1} D_S(x, y, z) dx dy dz}{\iiint x^{j-1} D_0(x, y, z) dx dy dz}, \quad (20)$$

$$\gamma = \sum_{j=2}^n \gamma_j. \quad (21)$$

The form of the above equations suggests a new set of coordinates $(X_1, Y_1, Z_1, X_2, Y_2, Z_2, \dots, X_n, Y_n, Z_n)$ to describe the configuration of a single molecule and thus take the place of the atomic Cartesian coordinates $(x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_n, y_n, z_n)$. Let X_1, Y_1 , and Z_1 represent the x, y , and z coordinates, respectively, of the center of gravity of the polymer molecule. Let X_j be defined by the expression:

$$X_j = M_j - M_{j-1}, \quad (22)$$

$$\text{where } M_j = \frac{\bar{L}_j}{\iiint x^j D_0(x, y, z) dx dy dz},$$

where \bar{L}_j = the average value of L_j for all segments of size j in the molecule under consideration, where L_j for a segment of size j is given by:

$$L_j = \frac{1}{8} \sum_{k=2}^j |x_k|,$$

and x_k is the x displacement of the k th chain atom of a given segment from the first atom of that segment. Thus just as γ_j represents the macroscopic x tensile strain due to the uncurling

and orientation of molecular chain segments containing j atoms when a given distribution of shapes is present, so X_j represents the mean relative uncurling and x orientation of the chain segments containing j atoms in a single polymer molecule of a definite shape.

If the new coordinates X_i, Y_i , etc., were a linear combination of the atomic Cartesian coordinates, $x_1, y_1, z_1, x_2, y_2, z_2, \dots$ etc., then they would represent an equivalent set of independent variables which together would define the configuration of a polymer molecule. Actually, the *absolute magnitudes* of certain quantities enter in place of the algebraic values. Hence the new "coordinates," X_1, X_2, \dots , do not represent a linear transformation of the original Cartesian coordinates. The X 's are not strictly a set of "normal coordinates" for the polymer molecule, although they are introduced for analogous reasons.

Just as a given distribution of molecular configurations results in a series of density distributions ${}^iD(x, y, z)$, so it also results in a series of probability distributions governing the various X 's—e.g., $D(X_j)$. The strain γ_j is given by:

$$\bar{X}_j = \gamma_j = \int_{-\infty}^{\infty} X_j D(X_j) dX_j. \quad (23)$$

In particular, the equilibrium unstressed distribution of molecular shapes, which gave rise to the density distributions ${}^mD_0(x, y, z)$, will also give rise to the distributions $D_0(X_j)$, such that

$$\gamma_j = \bar{X}_j = \int_{-\infty}^{\infty} X_j D_0(X_j) dX_j = 0. \quad (24)$$

In the presence of a stress, there will be a new equilibrium distribution of molecular shapes, and hence a new equilibrium distribution of the values of each of the X 's, and new equilibrium values of the macroscopic strain contributions $\gamma_2, \gamma_3, \gamma_4, \dots, \gamma_n$. The local kinkiness, defined by the X 's of low index, will take on its equilibrium distribution rather quickly; the long range convolutions, defined by the X 's of large index, will assume the new equilibrium distribution more slowly.

It follows from Eqs. (5) and (20) that the equilibrium value of γ_i is given by:

$$\gamma_i = S/5\rho kT. \quad (25)$$

Similarly, the equilibrium value of \bar{X}_j , the mean value of the coordinate X_j , has the value $S/5\rho kT$.

Finally, the contribution to the elastic compliance in tension which is furnished by the configurational changes of segments containing n atoms (in the range dn) is given by:

$$J(n)dn = (1/5\rho kT)dn. \quad (26)$$

We can now return to the question of the rate of attainment of elastic equilibrium. We have advanced the general hypothesis that the local kinkiness, defined by the X 's of low index, will take on its equilibrium distribution rather quickly, while the long range convolutions of the chains, defined by X 's of large index, will assume the new equilibrium distribution more slowly. Let us now specifically assume that each contribution to γ relaxes into its new equilibrium value in a simple exponential fashion, with a retardation time τ which is connected with the chain length of the corresponding segment in the same fashion that the melt viscosity of a linear polymer is connected with the molecular chain length.⁶

$$\tau_n = Ae^{b\sqrt{n}}e^{\Delta E/RT}. \quad (27)$$

This would seem to be a reasonable assumption as long as n is considerably greater than the length of the effective segments which act in flow and diffusion.

If we combine Eq. (27), which gives the retardation time for the configurational changes of a chain section of size n , with Eq. (26), which gives the elastic compliance associated with a range of sizes dn , we can deduce the function $J(\tau)$, which gives the elastic compliance as a function of retardation time. The function so obtained is:

$$\begin{aligned} &= 0 \quad \text{for} \quad \ln \tau < \alpha \\ J(\tau)d\tau &= \frac{2}{5b^2\rho kT} \cdot \left(\frac{\ln \tau - \ln A - \Delta E/RT}{\tau} \right) d\tau \quad (28) \\ &\quad \text{for} \quad \alpha < \ln \tau < \beta \\ &= 0 \quad \text{for} \quad \ln \tau > \beta \end{aligned}$$

where

$$\alpha = \ln A + \frac{\Delta E}{RT}, \quad \beta = \ln A + \frac{\Delta E}{RT} + b\sqrt{n}.$$

In the above form, the dependence on temperature as well as on τ is given. At a definite tem-

perature, the above equation can be expressed in the form:

$$J(\tau)d\tau = \frac{C \ln \tau - D}{\tau} d\tau \quad \text{for} \quad \alpha > \ln \tau > \beta. \quad (29)$$

The theory thus leads to precisely the sort of mechanical behavior which has been empirically assigned to amorphous polymers—i.e., a distribution of elastic compliance over a wide range of retardation times. The theory as presented here must certainly fall down very badly in the low τ region, which corresponds to the shape changes of very short segments. In the first place, the equilibrium distribution law (1) should not be applied to very short sections. Furthermore, the assumption that τ_n is given by Eq. (27) cannot be expected to hold for segments which are not several times as long as the "Eyring segments" which serve as the moving units of flow and diffusion. All assumptions involved in the theory are much more justified in the high τ region of the spectrum. In the case of very high molecular weight polymers, this high τ part of the spectrum should be relatively more important than in the case of a low molecular weight polymer, and hence the theory should be relatively more satisfactory for a very high polymer than for a low polymer.

In spite of the fact that the present treatment introduces specific assumptions which, at best, should be applied only to large segments, the writer feels that the general method involved represents a rational approach to the molecular theory of viscoelastic behavior in linear amorphous polymers. The theory can presumably be improved in the low τ region by the following extensions:

(1) Equation (1) is rigorously applicable only to chain atoms which are separated by a large number of chain units. A return should, therefore, be made to the original stochastic problem from which (1) is derived as a limiting form. A new distribution function $W(x, y, z, n)$, valid for small n as well as large, should replace (1) in the present treatment.

(2) An improved approximation to the function $\tau(n)$ should be developed to replace (27). An heuristic approach would seem indicated here. For example, the retardation times for shape changes of small segments might be expected to depend upon segment length in a manner analogous to that in which the viscosities of short molecules depend upon their length.

⁶ P. J. Flory, J. Am. Chem. Soc. **62**, 1057 (1940).