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AN ENGINEERING THEORY OF NONLINEAR VISCOELASTICITY WITH APPLICATIONS†

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Abstract—Relatively simple stress–strain equations are developed for nonlinear, initially isotropic, viscoelastic materials with constant temperature, and are shown to agree quite well with the actual behavior of unfilled and filled polymers. First, equations for a general state of strain are derived by extending Biot's linear thermodynamic theory to a restricted class of nonlinear behavior. Only two time-dependent relaxation functions appear, and these are just the familiar linear viscoelastic relaxation moduli. The general relations are then specialized to stress–strain equations applicable to uniaxial loading, radial and axial deformation problems of long, circular cylinders, and simple shear with lateral strain. The uniaxial equation yields, as a special case, a nonlinear relaxation modulus that has the familiar form for polymers wherein strain and time-dependence appear as separate factors. Results of experiments on highly-filled polymers are compared with theory for cases in which very small shear vibrations are superposed on static lateral compression and on static shear. Strong nonlinearities are observed with static strains of only a few percent.

INTRODUCTION

IT IS WELL-KNOWN that many unfilled and filled polymeric materials exhibit significant nonlinear viscoelastic behavior over a wide range of strains, strain rates, and temperatures encountered in certain technological applications. Composite systems consisting of soft polymers highly filled with hard particles, such as solid propellant, may have strongly nonlinear stress–strain response even at strain levels of only a few percent, as shown in this paper, and, for example, [1]. This appears to be due, in large part, to separation (dewetting) of the soft matrix from the hard filler particles in the presence of strain; the extent of this dewetting, and therefore nonlinearity, depends on the state of strain and its history. As a result, linear viscoelasticity theory may be severely limited in its application to systems whose hard-solids loading density is near its maximum value.

In this paper we shall develop relatively simple viscoelastic stress–strain equations which are suited especially for treating strong material nonlinearities, and then compare some experimental and theoretical results for solid propellants; no theoretical limitation is placed on strain magnitude. These equations are derived by extending Biot's linear thermodynamic theory [2] to a restricted class of nonlinear behavior. Consequently, our approach is considerably different from that followed by other workers. (For a discussion of the various theories see, for example, [3, 4]).

In an earlier paper by the author [5] it was pointed out that a relatively simple nonlinear theory could be developed by assuming viscoelastic material behaves thermodynamically as a linear viscoelastic system, but with nonlinear measures of strain in

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place of the classical linear strains and with modified stresses. As an example, the stress–strain equation for uniaxial loading was derived and shown to be consistent with large-strain relaxation data for several polymers. Specifically, this theory yielded the familiar relaxation modulus form wherein strain and time dependence appear as separate factors.

In the present paper, this theory is extended to general multiaxial loading of materials which are isotropic in their unstrained state. In addition, we admit a more general type of nonlinearity; it allows for nonlinear behavior under equilibrium (elastic) conditions which is different from that occurring under nonequilibrium conditions, and also includes a strain-reduced time analogous to temperature-reduced time for thermorheologically simple materials. These latter generalizations appear to be needed in the stress–strain equations of highly-loaded solid propellant.

The stress–strain equations so developed will be seen to be a natural generalization of the Boltzmann superposition principle to nonlinear, multiaxial behavior, and to contain two strain-independent relaxation moduli; only one relaxation modulus appears for materials that can be assumed to have a constant (or infinite) bulk modulus in the linear range of behavior. Because of our thermodynamic approach, these equations reduce to the most general, thermodynamically admissible forms for the limiting cases of linear viscoelasticity and nonlinear elasticity, and are consistent with thermodynamics for general strain histories.

In Section 1, pertinent thermodynamic equations derived earlier [2, 5] are reviewed and then extended to nonlinear behavior in terms of generalized coordinates and forces. Stress–strain equations for a general three-dimensional state of strain are given. In Sections 2 through 5 stress–strain equations for specific strain states are deduced, and then compared with some experimental results.

1. THERMODYNAMIC CONSIDERATIONS

The viscoelastic material is considered to be a closed thermodynamic system which is maintained at a constant temperature. Its state is assumed to be defined by (n) state variables q_i (generalized coordinates), with $i = 1, 2, \ldots n$. A generalized force Q_i, conjugate to the variable q_i, is defined by the condition that $Q_i \delta q_i$ is an incremental amount of external work done on the system, where δq_i denotes an incremental change in q_i.

The generalized coordinates will be divided into the two groups of hidden and observed. Hidden coordinates are defined by the condition that their conjugate forces are always zero, while the remaining coordinates are called observed variables. Although it is not necessary, for our purposes, to provide a physical interpretation for hidden coordinates, one can interpret some of them as being "molecular configurations" when dealing with polymers. On the other hand, a physical association must be made for observed variables in each application. For example, when a general state of uniform small strain is applied to a linear viscoelastic element of unit volume, one may take as observed variables the six components of the symmetric strain tensor; the conjugate generalized forces are the six components of the stress tensor.

Review of previous results

The general system defined above is governed by the following set of (n) equations of motion when in the neighborhood of an equilibrium state [5],

$$\frac{\partial F}{\partial q_i}+\sum_{j=1}^{n} b'_{ij}\frac{\mathrm{d}q_j}{\mathrm{d}t} = Q_i; \qquad i = 1,2,\ldots n. \tag{1}$$

where F is the Helmholtz free energy, and the coefficients b'_{ij} form a symmetric, positive semidefinite matrix as a consequence of Onsager's principle and the non-negative property of entropy production; in general, these coefficients may be functions of the generalized coordinates q_i.

In earlier studies [2, 5] the free energy F was expanded about an unstressed and unstrained reference state, and all terms higher than second order were neglected; viz. the quadratic form

$$F = \frac{1}{2}\sum_{i,j=1}^{n} a_{ij}q_iq_j \tag{2}$$

was used, where

$$a_{ij} = a_{ji} = \left(\frac{\partial^2 F}{\partial q_i \partial q_j}\right)_{\text{All } q\equiv 0}. \tag{3}$$

Also, the matrix of viscosity coefficients, b'_{ij}, was assumed constant, apart from thermal effects. These considerations reduced nonlinear system (1) to the set of linear equations,

$$\sum_{j=1}^{n} a_{ij}q_j+\sum_{j=1}^{n} b_{ij}\frac{\mathrm{d}q_j}{\mathrm{d}t} = Q_i \tag{4}$$

where b_{ij} is the value of b'_{ij} in the unstrained equilibrium state. Explicit relations between observed coordinates (strains) and generalized forces (stresses) were then derived by eliminating the hidden coordinates; this was accomplished by using the fact that $Q_i \equiv 0$ for all indices corresponding to hidden coordinates.

Although the resulting linear stress–strain relations are applicable to media with an arbitrary degree of anisotropy, we shall record here for reference purposes just the familiar isotropic relations. They can be written in the following form:†

$$Q_1 = \frac{2}{3}\int_0^t G(t-\tau)\frac{\mathrm{d}}{\mathrm{d}\tau}[2q_1-q_2-q_3]\,\mathrm{d}\tau+\int_0^t K(t-\tau)\frac{\mathrm{d}e}{\mathrm{d}\tau}\,\mathrm{d}\tau \tag{5a}$$

$$Q_2 = \frac{2}{3}\int_0^t G(t-\tau)\frac{\mathrm{d}}{\mathrm{d}\tau}[2q_2-q_1-q_3]\,\mathrm{d}\tau+\int_0^t K(t-\tau)\frac{\mathrm{d}e}{\mathrm{d}\tau}\,\mathrm{d}\tau \tag{5b}$$

$$Q_3 = \frac{2}{3}\int_0^t G(t-\tau)\frac{\mathrm{d}}{\mathrm{d}\tau}[2q_3-q_1-q_2]\,\mathrm{d}\tau+\int_0^t K(t-\tau)\frac{\mathrm{d}e}{\mathrm{d}\tau}\,\mathrm{d}\tau \tag{5c}$$

$$Q_4 = \int_0^t G(t-\tau)\frac{\mathrm{d}q_4}{\mathrm{d}\tau}\,\mathrm{d}\tau; \qquad Q_5 = \int_0^t G(t-\tau)\frac{\mathrm{d}q_5}{\mathrm{d}\tau}\,\mathrm{d}\tau; \qquad Q_6 = \int_0^t G(t-\tau)\frac{\mathrm{d}q_6}{\mathrm{d}\tau}\,\mathrm{d}\tau \tag{5d}$$

where $e \equiv q_1+q_2+q_3$, and $G(t)$ and $K(t)$ are the shear and bulk relaxation moduli, respectively. These moduli are restricted by thermodynamics to have the exponential form

