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## Elastic Loss and Relaxation Times in Cross-Linked Polymers

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The outlines of a theory of elastic loss in cross-linked polymers are developed on the basis of the ideas underlying the theory of dielectric loss of Fuoss and the writer and the three-dimensional network model of rubber structure proposed by James and Guth. The relaxation time distribution function for elastic loss is given in the approximation of free internal rotation of chain segments of the net. The influence of intermolecular hindering torques and network restraints on the relaxation time spectrum is discussed, but explicit calculations are postponed for a later report.

THE statistical theory of the equilibrium elastic behavior of rubber has contributed greatly to our understanding of the structure of cross-linked polymers, although from the quantitative point of view it still leaves something to be desired. The basic assumption of the theory is that the resistance offered to deformation by a cross-linked polymer network is principally due to the decrease in configurational entropy attending the elongation of the chain segments of the net.

If a time-dependent stress is applied to a polymer network, the finite time of response of the chain segments leads to a phase difference between strain and stress and a resultant energy dissipation in the specimen known as elastic loss. The elongation response of a chain segment of the network to the applied stress is accomplished by internal rotatory Brownian motion, which is associated with a relaxation time spectrum of the type described by Fuoss and the writer<sup>1</sup> in their theory of dielectric loss in polar polymers. It is

our purpose in the present article to sketch the outlines of a theory of elastic loss in cross-linked polymers on the basis of the ideas underlying the theory of dielectric loss.

As a preliminary step in the formulation of the theory of elastic loss, it is necessary to adopt a model for the polymer network spanning a specimen of a rubber-like material. Following the early qualitative theories of rubber elasticity,<sup>2</sup> two types of network model have been proposed in efforts to refine the theory. The one is the three-dimensional network of James and Guth<sup>3</sup> and the other is the model of Wall and Flory.<sup>4</sup> While it is not our purpose here to make a judgment on the relative merits of the two models in the equilibrium case, we have decided that the more detailed structural model of James and Guth offers the greater insight into the mechanism of the irreversible deformation of

<sup>2</sup> E. Guth and H. Mark, *Monats. f. Chemie* **65**, 93 (1934); Kuhn, *Kolloid Zeits.* **76**, 258 (1936).

<sup>3</sup> H. M. James and E. Guth, *J. Chem. Phys.* **11**, 455 (1943).

<sup>4</sup> F. T. Wall, *J. Chem. Phys.* **10**, 132, 485 (1942); P. Flory, *Chem. Rev.* **35**, 51 (1944); L. R. G. Treloar, *Trans. Faraday Soc.* **40**, 59 (1944).

<sup>1</sup> J. G. Kirkwood and R. M. Fuoss, *J. Chem. Phys.* **9**, 329 (1941).

the network associated with internal rotatory Brownian motion of the chain segments. At the same time, we recognize the possibility of developing a theory of elastic loss on the basis of the Flory-Wall model along the lines suggested by Alfrey.<sup>5</sup>

Before proceeding to the formulation of the theory, we must remark that it is not designed to account for all of the elastic loss, but only that part in excess of frequency independent loss associated with the permanent rupture of cross-linking bonds and with chemical alteration of the specimen. There is, of course, no experimental difficulty in separating the two types of loss for independent study.

We shall consider a rubber consisting of a cross-linked polymer network, possibly imbedded in a matrix of polymer chains not participating in the net structure. Following James and Guth,<sup>3</sup> we replace the irregular cross-linked network by a regular cubic array, each lattice point of which is connected to its nearest neighbors by a polymer chain segment composed of  $n$  bonds. We shall refer to each skeletal atom of the chain together with side chain groups bonded to it as a monomer unit. We denote the lattice parameter of the network by  $a$ , the number of chains per unit cross-section by  $\nu$ , and the number,  $\nu a$ , of chains per unit length by  $M$ .

