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A MODEL FOR VISCOELASTIC FLUID BEHAVIOR WHICH ALLOWS NON-AFFINE--ETC(U)
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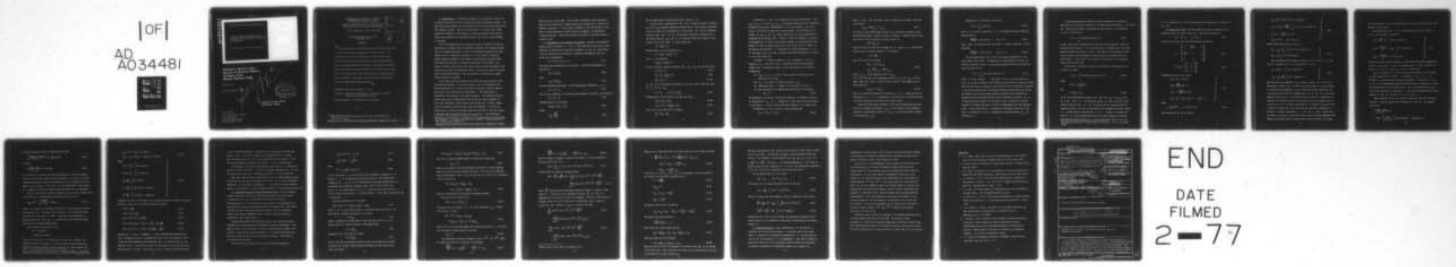

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A MODEL FOR VISCOELASTIC FLUID BEHAVIOR WHICH ALLOWS NON-AFFINE DEFORMATION

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ABSTRACT

A continuum theory of viscoelasticity is developed which allows non-affine deformation, defined in an appropriate manner. The constitutive equation is a generalization of that obtained from molecular theory with the addition of one scalar parameter which becomes important for large deformations. The theory is applied to simpler shear flows, the scalar parameter being determined to match certain experimental data. The theory shows good agreement with all data examined. The paper concludes with the development of a general non-affine thermodynamic theory.

AMS(MOS) Subject Classification - 76.00

Key Words - Nonlinear viscoelasticity, constitutive equations, Rheology, mathematical modeling.

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1. Introduction. A constitutive equation for viscoelastic fluids can be derived systematically from the molecular theory of Gaussian networks. The same constitutive equation can be derived from the molecular bead-spring model with Hookean springs. (See [1] for references). It, hence, has a sound theoretical foundation. Unfortunately, it does not describe, even qualitatively, some significant viscoelastic behavior such as the "shear thinning" of viscosity.

One of the assumptions of the molecular theory of networks is that the junctions move affinely with an equivalent continuum.* The anologous assumption of the bead-spring model is that the surrounding Newtonian fluid moves affinely with an equivalent continuum. It is our object to relax the affine assumption present in both models by developing a continuum theory that allows two histories of deformation which may be non-affine. One history is made to give rise to the current state of stress according to the constitutive equation from molecular theory. The second is made the observed smooth continuum deformation. The two motions are connected by an appropriate constitutive equation.

In the next section we develop the constitutive equation which allows non-affine deformation. It is just as easy to use as that based on the affine assumption, but is able to describe viscoelastic behavior considerably better for all the data we have examined. This improvement is purchased by the addition of one scalar parameter. The constitutive equation is then used to examine shear flow and the new scalar parameter in the theory determined to match certain experimental data. Steady, sudden start up and small oscillatory shear flows are examined. It is not our intention here to make an intensive comparison with data or with the results of the many empirical models found in the literature. Such comparisons

*Actually it is sufficient to assume only that boundary points of the network move affinely. It can then be proved that ensemble - average positions of all junctions move affinely [1].

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will follow in a later paper. We here wish to develop a sound theoretical basis for the theory and to compare results with enough data to indicate its potential usefulness. In this regard we develop in the last section of this paper a thermo-viscoelastic theory within the framework of generalized continuum mechanics. This theory contains the theory of the next section as a special case.

2. Development of the constitutive equation. Consider two deformation histories which we denote by α and β. The locations of particles in these histories are described by Cartesian coordinates x_i and ξ_i respectively. If the two histories are related by a compatible deformation, there is a one-to-one correspondence

$$\xi_i = \xi_i (x_1, x_2, x_3, t) \tag{2.1}$$

describing this deformation at every time t. The local deformation is described by

$$d\xi_i = F_{ij}\, dx_j \tag{2.2}$$

where

$$F_{ij} = \partial \xi_i / \partial x_j \tag{2.3}$$

are the deformation gradients. Define displacement components r_i by

$$\xi_i = x_i + r_i \tag{2.4}$$

The velocity components of particles in each history, $\dot{x}_i$ and $\dot{\xi}_i$, are related by

$$\dot{\xi}_i = \dot{x}_i + \dot{r}_i \tag{2.5}$$

Differentiation of (2.5) gives

$$A_{ir} F_{rk} = \dot{x}_{i,k} + \dot{r}_{i,k} \tag{2.6}$$

where

$$A_{ij} = \frac{\partial \dot{\xi}_i}{\partial \xi_j} \tag{2.7}$$

and the comma denotes differentiation with respect to x_i.