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† The equivalence of relations (5) and the operational form in [5] can be established by taking the Laplace transform of (5), and then relating the transformed bulk modulus to operational analogs of the Lamé elastic constants.

$$G(t) = G_e + \sum_s G_s \exp(-\lambda_s t) \tag{6a}$$

$$K(t) = K_e + \sum_s K_s \exp(-\lambda_s t) \tag{6b}$$

where the constants have the property $G_e \geqslant 0$, $K_e \geqslant 0$, $G_s \geqslant 0$, $K_s \geqslant 0$, and $\lambda_s > 0$. A delta function, $\delta(t)$, is thermodynamically admissible in (6), but is omitted here on physical grounds. Also, all variables q_i are assumed to vanish when $t < 0$.

The generalized variables in (5) are to be identified with stresses and strains referred to Cartesian coordinates (x, y, z) as follows:

$$Q_1 = \sigma_x; \quad Q_2 = \sigma_y; \quad Q_3 = \sigma_z; \quad Q_4 = \tau_{xy}; \quad Q_5 = \tau_{xz}; \quad Q_6 = \tau_{yz} \tag{7a}$$

$$q_1 = \varepsilon_x; \quad q_2 = \varepsilon_y; \quad q_3 = \varepsilon_z; \quad q_4 = \gamma_{xy}; \quad q_5 = \gamma_{xz}; \quad q_6 = \gamma_{yz} \tag{7b}$$

in which the familiar notation in [6] is used.

Extension to nonlinear behavior

It is important to recognize that equation (1) is *not* restricted to a neighborhood of the *unstrained* equilibrium state, but should be applicable as long as the system is close to any equilibrium state. Namely, if the imposed strain rates are not too high, it is reasonable to assume that equation (1) is valid almost regardless of the strain magnitudes†; it also seems reasonable to expect that the strain rate restriction will be practically the same as exists for infinitesimal strains, except possibly when failure is imminent.

Although equation (1) may be applicable, it is not practically useful unless the hidden coordinates can be eliminated so as to obtain explicit relations between forces and observed coordinates. We shall show that by introducing certain restricted forms of the free energy function and matrix b'_{ij}, the hidden variables can be easily eliminated, and that these restricted forms yield stress–strain equations which are (approximately) consistent with experimental data for filled and unfilled polymers.

Before introducing these restricted forms, it is of interest to make a comment concerning hidden coordinates, as this will serve to motivate further the choice of these restrictions. Specifically, let us first assume that each thermodynamic equilibrium state of the body depends on only observed variables. Then, without loss of generality, the hidden coordinates can be chosen so as to vanish at all equilibrium states.‡ If, for example, the body is strained very slowly so that thermodynamic equilibrium is maintained at each instant, these hidden coordinates remain at zero. Moreover, under nonequilibrium conditions these coordinates will be small if strain rates are sufficiently small, even though the applied strains (or observed variables) may be large enough to produce nonlinear behavior.

This observation indicates that it is meaningful, although strains may be large, to expand the free energy with respect to the hidden coordinates and neglect terms higher than second order. Moreover, it turns out that one can partially simplify the free energy with respect to observed coordinates also, and still obtain results which are consistent with a large amount of experimental data. Namely, we shall use the free energy expansion,

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† We are using "strain" rather loosely here, but will give specific definitions later in each application.

‡ Had we picked a set of hidden coordinates which, say, vanishes only in the unstrained equilibrium state, their values at all other equilibrium states would depend on the applied strains. By subtracting from the instantaneous value of each of these coordinates their equilibrium value, one obtains differences which represent the hidden coordinates chosen in the above text.

$$F = \Delta F_e + \tfrac{1}{2} \sum_{i,j=1}^{n} a_{ij} q_i q_j \tag{8}$$

where a_{ij} are the constants given in equation (3); ΔF_e is a function of only the observed coordinates, which is at least of third order in q_i. At an equilibrium state, the free energy is given by

$$F \equiv F_e \equiv \Delta F_e + \tfrac{1}{2} \sum_{i,j=1}^{k} a_{ij} q_i q_j \tag{9}$$

where it is assumed that there are k observed coordinates ($1 \leqslant i \leqslant k, 1 \leqslant j \leqslant k$).

Equation (8) represents a second-order approximation to free energy, apart from the value of free energy at equilibrium states; i.e. we have retained a completely general form of the free energy when under equilibrium conditions. Also, it should be emphasized that the observed variables reduce to strains when they are sufficiently small, but in general may be nonlinear functions of strains.

Note that if a_{ij} are assumed to depend on observed coordinates, expansion (8) will not involve any approximation with respect to these coordinates. A special form of this dependence is discussed in [7].

Considering now the matrix b'_{ij}, it will be assumed that

$$b'_{ij} = a_\varepsilon b_{ij}; \qquad a_\varepsilon > 0 \tag{10}$$

where a_ε depends on only observed coordinates (or strains) and b_{ij} is the same constant matrix appearing in (4). The function a_ε will be called a "strain shift-factor" since it is analogous to the familiar "temperature shift-factor" a_T[5]. It is observed that $a_\varepsilon = 1$ in the unstrained state. Experimental results to be given later indicate that such a shift factor is needed to achieve agreement with theory.

Upon substituting free energy (8) and the matrix (10) into equation (1), one finds the equations of motion:

$$\sum_{j=1}^{n} a_{ij} q_j + \sum_{j=1}^{n} b_{ij} \frac{\mathrm{d}q_j}{\mathrm{d}\rho} = Q_i - \frac{\partial \Delta F_e}{\partial q_i} \tag{11}$$

where ρ is a "strain-reduced time," defined by

$$\mathrm{d}\rho \equiv \frac{\mathrm{d}t}{a_\varepsilon} \quad \text{or} \quad \rho \equiv \int_0^t \frac{\mathrm{d}t}{a_\varepsilon} \tag{12}$$

and $Q_i = 0$ and $\partial \Delta F_e / \partial q_i = 0$ when $k+1 \leqslant i \leqslant n$.

Comparing equations (11) and (4), we see that solutions to (11) may be deduced immediately from solutions of the original linear set (4). Specifically, for a body which is isotropic in its unstrained state, equations (5) and (6) are applicable if we replace Q_i by $Q_i - \partial \Delta F_e / \partial q_i$ and real time by strain-reduced time (12). These modified equations represent a set of constitutive equations for three-dimensional, nonlinear viscoelastic behavior. In order to obtain explicit stress–strain equations one must relate the generalized forces to a stress tensor, and this association is made in the Appendix for a particular choice of strains.

For a general state of strain it is seen that there are only two relaxation moduli (which are the same as those occurring in the linear range of behavior), seven strain-dependent functions $q_1 \ldots q_6$, ΔF_e, and the strain-dependent shift factor a_ε. However, one can often expect to encounter considerable difficulty in applying these constitutive equations to specific problems and to simple configurations which are used in material property evaluation. Normally, it will be much easier to derive the constitutive equations for each application or class of problems of engineering interest; a convenient set of pertinent strains can be chosen for each case, without having to start with all six components of the strain tensor.

We shall illustrate this by deriving in the following two sections an equation for uniaxial loading of a bar, and then the stress–strain equations applicable to the analysis of symmetrically loaded, long cylinders.