When a stress  $\sigma$  is applied, let us say in the  $z$  direction, parallel to the axis of a thin cylindrical specimen of the polymeric material, we shall assume that it is distributed on the microscopic scale uniformly among the  $\nu$  lattice points per unit area in each cross-sectional plane of the network perpendicular to the axis of the specimen.\* Under this assumption, the terminal elements of each chain segment between successive

network planes are subjected to forces  $+F$  and  $-F$ , respectively, in the  $z$  direction, where

$$F = \sigma/\nu. \quad (1)$$

Under the action of the terminal forces the length  $z$  of the chain segment changes by internal rotatory Brownian motion, and a strain  $\epsilon_{zz}$  is developed.

$$\begin{aligned} \epsilon_{zz} &= \Delta z/a, \\ \Delta z &= z - a. \end{aligned} \quad (2)$$

As the length of the chain segments oriented in the  $z$  direction increases, the average force exerted by them on the chains oriented in the  $x$  and  $y$  directions is altered in such a manner that the latter contract. The resulting Poisson effect in rubbers is in general adequately described by the assumption of incompressibility and the strains  $\epsilon_{xx}$  and  $\epsilon_{yy}$  are approximately equal to  $-\epsilon_{zz}/2$ .

If the specimen is subjected to a time-dependent stress of the form of the real part of

$$\sigma = \sigma_0 e^{i\omega t} \quad (3)$$

of frequency  $\omega/2\pi$ , and the strain response is  $\epsilon_{zz}^0 e^{i\omega t}$ , the modulus of elasticity  $E$  is defined by the relation,

$$1/E = \epsilon_{zz}^0/\sigma_0. \quad (4)$$

It is the object of the present theory to determine the real and imaginary parts of the elastic modulus  $E$  as functions of frequency on the basis of the schematic model of polymer structure which has just been described. The elastic loss in the specimen is of course determined by the imaginary part of  $1/E$ . If we write

$$1/E = 1/E' - i/E'', \quad (5)$$

the rate of energy dissipation per unit volume is given by

$$-(du/dt) = \frac{\omega^2 \sigma_0^2}{4\pi E''}. \quad (6)$$

Since we wish to use the concept of relaxation time associated with the linear stimulus-response theory, we shall develop the theory in the linear approximation and will not consider departures from Hooke's law. However, it should be remarked that the theory will be valid for time-

<sup>5</sup> T. Alfrey, J. Chem. Phys. 12, 374 (1944).

\* This assumption is consistent with the perhaps oversimplified model of rubber structure of James and Guth, provided inertial effects are neglected. Equation (1), of course, represents the average terminal force on a chain segment arising from the applied stress, from which there will be fluctuations. However, we shall be interested only in the average force in the subsequent analysis.

A more drastic assumption presently to be made is that intermolecular hindering torques, acting on internal elements of a chain segment, have their equilibrium values even when the specimen is subjected to a time-dependent external stress. This assumption, equivalent to neglecting intermolecular relaxation effects, should be subjected to a more careful investigation, in future attempts to refine the preliminary theory to be described here.

dependent stresses of small amplitude superimposed upon static stresses of arbitrary magnitude. In the latter case the modulus  $E$  may, of course, depend upon the static stress in the initial state. It is sufficient to develop the theory for an harmonic time dependent stress of a single frequency. When the applied stress has arbitrary Fourier composition, each Fourier component can be treated independently by the methods to be described, insofar as the strain response  $\epsilon_{zz}$  is linear in the stress.

Each chain segment connecting neighboring lattice points is supposed to consist of  $n$  bonds  $\mathbf{r}_1 \cdots \mathbf{r}_n$ , each of length  $b$ . The vector  $\mathbf{R}$  connecting the terminal elements of the chain is

$$\mathbf{R} = \sum_{l=1}^n \mathbf{r}_l. \quad (7)$$

If we assume a fixed bond angle  $\gamma$ , the internal configuration of the chain is most simply described by coordinates  $\varphi_1, \dots, \varphi_{n-1}$ , where  $\varphi_l$  denotes the angle between the plane of bonds  $l$  and  $l+1$  and the plane of bonds  $l+1$  and  $l+2$ , in addition to the angles  $\vartheta$  and  $\varphi$  specifying the orientation of any one bond, say the central bond of the chain, relative to the external coordinate system. For brevity in notation, we shall denote the set of internal coordinates  $\varphi_1, \dots, \varphi_{n-1}, \varphi, \vartheta$  by  $q$ , when it is only necessary to consider them collectively.