We next derive transformation rules under a change of frame of reference for the various kinematic quantities defined above. The relative orientation of the two frames can be described by a translation $\underline{c}(t)$ and an orthogonal rotation tensor $Q(t)$. Let $\bar{x}_i$ be Cartesian coordinates associated with the second frame and Q_{ij} and C_i be components taken with respect to base vectors in the first frame. It can be shown that

$$x_i = Q_{ij}\bar{x}_j + C_i$$

Differentiation of this relation gives:

$$\dot{x}_i = Q_{ij}\dot{\bar{x}}_j + \dot{Q}_{ij}\bar{x}_j + \dot{C}_i$$

Since Q is orthogonal,

$$\dot{Q}_{ij}Q_{ik} + Q_{ij}\dot{Q}_{ik} = 0$$

If the two frames coincide at current time, $Q_{ij} = \delta_{ij}$ and the above give:

$$x_i = \bar{x}_i + C_i \tag{2.8}$$

$$\dot{x}_i = \dot{\bar{x}}_i + \dot{Q}_{ij}\bar{x}_j + \dot{C}_i \tag{2.9}$$

$$\dot{Q}_{ij} + \dot{Q}_{ji} = 0 \tag{2.10}$$

ξ_i and $\dot{\xi}_i$ also transform according to (2.8) and (2.9) so that the rules for r_i and $\dot{r}_i$ are:

$$r_i = \bar{r}_i \quad , \quad \dot{r}_i = \dot{\bar{r}}_i + \dot{Q}_{ij}\bar{r}_j \tag{2.11}$$

Differentiation of (2.9) and (2.11) give the rules:

$$\dot{x}_{i,k} = \dot{\bar{x}}_{i,k} + \dot{Q}_{ik} \tag{2.12}$$

$$\dot{r}_{i,j} = \dot{\bar{r}}_{i,j} + \dot{Q}_{ik}F_{kj} - \dot{Q}_{ij} \tag{2.13}$$

From (2.6), (2.12) and (2.13) we obtain

$$A_{ij} = \bar{A}_{ij} + \dot{Q}_{ij} \tag{2.14}$$

If histories α and β are identical, we say they are affine. Then, $F_{ij} = \delta_{ij}$, $r_i = 0$ and $A_{ij} = \dot{x}_{i,j}$. Non-affine histories may be incompatible in which case a global correspondence (2.1) is not defined. Eqs. (2.3), (2.4), (2.5) and (2.7) then cease to have meaning. We still make use of fields r_i, A_{ij}, x_i and F_{ij} which satisfy Eq. (2.6) and transformation relations (2.8) through (2.14). History α, which is assumed to be smooth and homogeneous, is taken as the history observed on the macroscopic scale. History β will be taken to give rise to the stress field in a manner to be made precise presently. F represents the local deformation of α to β according to Eq. (2.2) and A represents the velocity gradient of history β in a local sense also.

If tensor A is made to depend on $\dot{x}_{i,j}$ by making F and $\dot{r}_{i,j}$ depend on $\dot{x}_{i,j}$, there will result a continuum model which represents a simple fluid. We develop a theory of this type based on the following assumptions:

(a) $F_{ij}(t) = \delta_{ij}$. At current time the spatial labelling of both histories is the same.

(b) $\dot{r}_{i,j}$ is a linear isotropic function of $\dot{x}_{i,j}$.

(c) The Cauchy stress T depends on the history of tensor A.

(d) The deformation is incompressible according to the equation:

$$\dot{x}_{i,i} = 0 \tag{2.15}$$

By assumptions (a) and (b), the velocity gradient A becomes a function of the gradient $\dot{x}_{i,j}$ of α. Assumption (c) says that the stress depends on the history α, which is the constitutive relation of a simple fluid.

Assumptions (b) and (d) result in the following form:

$$\dot{r}_{i,j} = b\,\dot{x}_{i,j} + c\,\dot{x}_{j,i} \tag{2.16}$$

where b and c are constants. Use of assumption (a) and Eqs. (2.6) and (2.16) yield:

$$A_{ij} = (b+1)\dot{x}_{i,j} + c\,\dot{x}_{j,i} \tag{2.17}$$

We require (2.17), which plays the role of a constitutive equation, to be form invariant under a change of frame of reference. Substitution of (2.12) and (2.14) in (2.17) and use of (2.10) results in:

$$(c-b)\,\dot{Q}_{ij} = 0$$

which must hold for arbitrary antisymmetric $\dot{Q}$. Hence, $c = b$ and we write both in terms of another constant a, as follows:

$$c = b = \frac{a-1}{2}$$

Eqs. (2.16) and (2.17) become

$$\begin{aligned} \dot{r}_{i,j} &= (a-1)\,\dot{x}_{(i,j)} \\ A_{ij} &= \frac{a+1}{2}\,\dot{x}_{i,j} + \frac{a-1}{2}\,\dot{x}_{j,i} \end{aligned} \tag{2.18}$$

where $x_{(i,j)}$ is the symmetric part of $\dot{x}_{i,j}$.