2. STRESS–STRAIN EQUATION FOR UNIAXIAL LOADING

Consider a cubic specimen whose sides are unity in the undeformed and unstressed state. Let σ be a force applied normal to a face so as to develop a uniform, uniaxial state of stress, and let λ be the length of the sides parallel to the force direction; we shall call $\varepsilon \equiv \lambda - 1$ the strain.

For this case there is only one observed generalized coordinate, $q_1(\varepsilon)$, say, and one generalized force, Q_1. In view of the assumptions in Section 1, the relation between generalized force and coordinate is the same as for linear viscoelastic behavior, apart from the addition of a_ε and ΔF_e; thus, for an initially isotropic body,

$$Q_1 = \frac{\mathrm{d}\Delta F_e}{\mathrm{d}q_1} + \int_0^t E(\rho-\rho')\frac{\mathrm{d}q_1}{\mathrm{d}\tau}\,\mathrm{d}\tau \tag{13}$$

where $E(\rho)$ is the uniaxial relaxation modulus, and ρ is strain–reduced time defined in equation (12). Also, $\rho' \equiv \rho(\tau)$.

The virtual work is

$$\delta W = \sigma\delta\varepsilon = Q_1\delta q_1 = Q_1\frac{\mathrm{d}q_1}{\mathrm{d}\varepsilon}\,\delta\varepsilon. \tag{14}$$

Hence

$$\sigma = Q_1\frac{\mathrm{d}q_1}{\mathrm{d}\varepsilon} \tag{15}$$

and from equation (13) we derive the stress–strain equation,

$$\sigma = \frac{\mathrm{d}\Delta F_e}{\mathrm{d}\varepsilon} + \frac{\mathrm{d}q_1}{\mathrm{d}\varepsilon}\int_0^t E(\rho-\rho')\frac{\mathrm{d}q_1}{\mathrm{d}\tau}\,\mathrm{d}\tau. \tag{16}$$

Defining the equilibrium, small strain modulus as $E_e \equiv E(\infty)$, equation (16) can be written

$$\sigma = \frac{\mathrm{d}F_e}{\mathrm{d}\varepsilon} + \frac{\mathrm{d}q_1}{\mathrm{d}\varepsilon}\int_0^t [E(\rho-\rho')-E_e]\frac{\mathrm{d}q_1}{\mathrm{d}\tau}\,\mathrm{d}\tau \tag{17}$$

where F_e is the total free energy (strain energy) in equilibrium,

$$F_e = \Delta F_e + \tfrac{1}{2} E_e q_1^2. \tag{18}$$

For sufficiently small strains $q_1 = \varepsilon$, so that ΔF_e is at least third order in ε. If ΔF_e can be neglected, q_1 may be determined directly from the elastic strain energy,

$$q_1 = \sqrt{\left(\frac{2F_e}{E_e}\right)} \tag{19}$$

which corresponds to the result in [5].

Observe that there are three strain-dependent functions, F_e, q_1, and a_ε, appearing in (17), and one time-dependent function, $E(t)$. From the limit cases of nonlinear elastic and linear viscoelastic responses one can obtain the strain energy function $F_e(\varepsilon)$ and relaxation modulus $E(t)$.

In order to compare equation (16) with some experimental results, let the strain be a step-function of time,

$$\varepsilon = \begin{cases} 0; & t < 0 \\ \varepsilon_s; & t > 0 \end{cases} \tag{20}$$

where ε_s is constant. Equation (16) yields

$$\sigma = \frac{\mathrm{d}\Delta F_e}{\mathrm{d}\varepsilon} + \frac{1}{2}\frac{\mathrm{d}q_1^2}{\mathrm{d}\varepsilon} E(\rho) \tag{21}$$

and $\rho = t/a_\varepsilon$. If one considers the special case $\Delta F_e \equiv 0$ and $a_\varepsilon \equiv 1$, equation (21) yields the familiar product form observed for polymers [8, 9]. On the other hand, propellant data given in Section 5 for another state of strain indicate that we must take into account variations of ΔF_e and a_ε. The unfilled polymer data obtained by Mason[10] also suggests that a_ε is needed, at least with very large strains.

Finally, it should be clear that the form of the stress–strain equation (16), or (17), is the same as would be obtained for any case in which there is a single observed variable, such as equal biaxial strain or simple shear; it is necessary to replace only the relaxation modulus $E(\rho)$ by the appropriate linear viscoelastic relaxation modulus.

3. STRESS–STRAIN EQUATIONS FOR ANALYSIS OF LONG CYLINDERS

For engineering stress analysis purposes, case-bonded solid propellant grains are often approximated by infinitely long, hollow, circular cylinders. Under isothermal conditions, two types of axially symmetrical loading of particular interest in propellant problems are internal pressurization and axial acceleration. In this section we shall give a sufficient set of stress–strain equations for calculating displacement and stress distributions (apart from the axial stress) for such loading and configurations.

The viscoelastic cube shown in Fig. 1 may be interpreted as an infinitesimal element which has been cut from a cylinder; the x_1, x_2, x_3 directions correspond to the radial, circumferential, and axial directions, respectively. Without loss of generality, we may assume that the sides have unit length in the unstrained state.

The state of strain is assumed to be homogeneous and defined by three quantities: ε_1, ε_2, and γ_3. ε_1 and ε_2 are displacements between the faces whose normals are parallel to the x_1 and x_2 axes, respectively; γ_3 is equal to the displacement in the x_3-direction of the top surface relative to the bottom surface. The length of line elements in the x_3 direction

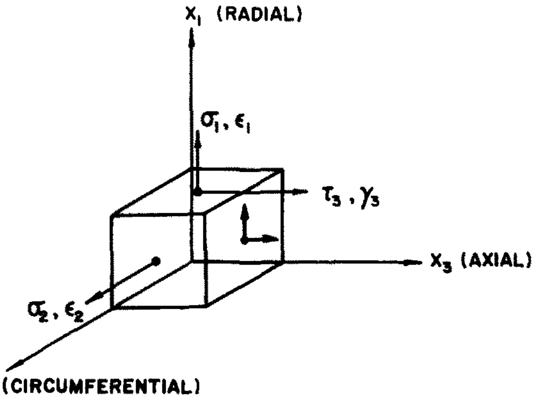

FIG. 1. Viscoelastic element and coordinate system.

are assumed constant. σ_1, σ_2, and τ_3 are the corresponding normal and shearing forces per unit undeformed area (i.e. stresses referred to the unstrained state).

Since three independent "strains" are used to describe the class of deformations of interest, we introduce three generalized coordinates, $q_i(\varepsilon_1, \varepsilon_2, \gamma_3)$ with $i = 1, 2, 3$. Their conjugate generalized forces satisfy the virtual work conditions,

$$\delta W = Q_1\delta q_1 + Q_2\delta q_2 + Q_3\delta q_3 = \sigma_1\delta\varepsilon_1 + \sigma_2\delta\varepsilon_2 + \tau_3\delta\gamma_3 \tag{22}$$

for arbitrary variations $\delta\varepsilon_1$, $\delta\varepsilon_2$ and $\delta\gamma_3$. Therefore

$$\sigma_1 = Q_1\frac{\partial q_1}{\partial\varepsilon_1} + Q_2\frac{\partial q_2}{\partial\varepsilon_1} + Q_3\frac{\partial q_3}{\partial\varepsilon_1} \tag{23a}$$

$$\sigma_2 = Q_1\frac{\partial q_1}{\partial\varepsilon_2} + Q_2\frac{\partial q_2}{\partial\varepsilon_2} + Q_3\frac{\partial q_3}{\partial\varepsilon_2} \tag{23b}$$

$$\tau_3 = Q_1\frac{\partial q_1}{\partial\gamma_3} + Q_2\frac{\partial q_2}{\partial\gamma_3} + Q_3\frac{\partial q_3}{\partial\gamma_3}\,. \tag{23c}$$