The ensemble representing the statistical behavior of the chains comprising a specimen of the polymeric material is characterized by a probability distribution function  $f(q, t)$  in the configuration space  $q$  of a chain. If  $\mathbf{e}_1$  is a unit vector in the  $z$  direction, the projection of the average length of a chain on the  $z$  axis is

$$\langle z \rangle_{av} = \int \mathbf{R} \cdot \mathbf{e}_1 f(q, t) dq. \quad (8)$$

In the equilibrium unstressed state  $\langle z \rangle_{av}$  is equal to the lattice parameter  $a$ , given by

$$\begin{aligned} a &= \int \mathbf{R} \cdot \mathbf{e}_1 f_0(q) dq, \\ f_0(q) &= A_0 \exp(-V_0/kT), \\ A_0^{-1} &= \int \exp(-V_0/kT) dq, \end{aligned} \quad (9)$$

where  $V_0$  is the potential of the average inter-

molecular and intramolecular forces inhibiting internal rotational motion of the chain.

As has been pointed out by James and Guth,<sup>3</sup> the system of forces  $+F$  and  $-F$  of Eq. (3) applied to the terminal elements of the chain can be derived from the potential,  $-F(\mathbf{R} \cdot \mathbf{e}_1)$ . Thus, according to our model, the potential of average force in the presence of an applied stress  $\sigma$  in the  $z$  direction is,

$$\begin{aligned} V &= V_0 - (\mathbf{R} \cdot \mathbf{e}_1)F, \\ F &= \sigma/\nu, \end{aligned} \quad (10)$$

where  $\nu$  is the number of chains per unit cross section.

By the theory of Brownian motion, the distribution function  $f(q, t)$  satisfies the generalized diffusion equation<sup>1</sup>

$$\begin{aligned} \nabla \cdot \mathbf{D} \cdot \{\nabla f + f \nabla V/kT\} &= \partial f / \partial t, \\ \mathbf{D} &= kT \zeta^{-1}, \end{aligned} \quad (11)$$

where  $\nabla$  is the gradient operator in the  $q$ -space of a chain and  $\mathbf{D}$  is the diffusion tensor, related by the second of Eqs. (11) to the resistance tensor  $\zeta$ . It is sufficient for our purposes to consider applied stresses with harmonic dependence on the time  $t$ ,

$$\sigma = \sigma_0 e^{i\omega t},$$

of frequency  $\omega/2\pi$ . When the stress has an arbitrary Fourier composition, each Fourier component of the form (3) can be treated independently by the methods to be described, insofar as the strain response  $\epsilon_{zz}$  is linear in the stress.

If we expand the distribution function  $f(q, t)$  satisfying Eq. (11) in powers of the stress amplitude  $\sigma_0$  in the form,

$$\begin{aligned} f &= A_0 \exp(-V_0/kT) \\ &\times \left[ 1 + \frac{\sigma_0}{\nu} e^{i\omega t} f_1(q, t) + O(\sigma_0^2) \right], \end{aligned} \quad (12)$$

we obtain the following differential equation for the function  $f_1(q, t)$ :

$$\begin{aligned} L(f_1 - (\mathbf{R} \cdot \mathbf{e}_1)/kT) - i\omega f_1 &= 0, \\ \omega \rightarrow 0; \quad f_1 \rightarrow [\mathbf{R} \cdot \mathbf{e}_1 - a]/kT, \end{aligned} \quad (13)$$

$$L = \exp(V_0/kT) \nabla \cdot [\exp(-V_0/kT) \mathbf{D} \cdot \nabla],$$

which has precisely the same form as in the theory of dielectric loss.<sup>1</sup> We expand the solution of Eq. (13) in the eigenfunctions  $\psi_\lambda$ , a complete orthonormal set, of the derived operator  $L_0$ .

