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Visco-Elastic Fluids: Prague 2006: by Barry Bernstein

strain, γ , stress, σ , temperature, ϑ , and heat flux, Q, removal rate of heat, the rate of deformation, $\dot{\gamma}$.

Elastic Solid

The stress-strain relation takes the form

 $\sigma = \mu \gamma$

 $\mu(\vartheta)$ is an elastic modulus.

The Helmholtz free energy, $A(\gamma,\vartheta)$ obeys

$$\sigma = \frac{\partial A}{\partial \gamma}$$

so that

$$A = \frac{1}{2}\gamma^2 + h(\vartheta)$$

The entropy, s, satisfies

$$s = -\frac{\partial A}{\partial \vartheta}$$

and the internal energy, E, is given by

$$E = A + \vartheta s$$

Balance of energy equations the rate of change in internal energy to the sum of the work done by the stresses and the rate of heat added, viz.

$$\dot{E} = \sigma \dot{\gamma} - Q$$

So

$$\dot{E} = \dot{A} + \dot{\vartheta}s + \vartheta\dot{s} = \frac{\partial A}{\partial \gamma}\dot{\gamma} + \frac{\partial A}{\partial \vartheta}\dot{\vartheta} + \vartheta\dot{s} + \dot{\vartheta}s$$
$$= s\dot{\gamma} - s\dot{\vartheta} + \vartheta\dot{s} + \dot{\vartheta}s = \sigma\dot{\gamma} + \vartheta\dot{s}$$

Putting these last two equations together yields

$$\vartheta \dot{s} + Q = 0$$

or

$$\dot{s} + \frac{Q}{\vartheta} = 0$$

Viscous Fluid

parameter, η , called *viscosity*

$$\sigma = \eta \dot{\gamma}$$

i.e. $\eta = \eta(\vartheta)$, Helmholtz Free energy, $A = A(\vartheta)$. entropy $s = -dA/d\vartheta$, internal energy $E = A + \vartheta s$. Balance of energy $\dot{E} = \sigma \dot{\gamma} - Q$. $\overline{A + \vartheta s} = \frac{dA}{d\vartheta} \dot{\vartheta} + \dot{\vartheta} s + \vartheta \dot{s} = -s \dot{\vartheta} + s \dot{\vartheta} + \vartheta \dot{s}$ $= \eta \dot{\gamma}^2 - Q$

Which sorts out to

$$\dot{s} + \frac{Q}{\vartheta} = \frac{\eta}{\vartheta} \dot{\gamma}^2 \ge 0$$

The second law is satisfied. Entropy is produced by viscosity and rate of production is > 0 if any flow.

Viscoelasticity

Time dependence.

relaxation modulus, $G(t, \vartheta)$, measured in a stress-relaxation experiment. (t = time.)

$$G = \sum_{n} a_n e^{-t/\tau_n}$$

 τ_n : relaxation times.

In a general deformation history

$$\begin{split} \sigma &= G(0)\gamma(t) + \int_{-\infty}^t \dot{G}(t-\tau)\gamma(\tau) \, d\tau \\ \gamma &= \begin{cases} 0 & \text{if } t < 0 \\ \gamma(t) & \text{if } t > 0 \end{cases} \end{split}$$

Then

$$\sigma = G(0)\gamma(t) + \int_0^t \dot{G}(t-\tau)\gamma(\tau) \, d\tau$$

Slowly changing modulus: i.e. if G is not large, apparent constant – apparently elastic. independently of $G(\infty)$. For fluid behavior, $G(\infty) =$ 0, - eventual complete relaxation. Then

$$\sigma = \int_0^\infty G(t-\tau) \dot{\gamma}(\tau) \, d\tau$$

 $G = \eta \delta(t)$ — viscous fluid again. Since the fluid point of view is unifying, we adopt it.