For sufficiently small strains, assume

$$\varepsilon_1 = q_1; \qquad \varepsilon_2 = q_2; \qquad \gamma_3 = q_3 \tag{24a}$$

so that for this limit case

$$\sigma_1 = Q_1; \qquad \sigma_2 = Q_2; \qquad \tau_3 = Q_3. \tag{24b}$$

Following the theory in Section 1, the relations between generalized coordinates and forces are determined directly from the limit case of linear viscoelastic behavior, apart from a_ε and ΔF_e. Thus,

$$Q_1 = \frac{\partial\Delta F_e}{\partial q_1} + \frac{2}{3}\int_0^t G(\rho-\rho')\frac{\mathrm{d}}{\mathrm{d}\tau}[2q_1 - q_2]\,\mathrm{d}\tau + \int_0^t K(\rho-\rho')\frac{\mathrm{d}e'}{\mathrm{d}\tau}\,\mathrm{d}\tau \tag{25a}$$

$$Q_2 = \frac{\partial\Delta F_e}{\partial q_2} + \frac{2}{3}\int_0^t G(\rho-\rho')\frac{\mathrm{d}}{\mathrm{d}\tau}[2q_2 - q_1]\,\mathrm{d}\tau + \int_0^t K(\rho-\rho')\frac{\mathrm{d}e'}{\mathrm{d}\tau}\,\mathrm{d}\tau \tag{25b}$$

$$Q_3 = \frac{\partial \Delta F_e}{\partial q_3} + \int_0^t G(\rho - \rho')\frac{dq_3}{d\tau}\,d\tau \tag{25c}$$

where $e' \equiv q_1 + q_2$, and $G(\rho)$ and $K(\rho)$ still denote the linear viscoelastic shear and bulk relaxation moduli, respectively.

Substitution of relations (25) into (23) will yield the desired stress–strain equations. However, before doing this, it is helpful to simplify equation (25) by introducing the familiar assumption that the bulk modulus is constant. We should emphasize that this implies the material is elastic with respect to volume changes in the linear range only; volume viscoelasticity arising from nonlinear phenomena, such as dewetting of solid propellant, is *not* excluded. With this simplification, the stress–strain equations become

$$\begin{aligned}\sigma_1 = {} & \frac{\partial F_e}{\partial \varepsilon_1} + \frac{2}{3}\frac{\partial q_1}{\partial \varepsilon_1}\int_0^t [G(\rho-\rho') - G_e]\frac{d}{d\tau}[2q_1 - q_2]\,d\tau \\ & + \frac{2}{3}\frac{\partial q_2}{\partial \varepsilon_1}\int_0^t [G(\rho-\rho') - G_e]\frac{d}{d\tau}[2q_2 - q_1]\,d\tau + \frac{\partial q_3}{\partial \varepsilon_1}\int_0^t [G(\rho-\rho') - G_e]\frac{dq_3}{d\tau}\,d\tau \end{aligned} \tag{26a}$$

$$\begin{aligned}\sigma_2 = {} & \frac{\partial F_e}{\partial \varepsilon_2} + \frac{2}{3}\frac{\partial q_1}{\partial \varepsilon_2}\int_0^t [G(\rho-\rho') - G_e]\frac{d}{d\tau}[2q_1 - q_2]\,d\tau \\ & + \frac{2}{3}\frac{\partial q_2}{\partial \varepsilon_2}\int_0^t [G(\rho-\rho') - G_e]\frac{d}{d\tau}[2q_2 - q_1]\,d\tau + \frac{\partial q_3}{\partial \varepsilon_2}\int_0^t [G(\rho-\rho') - G_e]\frac{dq_3}{d\tau}\,d\tau \end{aligned} \tag{26b}$$

$$\begin{aligned}\tau_3 = {} & \frac{\partial F_e}{\partial \gamma_3} + \frac{2}{3}\frac{\partial q_1}{\partial \gamma_3}\int_0^t [G(\rho-\rho') - G_e]\frac{d}{d\tau}[2q_1 - q_2]\,d\tau \\ & + \frac{2}{3}\frac{\partial q_2}{\partial \gamma_3}\int_0^t [G(\rho-\rho') - G_e]\frac{d}{d\tau}[2q_2 - q_1]\,d\tau + \frac{\partial q_3}{\partial \gamma_3}\int_0^t [G(\rho-\rho') - G_e]\frac{dq_3}{d\tau}\,d\tau. \end{aligned} \tag{26c}$$

We have introduced the equilibrium value of shear modulus, $G_e \equiv G(\infty)$, in order to write (26) in terms of the equilibrium free energy (strain energy) $F_e = F_e(\varepsilon_1, \varepsilon_2, \gamma_3)$.

Since the body is assumed to be isotropic in its unstrained equilibrium state, the functions F_e, a_ε, q_1, and q_2 are even functions of γ_3, while q_3 is an odd function of γ_3; this can be shown to follow from the fact that σ_1 and σ_2 must be even in γ_3 and τ_3 odd in γ_3. Furthermore, when $\gamma_3 = 0$ an interchange of the x_1 and x_2 axes should not affect the form of the stress–strain law, which implies the symmetry properties:

$$\begin{gathered} F_e(\varepsilon_1, \varepsilon_2, 0) = F_e(\varepsilon_2, \varepsilon_1, 0); \qquad a_\varepsilon(\varepsilon_1, \varepsilon_2, 0) = a_\varepsilon(\varepsilon_2, \varepsilon_1, 0) \\ q_1(\varepsilon_1, \varepsilon_2, 0) = q_2(\varepsilon_2, \varepsilon_1, 0) \end{gathered} \tag{27}$$

4. SMALL VIBRATIONS SUPERPOSED ON STATIC STRAIN

This section deals with application of the theory to two problems involving very small sinusoidal shear strain superposed on uniform static strain. Predictions of the equations derived here will be compared to experimental results in the following Section 5.

Shear vibrations superposed on lateral strain

Consider again the element shown in Fig. 1, but now assume that it is in a state of plane strain in the x_2 direction; i.e. $\varepsilon_2 \equiv 0$. The stress–strain equations can be deduced from (26) by setting $q_2 = 0$,

$$\sigma_1 = \frac{\partial F_e}{\partial \varepsilon_1} + \frac{4}{3}\frac{\partial q_1}{\partial \varepsilon_1}\int_0^t [G(\rho-\rho')-G_e]\frac{\mathrm{d}q_1}{\mathrm{d}\tau}\mathrm{d}\tau + \frac{\partial q_3}{\partial \varepsilon_1}\int_0^t [G(\rho-\rho')-G_e]\frac{\mathrm{d}q_3}{\mathrm{d}\tau}\mathrm{d}\tau \tag{28a}$$

$$\tau_3 = \frac{\partial F_e}{\partial \gamma_3} + \frac{4}{3}\frac{\partial q_1}{\partial \gamma_3}\int_0^t [G(\rho-\rho')-G_e]\frac{\mathrm{d}q_1}{\mathrm{d}\tau}\mathrm{d}\tau + \frac{\partial q_3}{\partial \gamma_3}\int_0^t [G(\rho-\rho')-G_e]\frac{\mathrm{d}q_3}{\mathrm{d}\tau}\mathrm{d}\tau \tag{28b}$$

where

$$F_e = F_e(\varepsilon_1, \gamma_3), \quad a_\varepsilon = a_\varepsilon(\varepsilon_1, \gamma_3), \quad q_1 = q_1(\varepsilon_1, \gamma_3), \quad \text{and} \quad q_3 = q_3(\varepsilon_1, \gamma_3).$$

It should be observed that equations (28) could have been derived directly from thermodynamic equation (11) by using only two observed variables, q_1 and q_3, without having to consider q_2. This latter generalized coordinate is not needed unless one deals directly with the more general equations (26), in which case $\varepsilon_2 \equiv 0$ does not necessarily imply $q_2 = 0$. (Note, however, that $q_2(\varepsilon_1, 0, \gamma_3)$ has no first-order terms because of the small-strain condition $q_2 = \varepsilon_2$). Whether or not $q_2(\varepsilon_1, 0, \gamma_3)$ vanishes in general cannot be determined without further experiments; for the present problem of small superposed vibrations, it can be shown that equations (26) and experimental data in Section 5 are consistent regardless of the value of $q_2(\varepsilon_1, 0, \gamma_3)$.