$$L_0\psi_\lambda - \lambda\psi_\lambda = 0,$$

$$L_0 = \nabla \cdot \mathbf{D} \cdot \nabla + u(q),$$

$$u(q) = (\nabla \cdot \mathbf{D} \cdot \nabla V_0)/2kT$$

$$- (\nabla V_0) \cdot \mathbf{D} \cdot (\nabla V_0)/(2kT)^2,$$

and calculate the average value of the  $z$ -extension of a chain,

$$\Delta z = \langle z \rangle_{Av} - a,$$

by Eqs. (8), (9), (12), and (13). The result is

$$\Delta z = \frac{\sigma_0}{\nu kT} \left[ \sum_\lambda \frac{|z_\lambda|^2}{1 + i\omega\tau_\lambda} \right] e^{i\omega t},$$

$$\tau_\lambda = 1/\lambda, \quad (15)$$

$$z_\lambda = A_0^{\frac{1}{2}} \int (\mathbf{R} \cdot \mathbf{e}_1) \exp(-V_0/2kT) \psi_\lambda^* dq,$$

where the sum extends over all eigenvalues  $\lambda$ . Since the details of the derivation of Eq. (15) are identical with those of the theory of dielectric polarization,<sup>1</sup> we have omitted the routine intermediate steps.\* The mean square component  $\langle z^2 \rangle_{Av}^0$  of the chain length along the  $z$  axis in the unstressed state is related to the coefficients  $z_\lambda$  in the following manner,

$$\sum_\lambda |z_\lambda|^2 = \langle z^2 \rangle_{Av}^0,$$

$$\langle z^2 \rangle_{Av}^0 = A_0 \int (\mathbf{R} \cdot \mathbf{e}_1)^2 \exp(-V_0/kT) dq. \quad (16)$$

Thus, if we define a function  $Q_\lambda$  by the relation

$$Q_\lambda = |z_\lambda|^2 / \langle z^2 \rangle_{Av}^0,$$

$$\sum_\lambda Q_\lambda = 1,$$

and employ Eq. (15) to obtain the elastic

\* Properly, in order to provide for the normalization of  $f_1(q, t)$ , the  $z_\lambda$  of Eq. (15) should be replaced by  $(\Delta z)_\lambda$  where

$$(\Delta z)_\lambda = z_\lambda - a A_0^{\frac{1}{2}} \int \exp(-V_0/2kT) \psi_\lambda^* dq.$$

However, for the small equilibrium extensions  $a$  in the unstressed state, the approximation  $z_\lambda$  is adequate and is introduced here largely for simplicity in the subsequent discussion.

modulus  $E$ , defined as  $\sigma_0/\epsilon_{zz}^0$ , we obtain

$$\frac{1}{E} = \frac{\langle z^2 \rangle_{Av}^0}{MkT} \sum_\lambda \frac{Q_\lambda}{1 + i\omega\tau_\lambda}. \quad (17)$$

If the discrete relaxation time spectrum  $\tau_\lambda$  is closely spaced relative to  $1/\omega$ , it may be approximated by a continuous spectrum with the result,\*

$$\frac{1}{E} = \frac{1}{E_0} \int_0^\infty \frac{\Phi(\tau)}{1 + i\omega\tau} d\tau,$$

$$\Phi(\tau) = -\frac{d\Omega}{d\tau}; \quad \Omega = \sum_{\lambda < 1/\tau} Q_\lambda, \quad (18)$$

$$\frac{1}{E_0} = \frac{\langle z^2 \rangle_{Av}^0}{MkT},$$

where  $E_0$  is the static modulus of elasticity. Before analyzing the relaxation time distribution function  $\Phi(\tau)$ , a few remarks concerning the static modulus are desirable. If the average force potential  $V_0$  is assumed constant, the free rotation approximation, the average value  $\langle z^2 \rangle_{Av}^0$  has the well-known form,

$$\langle z^2 \rangle_{Av}^0 = \langle R^2 \rangle_{Av}^0 / 3 = nl^2/3,$$

$$l = b \tan \gamma/2, \quad (19)$$

\* We remark here that  $\Phi(\tau)d\tau$  represents the fractional elastic compliance in tension associated with relaxation times in the interval between  $\tau$  and  $\tau + d\tau$ . For an incompressible material with a Poisson ratio of  $\frac{1}{2}$ , the shear modulus  $G$  is equal to  $E/3$ . Thus, if one wishes to speak of elastic compliance in shear, the function  $J(\tau)$  equal to  $3\Phi(\tau)/E_0$  may be used. The elastic compliance in shear associated with relaxation times between  $\tau$  and  $\tau + d\tau$  is then equal to  $J(\tau)d\tau$ .