Eq. (2.18) says that the antisymmetric parts of A_{ij} and $\dot{x}_{i,j}$ are the same. That is, α and β have the same vorticity. The symmetric parts are related by:

$$A_{(i,j)} = a\,\dot{x}_{(i,j)} \tag{2.19}$$

Hence, the rate-of-deformation of elements in β is a times the rate-of-deformation in α. $a = 1$ corresponds to affine motion, the deviation from this value measuring the deviation from affine motion.

There are various ways assumption (2.16) can be generalized and still result in a simple fluid theory. $\dot{r}_{i,j}$ can be allowed to be a nonlinear isotropic or anisotropic function of $\dot{x}_{i,j}$ or it can be allowed to depend on the history of $\dot{x}_{i,j}$.

Assumption (c) is written in the form:

$$T + pI = \overset{t}{\underset{\tau=-\infty}{F}} \{E(\tau,t)\} \tag{2.20}$$

where p is a scalar pressure and E is a deformation measure defined as the solution of:

$$\frac{\partial E(\tau,t)}{\partial t} = A(t)\ E(\tau,t), \qquad E(\tau,\tau) = I \tag{2.21}$$

where $\partial E/\partial t$ is a material time derivative. It can be shown that E also satisfies:

$$\frac{\partial E(\tau,t)}{\partial \tau} = -E(\tau,t)\ A(\tau), \qquad E(t,t) = I \tag{2.22}$$

With the generality of Eq. (2.20) this theory is equivalent to the usual simple fluid theory. Something new is obtained when a special constitutive equation is used. A constitutive equation derived from molecular theory is given by [1]:

$$T + pI = \int_{\tau=-\infty}^{t} m(t-\tau)K(\tau,t)K(\tau,t)^{\dagger}\, d\tau \tag{2.23}$$

where K is the gradient $\partial \underline{x}(t)/\partial \underline{x}(\tau)$ and m a scalar kernel function. Eq. (2.23) is derived from a molecular network model of Gaussian chains where the junctions are assumed to move affinely with an equivalent continuum. It can also be derived from a bead-spring molecular model where the springs are Hookean and the bead-spring system is assumed to be surrounded by a Newtonian fluid which moves affinely with an equivalent continuum. One of the most important features of this model is that it predicts a constant viscosity in steady shear flow, a result in disagreement with most measurements. We note that tensor K satisfies the equations (2.21) and (2.22) with E replaced by K and A replaced by velocity gradient $\dot{x}_{i,j}$ of deformation α.

A continuum model which relaxes the affine assumption is achieved by identifying the equivalent continuum of the models with the history α but allowing the molecular models to move affinely with history β by replacing K in Eq. (2.23) with E.

$$T + pI = \int_{-\infty}^{t} m(t-\tau)E(\tau,t)E(\tau,t)^{\dagger}\, d\tau \tag{2.24}$$

In what follows the consequences of (2.24) will be investigated. There is one additional parameter, a, in this new theory as compared with the affine molecular models which lead to (2.23). The choice of this parameter allows better agreement with experimental results than can be obtained with the affine model. In particular, the viscosity is now found to vary realistically with the shear rate.

An alternate constitutive equation is obtained by integrating (2.24) by parts, to obtain

$$T + pI = \int_{-\infty}^{t} G(t-\tau)E(\tau,t)D(\tau)E(\tau,t)^{\dagger}\, d\tau \tag{2.25}$$

where

$$m(t) = -\frac{1}{2}\frac{d}{dt}G(t)$$

and

$$D = \frac{1}{2}(A + A^{\dagger}) \tag{2.26}$$

is the rate-of-deformation tensor of β. Note that $D_{ij} = a\,\dot{x}_{(i,j)}$ from Eq. (2.19). When $a = 1$ the new model agrees, of course, with the affine molecular model (2.23). As $a \to 0$, it becomes the co-rotational model of Goddard and Miller [7]* that is discussed by Bird, Hassager and Abdel-Khalik [3]. In what follows we assume that $0 < a < 1$ because it is found that values of a in this range yield good results when compared with experiment whereas negative values of a do not yield good results. Note that

*In taking the limit, Ga is held fixed as the kernel in the co-rotational model.

$a = -1$ corresponds to a so called covariant model (equation 2 of table 6.4, ref. [1]).