The variables q_1 and q_3 satisfy the same conditions stated in Section 3. Specifically, $q_1 = \varepsilon_1$ and $q_3 = \gamma_3$ when $|\varepsilon_1| \ll 1$ and $|\gamma_3| \ll 1$. Also, F_e and q_1 are even in γ_3 and q_3 is an odd function of γ_3. In the following analysis, it will be helpful to use q_3 in the form,

$$q_3 = \gamma_3[1+\gamma_3^2 f + \varepsilon_1 g] \tag{29}$$

in which we have introduced arbitrary functions of ε_1 and γ_3^2: $f = f(\varepsilon_1, \gamma_3^2)$ and $g = g(\varepsilon_1, \gamma_3^2)$.

Suppose now that a finite, constant strain $\varepsilon_1 = \varepsilon_s$ is applied and maintained indefinitely. After the element has relaxed to a steady state of stress, apply a small harmonic shear strain, $\gamma_3 = \gamma_0 \exp(i\omega t)$, with amplitude $\gamma_0 \ll 1$ and frequency ω. The terms in (28) can be approximated as follows:

$$\frac{\partial F_e}{\partial \varepsilon_1} \simeq \left(\frac{\partial F_e}{\partial \varepsilon_1}\right)\bigg|_{\substack{\gamma_3=0\\ \varepsilon_1=\varepsilon_s}} \equiv \left(\frac{\partial F_e}{\partial \varepsilon_1}\right)_s \tag{30a}$$

$$\frac{\partial F_e}{\partial \gamma_3} \simeq c\gamma_3 : c \equiv \left(\frac{\partial^2 F_e}{\partial \gamma^2}\right)\bigg|_{\substack{\gamma_3=0\\ \varepsilon_1=\varepsilon_s}} \tag{30b}$$

$$\frac{\partial q_3}{\partial \gamma_3} \simeq 1+\varepsilon_s g_s : g_s \equiv g(\varepsilon_s, 0) \tag{30c}$$

Also, both integral terms in (28a) and the first integral in (28b) either vanish or are negligible. The second integral term in (28b) becomes

$$\frac{\partial q_3}{\partial \gamma_3}\int_0^t [G(\rho-\rho')-G_e]\frac{\mathrm{d}q_3}{d\tau}\mathrm{d}\tau \simeq (1+\varepsilon_s g_s)^2(G^*-G_e)\gamma_3 \tag{31}$$

where G^* is the complex linear viscoelastic shear modulus,

$$G^* = G'(\omega a_\varepsilon)+iG''(\omega a_\varepsilon) : i \equiv \sqrt{-1} \tag{32}$$

in which G' is the "storage modulus" and G'' is the "loss modulus"; these moduli are functions of only "reduced frequency," ωa_ε.

With these considerations, one derives the stress–strain equations,

$$\sigma_1 = \left(\frac{\partial F_e}{\partial \varepsilon_1}\right)_s \tag{33a}$$

$$\tau_3 = G^*_\varepsilon \gamma_3 = (G'_\varepsilon + iG''_\varepsilon)\gamma_3 \tag{33b}$$

in which the components of the nonlinear complex modulus, G^*_ε, are

$$G'_\varepsilon \equiv [c-(1+\varepsilon_s g_s)^2 G_e]+(1+\varepsilon_s g_s)^2 G' \tag{34a}$$

$$G''_\varepsilon \equiv (1+\varepsilon_s g_s)^2 G''. \tag{34b}$$

It is interesting to observe that the nonlinear storage modulus, G'_ε, consists of a frequency-independent term, $[c-(1+\varepsilon_s g_s)^2 G_e]$, and a frequency-dependent term that is similar to the nonlinear loss modulus, G''_ε. It will be seen later that this character of the nonlinear complex modulus, as well as its dependence on reduced frequency, ωa_ε, can be used as a direct experimental check on validity of the theory.

Shear vibrations superposed on static shear strain

Let us now derive the stress–strain equation for the element in Fig. 1 when $\varepsilon_1 \equiv \varepsilon_2 \equiv 0$ and

$$\gamma_3 = \gamma_s + |\Delta\gamma_3| \exp(i\omega t) = \gamma_s + \Delta\gamma_3 \tag{35}$$

where γ_s is a static shear strain and $|\Delta\gamma_3|$ is a very small vibration amplitude.

For this case, we have to consider just one observed generalized coordinate, $q_3 = q_3(\gamma_3)$, which is related to shear force per unit undeformed area, τ_3, by the equation

$$\tau_3 = \frac{\mathrm{d}F_e}{\mathrm{d}\gamma_3} + \frac{\mathrm{d}q_3}{\mathrm{d}\gamma_3}\int_0^t [G(\rho-\rho')-G_e]\frac{\mathrm{d}q_3}{\mathrm{d}\tau}\,\mathrm{d}\tau \tag{36}$$

which has the same form as uniaxial equation (17).

Substitution of shear strain (35) into (36) yields the incremental stress–strain equation,

$$\Delta\tau_3 = G^*_\gamma \Delta\gamma_3 = (G'_\gamma + iG''_\gamma)\Delta\gamma_3 \tag{37}$$

where τ_3 is assumed constant prior to applying $\Delta\gamma_3$, and

$$\Delta\tau_3 \equiv \tau_3 - \left(\frac{\mathrm{d}F_e}{\mathrm{d}\gamma_3}\right)_{\gamma_s} \tag{38}$$

$$G'_\gamma \equiv \left[\left(\frac{\mathrm{d}^2F_e}{\mathrm{d}\gamma_3^2}\right)_{\gamma_s} - \left(\frac{\mathrm{d}q_3}{\mathrm{d}\gamma_3}\right)^2_{\gamma_s} G_e\right] + \left(\frac{\mathrm{d}q_3}{\mathrm{d}\gamma_3}\right)^2_{\gamma_s} G' \tag{39a}$$

$$G''_\gamma \equiv \left(\frac{\mathrm{d}q_3}{\mathrm{d}\gamma_3}\right)^2_{\gamma_s} G'' \tag{39b}$$

in which $G' = G'(\omega a_\varepsilon)$ and $G'' = G''(\omega a_\varepsilon)$ are the familiar components of the linear viscoelastic complex modulus. All strain-dependent functions noted are evaluated at $\gamma_3 = \gamma_s$.

It is seen that nonlinear moduli (39) have the same form as those with static lateral strain, equation (34), and consequently will permit a further check on the theory.

From an experimental stand-point, it will not always be convenient to wait until a steady state of stress is reached before applying the cyclic strain. The nonlinear storage moduli (34a) and (39a) are found to contain a time-dependent term which must be considered in the presence of simultaneous stress relaxation.

5. DISCUSSION OF EXPERIMENTS AND RESULTS

We now turn to a discussion of experiments* using the specimen shown in Fig. 2, and make a comparison of data with nonlinear moduli (34) and (39). The objective of these tests was not to carefully evaluate material properties, but rather was to obtain a preliminary evaluation of the theory. In fact, only a single specimen was used for each of the two loading conditions.

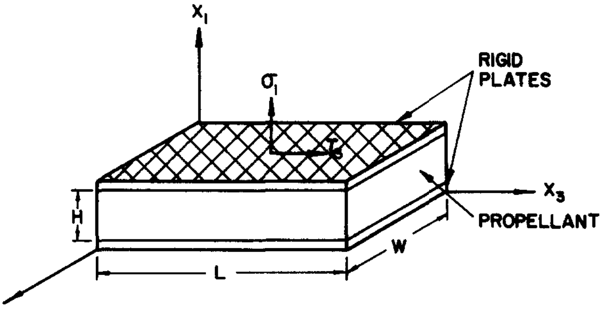

FIG. 2. Shear specimen.