The theory which we have developed leads directly to a distribution of the elastic compliance, not the elastic modulus, in the relaxation time spectrum. The distribution is therefore not Maxwellian. In order to bridge the gap between the viscous fluid and the elastic solid, Maxwell proposed a relaxation mechanism, which for a single relaxation time is described by the equation,

$$\frac{d\sigma}{dt} + \frac{\sigma}{\tau} = E_\infty \frac{d\epsilon}{dt}.$$

Under a constant stress the material creeps. For a stress with harmonic dependence on time, the elastic modulus  $E$  is

$$E = i\omega\tau E_\infty / (1 + i\omega\tau).$$

Thus, if the frequency is large relative to  $1/\tau$ ,  $E$  approaches  $E_\infty$ , and the stress approaches proportionality with the strain. When the frequency is small relative to  $1/\tau$ , the stress approaches proportionality with the rate of strain.

Although a part of the elastic loss of cross-linked polymers, in which creep is observed, is no doubt due to mechanisms formally described by the Maxwellian scheme, such contributions are not included in the present theory.

where  $n$  is the number of bonds comprising the chain segment,  $b$  the bond length, and  $\gamma$  the bond angle. The same result is obtained if each bond is an axis of symmetry or contains a plane of symmetry of the intramolecular torque hindering rotation around that bond. The influence of the average intermolecular hindering torque on  $\langle z^2 \rangle_{Av}^0$  is much more difficult to determine. If we make the assumption of James and Guth<sup>3</sup> that the average intermolecular force hindering the internal motion of the chain can be represented by an internal stress  $\sigma_i$  distributed over the lattice points of the net, with

$$V_0 = -(\mathbf{R} \cdot \mathbf{e}_1)\sigma_i/\nu,$$

for a chain oriented in the  $z$  direction, we obtain

$$\begin{aligned} \langle z^2 \rangle_{Av}^0 &= nl^2/9, \\ l &= b \tan \gamma/2, \end{aligned} \quad (20)$$

a result which differs from that of Eq. (19) by the factor  $\frac{1}{3}$ . The elastic modulus  $E_0$  in the unstressed state then agrees with that of James and Guth.<sup>3</sup> Undoubtedly, an entirely satisfactory quantitative theory of the elastic modulus  $E_0$  depends upon an exact analysis of the potential  $V_0$  of the intramolecular and intermolecular hindering torques acting on a chain segment of the network.

In investigating the relaxation time distribution,  $\Phi(\tau)$ , we must first determine the internal rotatory diffusion tensor  $\mathbf{D}$  entering into Eq. (11). Fuoss and the writer<sup>1</sup> have estimated  $\mathbf{D}$  for the most probable configuration of a freely rotating polymer chain. It was assumed that each monomer unit, moving subject to the restraints imposed upon it by the other elements of the chain, was subject to a resistance proportional to its velocity. The friction constant  $\zeta_0$  of each such monomer unit was further supposed to be independent of the chain length  $n$ , but of course dependent upon the environment of the chain. The existence of the friction constant  $\zeta_0$  implies merely the validity of the theory of Brownian motion. Although Fuoss and the writer suggested the use of the usual hydrodynamic estimate of  $\zeta_0$  by Stokes' law, none of the general results of the theory of dielectric loss nor those of the present theory depend upon

this estimate, as implied by Kauzmann.<sup>6</sup> If one desires, one may use the transition state theory for estimating  $\zeta_0$ , as advocated by Kauzmann and Eyring.<sup>6</sup> that the activation energy for viscous flow in fluids composed of long chain molecules becomes independent of chain length for  $n$  of the order of 20, lends support to our assumption that  $\zeta_0$  can be treated as independent of  $n$ .