3. Simple shear flow. We next examine the results predicted by the non-affine model for simple shear flow. This flow is defined by:

$$\dot{x}_1 = \kappa(t)\, x_2 \quad , \quad \dot{x}_2 = \dot{x}_3 = 0 \tag{3.1}$$

the velocity gradient and rate-of-deformation tensors are

$$A = \begin{bmatrix} 0 & \frac{a+1}{2}\kappa & 0 \\ \frac{a-1}{2}\kappa & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{3.2}$$

$$D = \frac{1}{2}\, a\, \kappa \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{3.3}$$

Integrating system (2.21) yields

$$\left.\begin{aligned} E_{11} &= E_{22} = \cos(\lambda\, s) \\ E_{12} &= \sqrt{\frac{1+a}{1-a}}\, \sin(\lambda\, s) \\ E_{21} &= -\sqrt{\frac{1-a}{1+a}}\, \sin(\lambda\, s) \\ E_{31} &= E_{13} = E_{32} = E_{23} = 0 \quad , \quad E_{33} = 1 \end{aligned}\right\} \tag{3.4}$$

where

$$\lambda = \frac{1}{2}\sqrt{1-a^2} \quad , \quad s = \int_\tau^t \kappa(t')\, dt' \tag{3.5}$$

The constitutive Eq. (2.25) yields:

$$
\left.
\begin{aligned}
T_{12} &= \frac{1}{2}\, a \int_{-\infty}^{t} G(t-\tau)\, \kappa(\tau)\, \cos(2\lambda s)\, d\tau \\
T_{11} + p &= \frac{1}{2}\, a \sqrt{\frac{1+a}{1-a}} \int_{-\infty}^{t} G(t-\tau)\, \kappa(\tau)\, \sin(2\lambda s)\, d\tau \\
T_{22} + p &= -\frac{1-a}{1+a}\,(T_{11} + p) \\
T_{33} + p &= 0 \quad , \quad T_{13} = T_{23} = 0
\end{aligned}
\right\} \qquad (3.6)
$$

Normal stress differences are given by:

$$
\left.
\begin{aligned}
T_{11} - T_{22} &= \frac{a}{2\lambda} \int_{-\infty}^{t} G(t-\tau)\, \kappa(\tau)\, \sin(2\lambda s)\, d\tau \\
T_{22} - T_{33} &= -\frac{1}{2}\,(1-a)(T_{11}-T_{22})
\end{aligned}
\right\} \qquad (3.7)
$$

For the sudden start of shear defined by $\kappa(t) = 0$ for $t < 0$ and $\kappa(t) = k$ = constant for $t \geq 0$, we obtain for $t \geq 0$,

$$
\left.
\begin{aligned}
T_{12} &= \frac{1}{2}\, a\, k \int_{0}^{t} G(\tau)\, \cos(2\lambda k\tau)\, d\tau \\
T_{11} - T_{22} &= \frac{ak}{2\lambda} \int_{0}^{t} G(\tau)\, \sin(2\lambda k\tau)\, d\tau
\end{aligned}
\right\} \qquad (3.8)
$$

Note that the first maximum of T_{12} occurs at strain $kt = \pi/4\lambda$ and is independent of shear rate. In this theory the parameter a can be chosen to cause the first maximum to occur at any given strain, whereas in the co-rotational limit the first maximum must occur at $kt = \pi/2$. The affine molecular model, with $\lambda = 0$, does not predict overshoot. Examination of same data for solutions given in [3] indicates that the maximum occurs at a strain of 2.9 to 3.4, which corresponds to λ between 0.23 and 0.27 and a between 0.84 and 0.89. For a melt data [8] indicates a maximum at a strain of 4.7 which corresponds to $\lambda = 0.17$ and $a = 0.94$. We note that our model, as does the co-rotational model, predicts stress components that undergo an infinite number of damped oscillations with time. For normal

stress differences, the first maximum occurs at twice the strain as the first maximum of shear stess.

For steady shear flow, $\kappa = k = \text{constant}$ for all time, we obtain $s = k(t-\tau)$ and viscometric functions:

$$\left.\begin{aligned} \eta(k) &= \frac{T_{12}}{k} = \frac{1}{2}\, a \int_0^\infty G(\tau)\, \cos(2\lambda k\tau)\, d\tau \\ \Psi_1(k) &= \frac{T_{11}-T_{22}}{k^2} = \frac{a}{2\lambda k} \int_0^\infty G(\tau)\, \sin(2\lambda k\tau)\, d\tau \\ \Psi_2(k) &= \frac{T_{22}-T_{33}}{k^2} = -\frac{1}{2}\,(1-a)\,\Psi_1(k) \end{aligned}\right\} \qquad (3.9)$$

The present model predicts negative Ψ_2, which agrees with most experimental results. If we take $a = 0.87$ for solutions and $a = 0.94$ for melts, we obtain $\Psi_2 = -0.07\ \Psi_1$ and $\Psi_2 = -0.03\ \Psi_1$, respectively.

Any of relations (3.9), which are Fourier transforms, can be inverted to yield expressions for kernel G in terms of η, Ψ_1 or Ψ_2. In principle, we can use these relations to determine G from data on η, Ψ_1 or Ψ_2. If the experimental material behaves exactly according to our model, each equation will yield the same result. The co-rotational model can be used in the same manner to determine G. The affine molecular model predicts constant η and Ψ_1 and gives $\Psi_2 = 0$ for every G.