The specimen dimensions were approximately $L = 0{\cdot}50$ in., $H = 0{\cdot}13$ in., and $W = 0{\cdot}34$ in. With these dimensions the load–displacement response of the specimen is influenced somewhat by the free surfaces, which were not accounted for in deriving the stress–strain relations. However, in view of our objective, this is not significant; for the usual case in which $G/K \ll 1$, application of the thermodynamic theory for arbitrary values of L, H, and W yields force–displacement relations that have the same form as stress–strain equations (28) and (36).

The vibration test apparatus that was used has been described in detail elsewhere [11]. It employs a piezoelectric driver which, in the present tests, subjected the specimen to a shear strain amplitude of 6×10^{-3} per cent over the frequency range of 20–1000 c/s.

Shear vibrations superposed on lateral strain

The specimen used for this case was an 84 wt.%-loaded polybutadiene acrylic acid (PBAA) propellant. (Greatest loading possible is approximately 90 per cent).

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* The experiments were conducted by Mr. Dalton Cantey of Lockheed Propulsion Company, Redlands, California.

The measured nonlinear storage modulus, $G'_\varepsilon(\omega)$, and loss modulus, $G''_\varepsilon(\omega)$, are illustrated in Fig. 3 using logarithmic scales ($\log \equiv \log_{10}$). (Note that the static strain was

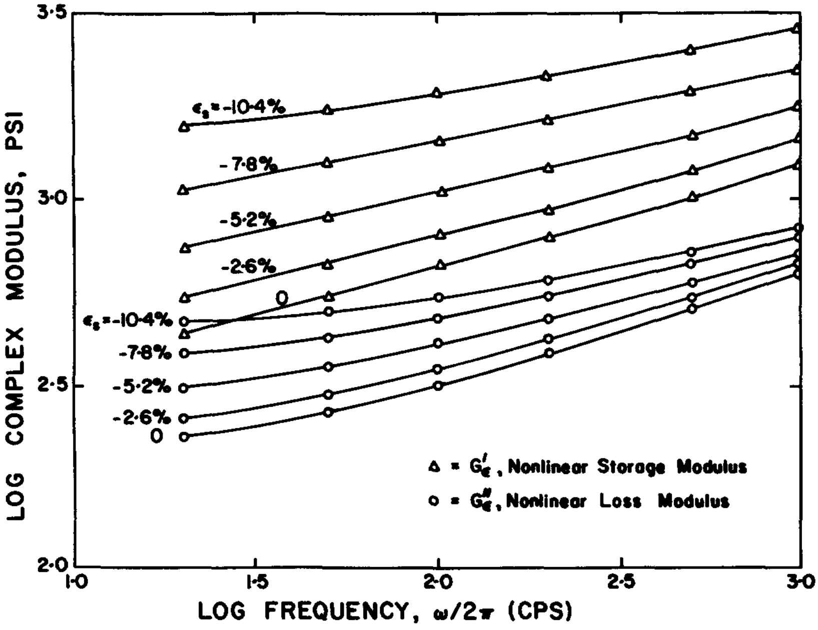

FIG. 3. Complex shear modulus with static lateral compression, PBAA propellant, 84 wt.% loading.

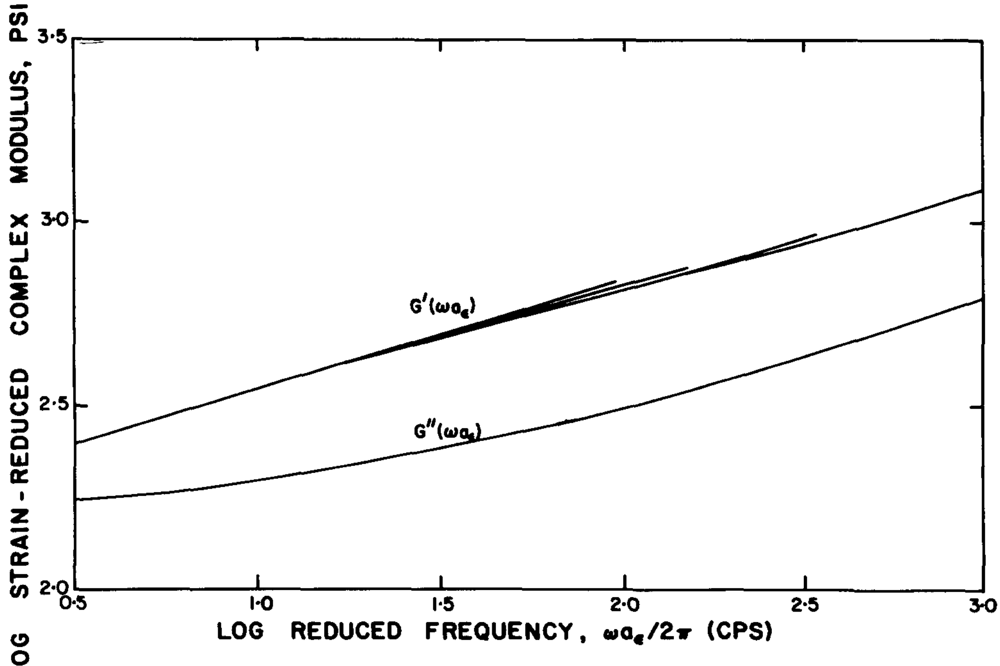

FIG. 4. Lateral strain-reduced complex shear modulus, PBAA propellant, 84 wt.% loading.

either compressive or zero in this test). Especially interesting is the strong nonlinearity that is seen to exist even though this lateral strain is relatively small.

According to equation (34b), the G''_ε curves in Fig. 3 should form a continuous curve of $G''(\omega a_\varepsilon)$ by translating them vertically an amount $\log(1+\varepsilon_s g_s)^2$, and horizontally an amount $\log a_\varepsilon$. Figure 4 shows the result of these translations; all five G''_ε curves blend together within graphical accuracy. Similarly, the quantity $\{G'_\varepsilon - [c-(1+\varepsilon_s g_s)^2 G_e]\}/(1+\varepsilon_s g_s)^2$ should form a continuous curve of $G'(\omega a_\varepsilon)$, in which the denominator and a_ε have been obtained previously by shifting the G''_ε data. Superposition of the storage modulus curves is seen to be quite good, with the maximum deviation from the $\varepsilon_s = 0$ curve being seven per cent. Graphically determined pertinent values are given in Table 1.

TABLE 1

Compressive strain, $-\varepsilon_s$ (%)	a_ε	$c-(1+\varepsilon_s g_s)^2 G_e$ (psi)	g_s
	1	0	
2·6	0·74	70	−3·46
5·2	0·35	228	−5·20
7·8	0·18	508	−6·16
10·4	0·10	962	−6·35

We should point out that the small difference between reduced storage modulus curves in Fig. 4 can be removed by a slight adjustment of the values in this table. However, this change leads to reduced loss modulus curves which do not blend together as well as indicated in Fig. 4.

Shear vibrations superposed on static shear strain

In this case, a specimen made of 88 wt. %-loaded carboxy-terminated polybutadiene propellant (CTPB) was used. (Greatest loading possible is approximately 90 per cent).

Figure 5 shows the measured complex modulus components, which are seen to be quite sensitive to the static shear strain. If the theoretical moduli (39) are valid, this data should superpose in the same way as the moduli with lateral compression. However, it is clear from the figure that G''_γ curves cannot be shifted to form a single curve. Nevertheless, the storage moduli values do superpose very well, as shown in Fig. 6. Graphically determined values are given in Table 2. The a_ε values were estimated by trial-and-error such that the loss modulus values would blend together at the lower frequencies.*

Although the nonlinear loss moduli for this very highly-loaded propellant do not superpose very well, especially at the higher frequencies, equation (36) may still be a valid approximation for some other strain histories; this follows from the good superposition exhibited by the storage modulus, and the fact that for many materials the relaxation modulus and storage modulus are practically identical [12]. However, further study is certainly needed in order to determine the range of validity of equation (36) for this material.