The estimate of the diffusion tensor  $\mathbf{D}$  of Fuoss and the writer<sup>1</sup> leads to the following expression for the operator  $\nabla \cdot \mathbf{D} \cdot \nabla$  of Eq. (11),

$$\begin{aligned} \nabla \cdot \mathbf{D} \cdot \nabla &= \frac{D_0}{2n^2} \left[ \frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left( \sin \vartheta \frac{\partial}{\partial \vartheta} \right) \right. \\ &\quad \left. + \frac{1}{\sin^2 \vartheta} \frac{\partial^2}{\partial \varphi^2} \right] + \sum_{s=1}^{n-2} D_s \frac{\partial^2}{\partial \varphi_s^2}, \quad (21) \\ D_s &= \frac{4D_0}{[n - |2s - n|]^2}, \\ D_0 &= 3kT/b^2\zeta_0, \end{aligned}$$

where  $b$  is the bond length. We remark that  $D_s$  is of the order  $D_0$  for bonds near the chain ends and of the order of  $D_0/n^2$  for bonds near the middle of the chain. This result appears reasonable, if we remember that  $D_s$  measures the resisting torque experienced by the molecule when rotation occurs around bond  $s$  alone, the configuration of the other bonds remaining fixed.

Use of Eq. (21) in Eq. (11) and the approximation of free rotation lead to the following relaxation time distribution function for elastic loss,

$$\begin{aligned} \Phi(\tau) &= \frac{\tau_m}{(\tau + \tau_m)^2}, \\ \tau_m &= n\tau_0, \\ \tau_0 &= 2b^2\zeta_0/kT. \end{aligned} \quad (22)$$

The details of the determination of  $G(\tau)$  are formally identical with those of the theory of dielectric loss.<sup>1</sup> It should be emphasized, however, that the theory of elastic loss applies only

<sup>6</sup> W. Kauzmann, *Rev. Mod. Phys.* **14**, 12 (1942); W. Kauzmann and H. Eyring, *J. Am. Chem. Soc.* **62**, 3113 (1940).

to cross-linked polymers. A polar *cross-linked* polymer should exhibit the same relaxation time spectrum in elastic and dielectric loss. This will not in general be true of a thermoplastic polymer such as polyvinyl chloride to which the model underlying the theory of elastic loss here described does not apply. It is possible that temporary cross-linkages due to intermolecular forces can be regarded as existing in thermoplastic polymers. On this assumption, elastic loss might consist of a contribution of the type described here superposed upon creep due to slippage at the temporary cross links.

The frequency of maximum loss for the distribution (22) is given by

$$\omega_m = 1/n\tau_0, \quad (23)$$

and is thus inversely proportional to the length  $n$  of the chain segments between cross-links. In a rubber, the use of Stokes' law with an effective viscosity coefficient for estimating  $\zeta_0$  and  $\tau_0$  can scarcely be defended, although such an estimate is adequate in order of magnitude for a polymer chain dispersed in a low molecular weight solvent. In the absence of an adequate theoretical

method for estimating  $\tau_0$ , we remark that

$$\tau_0 = 2b^2/D^0, \quad (24)$$

where  $D^0$  is the translational diffusion constant of a monomer unit of the chain. We therefore suggest that reasonable, although perhaps rough, estimates of  $\tau_0$  might be obtained from experimental diffusion constants in the rubber, of small molecules of the approximate size and shape of the representative monomer unit. For example in a Buna S rubber, one might measure the diffusion constant of benzene or toluene in the rubber itself for use in Eq. (24) to estimate  $\tau_0$  for the styrene units of the polymer, to which most of the loss could probably be attributed.

In conclusion we remark that the relaxation time distribution, Eq. (22), is to be regarded only as a first rough approximation. Properly, the influence of the intermolecular hindering torques should be taken into account in order to improve the free rotation approximation. A possible method of accomplishing this could be based upon the internal stress concept of James and Guth. An investigation along these lines is in progress and will be reported at a later time.