These equations can be used to derive relations between the viscosity function η and the normal stress functions Ψ_1 and Ψ_2. For example, from (3.9),

$$\int_0^\infty \frac{\eta(x) - \eta(k)}{k^2 - x^2}\, dx =$$

$$= \frac{1}{2}\, a \int_0^\infty \frac{dx}{k^2 - x^2} \int_0^\infty G(\tau)[\cos(2\lambda\tau x) - \cos(2\lambda\tau k)]\, d\tau$$

On interchanging the order of integration and using

$$\int_0^\infty \frac{\cos(ax) - \cos(ak)}{k^2 - x^2}\, dx = \frac{\pi}{2k} \sin(ak) \tag{3.10}$$

we obtain

$$\int_0^\infty \frac{\eta(x) - \eta(k)}{k^2 - x^2}\, dx = \frac{\pi\lambda}{2} \Psi_1(k) \tag{3.11}$$

Eq. (3.10) can be derived by writing the integral as a Cauchy principal value and evaluating it using contour integration. Eq. (3.11) can be made to match experimental results for polymer melts and for polymer solutions given in [3] by taking $\lambda = 1/6$ and $\lambda = 1/4$ respectively*. These values of λ agree well with those obtained from the shear start up experiments.

Note that the value of the first maximum of shear stress in sudden start up is related to the steady shear viscosity given by (3.9) by

$$T_{max} = \frac{2}{\pi} k \int_0^\infty \frac{\cos(\frac{\pi}{2} x)}{1 - x^2}\, \eta(kx)\, dx \tag{3.12}$$

where k is taken to be the same in each flow. This equation is obtained by inverting (3.9) to obtain $G(\tau)$ in terms of $\eta(k)$ and substituting the result in $(3.8)_1$ with $t = \pi/4\lambda k$. This result is independent of material quantities $G(t)$ and a. In particular this prediction agrees with that of the Goddard-Miller model.

For oscillatory shear flow, we set

$$\kappa(t) = k \cos(\omega t)$$

$$s = \frac{k}{\omega} (\sin\omega t - \sin\omega\tau)$$

in Eqs. (3.6) and (3.7). If the factors $\cos(2\lambda s)$ and $\sin(2\lambda s)$ are expanded in series of powers of k and the leading terms retained, we obtain the following results for small amplitude oscillatory shear flow:

*Eq. (3.11) was derived in [3] for the co-rotational model, $\lambda = 1/2$, and empirically modified to the form (3.11) in order to fit experimental data.

$$T_{12} = k\,(\eta' \cos\omega t + \eta'' \sin\omega t)$$

$$T_{11} - T_{22} = k^2(\theta_m + \theta' \cos 2\omega t + \theta'' \sin 2\omega t) \tag{3.13}$$

where

$$\left.\begin{aligned}
\eta'(\omega) &= \frac{1}{2}\, a \int_0^\infty G(\tau) \cos\omega\tau \, d\tau \\
\eta''(\omega) &= \frac{1}{2}\, a \int_0^\infty G(\tau) \sin\omega\tau \, d\tau \\
\theta_m &= \frac{a}{2\omega} \int_0^\infty G(\tau) \sin\omega\tau \, d\tau \\
\theta' &= \frac{a}{2\omega} \int_0^\infty G(\tau)(\sin 2\omega\tau - \sin\omega\tau) \, d\tau \\
\theta'' &= \frac{a}{2\omega} \int_0^\infty G(\tau)(\cos\omega\tau - \cos 2\omega\tau) \, d\tau
\end{aligned}\right\} \tag{3.14}$$

Comparison with Eqs. (3.9) shows that the large deformation viscosity functional forms are related to the oscillatory forms as follows:

$$\eta'(x) = \eta\left(\frac{x}{2\lambda}\right) \tag{3.15}$$

$$\eta''(x) = \frac{1}{2}\, x\, \Psi_1\left(\frac{x}{2\lambda}\right) \tag{3.16}$$

$$\theta_m(x) = \frac{1}{x}\,\eta''(x) = \frac{1}{2}\,\Psi_2\left(\frac{x}{2\lambda}\right) \tag{3.17}$$

$$\theta'(x) = \frac{1}{x}\,[\eta''(2x) - \eta''(x)] = \Psi_1\left(\frac{x}{\lambda}\right) - \frac{1}{2}\,\Psi_2\left(\frac{x}{2\lambda}\right) \tag{3.18}$$

$$\theta''(x) = \frac{1}{x}\,[\eta'(x) - \eta'(2x)] = \frac{1}{x}\left[\eta\left(\frac{x}{2\lambda}\right) - \eta\left(\frac{x}{\lambda}\right)\right] \tag{3.19}$$

From data on η' and η parameter λ can be determined by shifting curve $\eta'(x)$ horizontally until it coincides with curve $\eta(x)$ and using Eq. (3.15). It can also be determined by shifting curve $\frac{2}{x}\eta''$ to coincide with Ψ_1 and using Eq. (3.16). The horizontal shifts are performed with the data plotted on semi-log paper, of course. Data given in [3] for a polymer solution determine

$\lambda = 1/4$ from both equations. From data for a melt given in [3] both also give $\lambda = 1/4$. This is the one melt in six discussed in [3] for which Eq. (3.11) also gives $\lambda = 1/4$. For the other five (3.11) yields $\lambda = 1/6$. For a soap solution, data given in [4] gives $\lambda = 1/4$ for both shifts.