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* Recall for the previous case of lateral compression that the shift-factor was determined by superposing loss moduli, and a trial-and-error procedure was not needed.

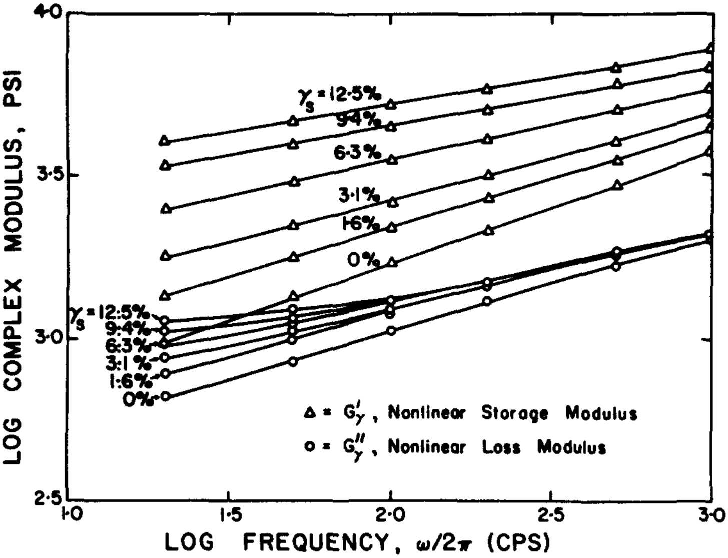

Fig. 5. Complex shear modulus with static shear strain, CTPB propellant, 88 wt.% loading.

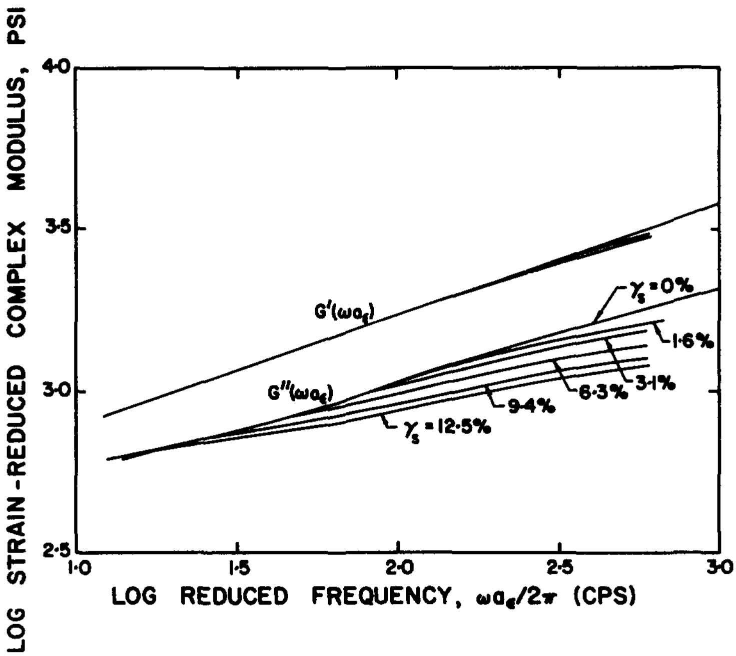

Fig. 6. Shear strain–reduced complex shear modulus, CTPB propellant, 88 wt.% loading.

As a final item of interest, the data in Table 2 enable us to determine whether or not the third and higher order portion of the free energy, ΔF_e, can be neglected. First, observe that $F_e \equiv \Delta F_e + G_e q_3^2/2$; hence

$$\frac{d^2F_e}{d\gamma_3^2}-\left(\frac{dq_3}{d\gamma_3}\right)^2 G_e = \frac{d^2\Delta F_e}{d\gamma_3^2}+\frac{d^2q_3}{d\gamma_3^2}q_3 G_e \tag{40}$$

TABLE 2

Static shear strain, γ_s (%)	a_ε	$\left(\frac{d^2F_e}{d\gamma_3^2}\right)_{\gamma_s} - \left(\frac{dq_3}{d\gamma_3}\right)^2_{\gamma_s} G_e$ (psi)	$\left(\frac{dq_3}{d\gamma_3}\right)_{\gamma_s}$
0	1·0	0	1·0
1·6	0·7	300	1·12
3·1	0·6	700	1·17
6·3	0·6	1300	1·25
9·4	0·6	2100	1·30
12·5	0·6	2700	1·33

For this material, the equilibrium shear modulus is $G_e \simeq 200$ psi, and values of $q_3 d^2 q_3/d\gamma_3^2$ can be estimated from $dq_3/d\gamma_3$ in Table 2. Upon comparing terms in (40) one finds, over most of the strain range covered in this test, that ΔF_e must not only be retained, but actually provides the greatest contribution to the frequency-independent portion of the nonlinear storage modulus, G'_γ.

6. CONCLUDING REMARKS

Irreversible thermodynamics has been used to derive nonlinear stress–strain equations. Comparison of theoretical results with experimental data shown herein, and with some data obtained by others, indicates that the proposed equations are applicable to highly viscoelastic media with strong material nonlinearities. It was shown that a simple graphical method can be used to evaluate strain-dependent material functions and to check validity of this theory.

Considering the fact that data presently available on any given material are very limited in the nonlinear range, there is a major need for further critical experiments in order to establish the range of validity of the theory. In this connection, it is believed that experiments involving harmonic strain, similar to those discussed in this paper, provide an especially critical check on theory since two interrelated response quantities (i.e. amplitude and phase angle) are obtained. Of course, additional strain histories, such as constant finite strain step and constant strain rate should be applied in order to further check accuracy of the theory in predicting response in the nonlinear range.

On the basis of the similarity between the linear and nonlinear forms of the constitutive equations in generalized notation, it is possible to represent the nonlinear equations by mechanical models consisting of springs and dashpots. This point is discussed further in [7], where the present theory is extended to include transient temperatures and thermomechanical coupling.

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APPENDIX

Relation Between Generalized Forces and the Stress Tensor

We choose as strains the covariant components of the strain tensor γ_{ij} [13] referred to a convected set of coordinates $(\theta_1, \theta_2, \theta_3)$; these are called sometimes the Lagrangian components of strain [14], and are quantities that define completely the state of deformation of each material element, independently of rigid body motion. Equation (7) is not applicable with nonlinear behavior, but the appropriate generalized force and stress relations can be determined from a virtual work condition.

To accomplish this, we first introduce the single index notation,

$$P^1 \equiv \tau^{11};\ P^2 \equiv \tau^{22};\ P^3 \equiv \tau^{33};\ P^4 \equiv \tau^{12};\ P^5 \equiv \tau^{13};\ P^6 \equiv \tau^{23} \tag{41a}$$

$$\xi_1 \equiv \gamma_{11};\ \xi_2 \equiv \gamma_{22};\ \xi_3 \equiv \gamma_{33};\ \xi_4 \equiv 2\gamma_{12};\ \xi_5 \equiv 2\gamma_{13};\ \xi_6 \equiv 2\gamma_{23} \tag{41b}$$

where τ^{ij} are components of the contravariant stress tensor [13] referred to $(\theta_1, \theta_2, \theta_3)$. Assuming that the volume of the body is unity in the unstrained state, and that it is strained homogeneously, the virtual work δW is [13]

$$\delta W = \sqrt{\left(\frac{G}{g}\right)} \sum_{i=1}^{6} P^i \delta\xi_i \tag{42}$$

where g and G are the determinants of the covariant metric tensors of the unstrained and strained bodies, respectively. For arbitrary variations $\delta\xi_i$

$$\sqrt{\left(\frac{G}{g}\right)} \sum_{i=1}^{6} P^i \delta\xi_i = \sum_{i,j=1}^{6} Q_j \frac{\partial q_j}{\partial \xi_i} \delta\xi_i . \tag{43}$$

Thus,

$$P^i = \sqrt{\left(\frac{g}{G}\right)} \sum_{j=1}^{6} Q_j \frac{\partial q_j}{\partial \xi_i} \tag{44}$$

where, for an initially isotropic body with initially Cartesian coordinates,*

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*The derivative $(d/d\tau)$ is defined as a time derivative for fixed values of the convected coordinates $(\theta_1, \theta_2, \theta_3)$.

$$Q_1 = \frac{\partial \Delta F_e}{\partial q_1}+\frac{2}{3}\int_0^t G(\rho-\rho')\frac{\mathrm{d}}{\mathrm{d}\tau}(2q_1-q_2-q_3)\mathrm{d}\tau+\int_0^t K(\rho-\rho')\frac{\mathrm{d}e}{\mathrm{d}\tau}\mathrm{d}\tau \tag{45a}$$

$$Q_2 = \frac{\partial \Delta F_e}{\partial q_2}+\frac{2}{3}\int_0^t G(\rho-\rho')\frac{\mathrm{d}}{\mathrm{d}\tau}(2q_2-q_1-q_3)\mathrm{d}\tau+\int_0^t K(\rho-\rho')\frac{\mathrm{d}e}{\mathrm{d}\tau}\mathrm{d}\tau \tag{45b}$$

$$Q_3 = \frac{\partial \Delta F_e}{\partial q_3}+\frac{2}{3}\int_0^t G(\rho-\rho')\frac{\mathrm{d}}{\mathrm{d}\tau}(2q_3-q_1-q_2)\mathrm{d}\tau+\int_0^t K(\rho-\rho')\frac{\mathrm{d}e}{\mathrm{d}\tau}\mathrm{d}\tau \tag{45c}$$

$$Q_4 = \frac{\partial \Delta F_e}{\partial q_4}+\int_0^t G(\rho-\rho')\frac{\mathrm{d}q_4}{\mathrm{d}\tau}\mathrm{d}\tau; \qquad Q_5 = \frac{\partial \Delta F_e}{\partial q_5}+\int_0^t G(\rho-\rho')\frac{\mathrm{d}q_5}{\mathrm{d}\tau}\mathrm{d}\tau;$$

$$Q_6 = \frac{\partial \Delta F_e}{\partial q_6}+\int_0^t G(\rho-\rho')\frac{\mathrm{d}q_6}{\mathrm{d}\tau}\mathrm{d}\tau \tag{45d}$$

$$\rho \equiv \int_0^t \frac{\mathrm{d}t}{a_\varepsilon}; \qquad \rho' \equiv \int_0^\tau \frac{\mathrm{d}t}{a_\varepsilon}; \qquad g = 1. \tag{45e}$$

The equilibrium free energy term ΔF_e and the shift-factor a_ε are functions of the three strain invariants only; the generalized coordinates must reduce to strains for sufficiently small strains, but, in general, will be isotropic tensor functions [3] of the strain tensor.

In deriving equation (44), we have been careful to define stresses and strains in terms of a coordinate system that moves with the body. Also, the strains (41b) are nonlinear functions of displacement, and are valid regardless of the amount of deformation. However, as a practical point, there will be cases for which material nonlinearities exist but geometric nonlinearities can be neglected; i.e., when deformations are small enough that no distinction between coordinates in undeformed and deformed states is needed, and the strain–displacement relations can be linearized. Under these circumstances, one can set $(g/G) = 1$ in (44) and use as stresses and strains the familiar ones appearing in [6].

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Résumé—Des équations relativement simples de tension—deformation on été développées pour des matériaux viscoélastiques, non linéaires, initialement isotropes à une température constante, et démonstration a été faite qu'ils peuvent s'accorder assez bien avec le comportement réel des polymères remplis ou non-remplis. Tout d'abord, des équations pour une condition générale de contrainte sont dérivés en étendant la théorie thermodynamique linéaire de Biot à une catégorie restreinte de comportement non-linéaire. Seulement deux fonctions de relaxation tributaires du temps apparaissent, et celles-ci sont les modules familières de viscoélasticité linéaire. Les relations générales sont alors spécialisées aux équations de résistance–effort applicables aux chargements uniaxes, aux problèmes des déformations radiales et axiales de cylindres longs, circulaires et de simple cisaillement avec contrainte latérale. L'équation uniaxiale produit, comme cas spécial, un module de relaxation non-linéaire qui possède la forme familière pour les polymères dans lesquels la contrainte et la dépendance au temps apparaissent comme des facteurs différents. Les résultats d'expériences sur des polymères hautement remplis sont comparés avec la théorie pour les cas dans lesquels des vibration de cisaillement très légères sont superposées à une compression latérale statique et sur un cisaillement statique. De fortes non-linéarités sont notées avec un léger pourcentage de contrainte statique.

Zusammenfassung—Relative einfache Spannungs–Dehnungsgleichungen wurden für nichtlineare, anfängliche isotrop viskoelashschi Materialien mit beständiger Temperatur entwickelt und stimmen sehr gut mit dem tatsächlichen Verhalten von ungefüllten und gefüllten Polymern überein. Erstens, Gleichungen für einen allgemeinen Zustand der Spannung, werden bei Erweiterung der Biot-linearen wärmemechanischen Theorie, zu einer beschränkten Klasse von nichtlinearen Verhalten abgeleitet. Es erscheinen nur zwei zeitabhängige Entspannungs Funktionen, und diese sind gerade die wohlbekannten linearen viskoelastischen Module. Die allgemeinen Beziehungen sind dann zu Spannungs–Dehnungsgleichungen spezialisiert, anwendbar für einachsige Belastung, radiale und axiale Verformungsprobleme von langen, kreisförmigen Zylindern und einfachen Schub mit seitlicher Beanspruchung. Die einachsige Gleichung ergibt, als ein besonderer Fall, einen nichtlinearen Modul, welches die wohlbekannte Form für Polymer hat, in welchem Beanspruchungen und Zeitabhängigkeit als getrennte Faktoren erscheinen. Ergebnisse von Versuchen an hochgefüllten Polymern werden mit der Theorie von Fällen verglichen, in welchen sehr kleine Schubschwingungen an statischen seitlichen Kompressionen und an statischen Beanspruchungen überlagert sind. Starke Nichtlinearitäten werden mit statischen Deformationen von nur wenigen Prozenten beobachtet.

Абстракт—Выведены относительно простые уравнения "напряжения-деформации" для нелинейных первоначально изотропных, вязкоупругих материалов с постоянной температурой и показано, что они совершенно согласуются с действительным поведением полимеров с наполнителями и без наполнителей. Во-первых, уравнения общего состояния деформации выводятся распространением линейной термодинамической теории Биота (Biot) на ограниченную группу нелинейного поведения. Выявляются только две, зависящие от времени функции релаксации и они представляют из себя именно хорошо известные линейные вязкоупругие релаксационные модули. Общие соотношения, затем, ограничиваются уравнениями напряжения-деформации, применимыми при одноосном нагружении, при радиальных и осевых проблемах деформации длинных, круговых цилиндров и простого сдвига с поперечной деформацией. Одноосное уравнение поддаётся, как специальный случай, нелинейному релаксационному модулю, который обладает хорошо известной формой для полимеров, в то время, как деформация и зависимость от времени представляют из себя отдельные факторы. Результаты опытов с полимерами с высоким содержанием наполнителя сравниваются с теорией для случаев, в которых вибрации очень малого сдвига совмещаются со статическим поперечным сжатием и со статическим сдвигом. Больмая нелинейностб наблюдается для статических деформации которые только несколько ироцент.