In conclusion, all data we have examined give values of λ between 1/6 and 1/4. We have found that $\lambda = 1/4$ for all polymer solutions and $\lambda = 1/6$ for all polymer melts save one. Corresponding values of a^2 are 3/4 and 8/9.

Note that, from the form of expressions (3.14), the small amplitude oscillatory motion can be used to determine the product aG, but cannot determine a separately. In this sense, the parameter a is relevant to finite amplitude motions. Note that $\frac{1}{2}$ aG is the "relaxation modulus" of linear viscoelasticity [9].

4. A non-affine general thermo-viscoelastic theory. We now formulate a theory within the frame work of generalized mechanics [2] that permits a deformation which is not affine with an equivalent continuum. The assumptions of §2 are relaxed so that a theory of some generality is achieved which includes the previous results as a special case. This theory is useful in that it shows the assumptions made in §2 are consistent within a more general framework; and it provides a proper setting for extensions of the special theory.

The governing equations are derived from the first and second laws of thermodynamics by application of appropriate invariance requirements. This method is due to Rivlin and Green. We do not include kinetic energy or the work due to body forces in this formulation. As a result both inertia and body force terms are left out of the equations of motion. These effects can be added if one wishes.

The law of energy balance and the Clausius-Duhem inequality are:

$$\int_R \dot{u}\,\rho\,dV = \dot{w} - \int_A q\,dA \tag{4.1}$$

$$\int_R \dot{s}\,\rho\,dV \geq - \int_A \frac{q}{\theta}\,dA \tag{4.2}$$

where

$$\dot{w} = \int_A [p_i \dot{x}_i + m_i \dot{r}_i]\,dA \tag{4.3}$$

is the rate-of-work. $\underline{p}$ is the stress vector conjugate to velocity $\dot{\underline{x}}$ of history α. $\dot{\underline{r}}$ is a generalized velocity field and $\underline{m}$ the stress vector conjugate to it. $\dot{\underline{x}}$ and $\dot{\underline{r}}$ are identified with the same quantities of §2 by assuming they transform according to Eqs. (2.9), (2.11), (2.12) and (2.13). R is a neighborhood in the x_i - coordinate space with surface A. u is the internal energy density, ρ the mass density, q heat flux, θ temperature and s the entropy.

Tetrahedron analysis of (4.1) yields:

$$p_i \dot{x}_i + m_i \dot{r}_i - q = (P_{ij}\dot{x}_i + M_{ij}\dot{r}_i - q_j)m_j \tag{4.4}$$

where P and M are stress tensors, $\underline{q}$ the heat flux vector and $\underline{n}$ the unit normal. Tetrahedron analysis of (4.2) gives

$$q = q_i n_i \tag{4.5}$$

Under a translation of frame given by (2.9) and (2.11) with $\dot{Q} = 0$ we require that (4.4) remain invariant. This implies that

$$p_i = P_{ij} n_j \tag{4.6}$$

Equations (4.4), (4.5) and (4.6) imply

$$m_i = M_{ij} n_j \tag{4.7}$$

Use of (4.4) and the divergence theorem in Eq. (4.1) allows one to write the latter as a single volume integral from which the local form of the first law follows.

$$\rho\dot{u} = P_{ij,j}\dot{x}_i + P_{ij}\dot{x}_{i,j} + M_{ij,j}\dot{r}_i + M_{ij}\dot{r}_{i,j} - q_{i,i} \tag{4.8}$$

For (4.8) to remain invariant under a translation, we must have

$$P_{ij,j} = 0 \tag{4.9}$$

which is an equation of motion expressing the balance of linear momentum. With (4.9) one term can be deleted from (4.8). For (4.8) to be invariant under transformations (2.9), (2.11), (2.12) and (2.13) for all $\dot{Q}$ satisfying (2.10), we must have

$$\begin{aligned} &P_{ij} + M_{ik,k}r_j + M_{ik}F_{jk} - M_{ij} \\ &\quad = P_{ji} + M_{jk,k}r_i + M_{jk}F_{ik} - M_{ji} \end{aligned} \tag{4.10}$$

which is an expression of the balance of angular momentum.

The local form of law (4.2) is

$$\rho\theta\dot{s} \geq - q_{i,i} + \frac{1}{\theta} q_i \theta_{,i} \tag{4.11}$$

Introducing the free energy $h = u - \theta s$ and eliminating $q_{i,i}$ between (4.8) and (4.11) gives:

$$\begin{aligned} \rho\dot{h} \leq &- \rho s\dot{\theta} + P_{ij}\dot{x}_{i,j} + M_{ij,j}\dot{r}_i \\ &+ M_{ij}\dot{r}_{i,j} - \frac{1}{\theta} q_i \theta_{,i} + p\,\delta_{ij}\dot{x}_{i,j} \end{aligned} \tag{4.12}$$

where the last term has been added with a pressure multiplier p to account for the assumed incompressibility constraint

$$\dot{x}_{i,i} = 0 \tag{4.13}$$

As thermodynamic extensive variables we use θ, $H^{(1)}$ and $H^{(2)}$ where the latter are defined as solutions of the systems

$$\frac{\partial H^{(1)}_{ij}}{\partial t}(t,\tau) = \dot{x}_{i,k}H^{(1)}_{kj} \quad , \quad H^{(1)}_{ij}(\tau,\tau) = \delta_{ij} \tag{4.14}$$

$$\frac{\partial H^{(2)}_{ij}}{\partial t}(t,\tau) = \dot{r}_{i,k} H^{(2)}_{kj} \quad , \quad H^{(2)}_{ij}(\tau,\tau) = \delta_{ij} \tag{4.15}$$

The free energy is assumed to depend on the history of these variables as well as explicitly on $\theta(t)$.

$$h(t) = \bar{h}_{\tau=-\infty}^{t} \{t, \theta(t), \theta(\tau), H^{(1)}(t,\tau), H^{(2)}(t,\tau)\} \tag{4.16}$$

A chain rule* for nonlinear mappings yields:

$$\dot{h}(t) = \frac{\partial \bar{h}}{\partial t} + \frac{\partial \bar{h}}{\partial \theta(t)} \dot{\theta}(t) + \delta\bar{h}_{1\,\tau=-\infty}^{t}(t,\theta(t),\theta(\tau), H^{(1)}, H^{(2)}; \frac{\partial H^{(1)}}{\partial t})$$

$$\delta\bar{h}_{2\,\tau=-\infty}^{t}(t,\theta(t),\theta(\tau), H^{(1)}, H^{(2)}; \frac{\partial H^{(2)}}{\partial t}) \tag{4.17}$$

where $\frac{\partial \bar{h}}{\partial t}$ indicates partial differentiation with respect to explicit dependence on t holding the other arguments fixed and $\delta\bar{h}_1$ and $\delta\bar{h}_2$ are mappings which are linear in their last arguments. The use of this linearity and Eqs. (4.14) and (4.15) allows us to conclude that $\delta\bar{h}_1$ is linear in $\dot{x}_{i,k}(t)$ and $\delta\bar{h}_2$ linear in $\dot{r}_{i,k}(t)$ to obtain the forms:

$$\delta\bar{h}_{1\,\tau=-\infty}^{t}(t,\theta(t), \theta(\tau), H^{(1)}, H^{(2)}; \frac{\partial H^{(1)}}{\partial t}) \tag{4.18}$$

$$= \delta h^{(1)}_{ij\,\tau=-\infty}^{t}(t,\theta(t),\theta(\tau), H^{(1)}, H^{(2)})\, \dot{x}_{i,j}(t)$$

$$\delta\bar{h}_{2\,\tau=-\infty}^{t}(t,\theta(t), \theta(\tau), H^{(1)}, H^{(2)}; \frac{\partial H^{(2)}}{\partial t} \tag{4.19}$$

$$= \delta h^{(2)}_{ij\,\tau=-\infty}^{t}(t,\theta(t), \theta(\tau), H^{(1)}, H^{(2)})\, \dot{r}_{i,j}(t)$$

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*Chain rules of this type are discussed in [5].

Using (4.17), (4.18) and (4.19), the second law, Eq. (4.12), takes the form:

$$\rho \frac{\partial \bar{h}}{\partial t} + \frac{1}{\theta} q_i \theta_{,i} \leq - \rho(s + \frac{\partial \bar{h}}{\partial \theta(t)}) \dot{\theta}(t) + M_{ij,j} \dot{r}_i$$

$$+ (P_{ij} + p \delta_{ij} - \rho \delta h_{ij}^{(1)}) \dot{x}_{i,j} \qquad (4.20)$$

$$+ (M_{ij} - \rho \delta h_{ij}^{(2)}) \dot{r}_{i,j}$$

If the rates $\dot{\theta}$, $\dot{r}_i$, $\dot{x}_{i,j}$ and $\dot{r}_{i,j}$ are independent, (4.20) can hold for all values of the extensive variables only if

$$s = - \frac{\partial \bar{h}}{\partial \theta(t)} \qquad (4.21)$$

$$M_{ij,j} = 0 \qquad (4.22)$$

$$P_{ij} + p \delta_{ij} = \rho \delta h_{ij}^{(1)} \qquad (4.23)$$

$$M_{ij} = \rho \delta h_{ij}^{(2)} \qquad (4.24)$$

The Cauchy stress tensor is given by

$$T_{ij} = P_{ij} + M_{ij} = - p\delta_{ij} + \rho \delta h_{ij}^{(1)} + \rho \delta h_{ij}^{(2)} \qquad (4.25)$$

The second law (4.20) reduces to

$$\rho \frac{\partial \bar{h}}{\partial t} + \frac{1}{\theta} q_i \theta_{,i} \leq 0 \qquad (4.26)$$

With (4.22), Eq. (4.10) takes the form

$$P_{ij} + M_{ik} F_{jk} - M_{ij} = P_{ji} + M_{jk} F_{ik} - M_{ji} \qquad (4.27)$$

while the first law (4.8) becomes

$$\rho \dot{u} = P_{ij} \dot{x}_{i,j} + M_{ij} r_{i,j} - q_{i,i} \qquad (4.28)$$

When the rates in (4.20) are dependent, we postulate that Eqs. (4.21) through (4.28) still hold. These equations then imply that the second law in the form (4.20) holds but are more restrictive.

The basic equations are (4.9), (4.13), (4.14), (4.15), (4.21), (4.22), (4.23), (4.24), and (4.28). To these must be added a vector equation of heat conduction. The variables in these equations are P_{ij}, M_{ij}, x_i, r_i, q_i, s, θ, p, $H^{(1)}_{ij}$ and $H^{(2)}_{ij}$. Note that ρ is considered known and u in (4.28) is given in terms of other variables by $u = h + \theta s$. The constitutive equations (4.23) and (4.24) must be compatible with (4.26) and (4.27).

In the special theory of §2, we have

$$F_{ij} = \delta_{ij} \quad , \qquad A_{ij} = \dot{x}_{i,j} + \dot{r}_{i,j} \tag{4.29}$$

If we take the free energy functional (4.16) in the form

$$h(t) = \frac{1}{2\rho a} \int_{-\infty}^{t} m(t-\tau)\ \mathrm{tr}\ (E\, E^{+})\, d\tau \tag{4.30}$$

and carry through the steps leading to (4.17), (4.18) and (4.19), we get

$$\frac{\partial \bar{h}}{\partial t} = \frac{3}{2\rho a}\,\eta(0) + \frac{1}{2a\rho} \int_{-\infty}^{t} \frac{\partial m}{\partial t}\,(t-\tau)\ \mathrm{tr}\ (E\, E^{+})\, d\tau \tag{4.31}$$

$$\delta h^{(1)}_{ij} = \delta h^{(2)}_{ij} = \frac{1}{2\rho} \int_{-\infty}^{t} m(t-\tau)\, E_{ik} E_{jk}\, d\tau \tag{4.32}$$

Substitution of (4.32) in (4.25) yields the constitutive equation (2.24). Substituting (4.31) in inequality (4.26) gives a restriction on the kernel function m.

5. *Concluding Remarks.* Under assumptions of §2 the history β coincides with the smooth deformation α at current time, but at other times β represents an incompatible deformation of α. In this sense we can say that the deformation β is inhomogeneous. This idea is similar to that used by Noll [2] [4] in developing a theory suitable for describing a continuous distribution of dislocations where use is made of an

inhomogeneous reference state. Noll's theory would seem to be more suitable for describing the behavior of materials with a preferred reference state whereas the present theory is more suited to fluids.

We note that in the thermodynamic theory developed by Coleman (see [5] for references) the free energy is assumed to depend explicitly on the current value of a strain measure and to be differentiable with respect to this measure. In the present theory an assumption of this kind is not needed, the free energy functional (4.16) depending only on the history of strain measures $H^{(1)}$ and $H^{(2)}$. It has been pointed out by Astarita and Sarti [6] that this assumption made in the Coleman theory is a serious one, implying that the material can support a jump in strain, a deformation not possible in a Newtonian fluid. Thus the Coleman model excludes Newtonian fluid behavior. Since this assumption is not made in our model, it may be more suitable for the description of fluid behavior, both viscous and viscoelastic. The reason the assumption is not needed here is because of the use of strain measures $H^{(1)}$ and $H^{(2)}$ defined by differential equations (4.14) and (4.15).

Finally we wish to thank our colleagues in the Rheology Research Center for their helpful discussion of this paper. We especially thank Professor R. B. Bird for his detailed suggestions and Professor Arthur Lodge who provided the motivation for this paper by pointing to the need to relax the affine assumption of the molecular network theory (Ref. [1], pp. 232-235).

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A continuum theory of viscoelasticity is developed which allows non-affine deformation, defined in an appropriate manner. The constitutive equation is a generalization of that obtained from molecular theory with the addition of one scalar parameter which becomes important for large deformations. The theory is applied to simple shear flows, the scalar parameter being determined to match certain experimental data. The theory shows good agreement with all data examined. The paper concludes with the development of a general non-affine thermodynamic theory.

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