Helmholtz free energy

$$\begin{split} A &= -\frac{1}{2} \int_{-\infty}^t \dot{G}(t - \tau, \vartheta) [\gamma(t) - \gamma(\tau)]^2 \, d\tau + h(\vartheta), \\ &\qquad \qquad \frac{\partial}{\partial \vartheta} (-\dot{G}) \geq 0 \end{split}$$

where
$$h = h(\vartheta)$$
:
 $s = \frac{1}{2} \int \frac{\partial}{\partial \vartheta} \dot{G}(t - \tau, \vartheta) [\gamma(t) - \gamma(\tau)]^2 d\tau - h'(\vartheta)$
 $E = A + \vartheta s$
 $\dot{E} = \sigma \dot{\gamma} + \vartheta \dot{s} - \frac{1}{2} \int_{-\infty}^t \ddot{G}(t - \tau, \vartheta) [\gamma(t0 - \gamma(\tau))]^2 d\tau$

energy balance equation \Rightarrow

$$\dot{s} + \frac{Q}{\vartheta} = \frac{1}{2\vartheta} \int_{-\infty}^{t} \ddot{G}(t - \tau, \vartheta) [\gamma(t) - \gamma(\tau)]^2 d\tau$$

Since G is a sum of decaying exponentials, $\ddot{G} \geq 0$ and so the second law holds.

Consider $G \sim \vartheta$ (as in perfect gas or ideal rubber).

$$G(t - \tau, \vartheta) = \vartheta \overline{G}(t - \tau)$$

Internal energy, E, then becomes

$$E = h(\vartheta) - \vartheta h'(\vartheta)$$

So during an isothermal stress relaxation, there is no work being done, the internal energy is not changing and so no heat is flowing. What is happening?

Ideal Gas

- Phase 1: work put into internal energy, ϑ rises
- Phase 2: heat flows into surroundings, internal energy returns to original value. All work is stored in the surroundings
- Phase 3: gas does work to return to original pressure. It cools.
- Phase 4: heat flows back from room gas returns to original state.

Our material: During relaxation no heat is flowing; Material is losing its ability to remove heat from its surroundings and return the corresponding energy as work. Let

$$\Sigma = \frac{1}{2} \int \frac{\partial}{\partial \vartheta} \dot{G}(t - \tau, \vartheta) [\gamma(t) - \gamma(\tau)]^2 \, d\tau$$

then $s + \Sigma = -h'(\vartheta)$ Consider, now, a stress relaxation experiment. Since for times t < 0 and $\tau \leq t \ \gamma(t) - \gamma(\tau) = 0, \ \Sigma = 0$. The load is put on, the temperature returns to room temperature and $s + \Sigma$ is the same as it was originally. But now, $\sigma > 0$ and so s has decreased. As time goes on, Σ decays toward zero, and so s rises to its original value.

Perhaps more importantly, one should note that if $\Sigma > 0$, and nothing else is changing, then Σ is changing. Equilibrium is possible only if $\Sigma = 0$. So we are dealing with thermodynamic non-equilibrium. We proposed that Σ be called *entaxy*, i.e. internal form.

Time-temperature superposition: Let $b_T(\tau)$ be the ratio between the rate of the material clock and the laboratory clock.

$$\beta(t) = \int_0^t b_T(\xi) \, d\xi$$

be the material time when the laboratory time is t. Then the Helmholtz free energy becomes

$$A = -\frac{1}{2} \int_{-\infty}^{t} \dot{G}(\beta(t) - \beta(\tau), \vartheta) [\gamma(t) - \gamma(\tau)]^2 b_T(\tau) d\tau + h(\vartheta)$$

and, except for such modifications, nothing important changes.

Ideas to be carried over to theory which

- 1. Allows finite strain.
- 2. is properly invariant and
- 3. is three dimensional.

To these ends, then, we consider a motion, which is a time dependent mapping of the material points into space. We choose a reference configuration, which is just some mapping of material points into space: We suppose, then, that X_{α} , $\alpha = 1, 2, 3$, varies over a given material region in the reference configuration and that $x_i = x_i(X_{\alpha}, t)$ maps the material point X_{α} into the spatial point x_i at time t. The deformation tensor is given by

$$x_{i\alpha} \stackrel{\text{def}}{=} \frac{\partial x_i}{\partial X_\alpha}$$

Right Cauchy-Green tensor

$$C_{\alpha\beta} = x_{i\alpha} x_{i\beta}$$

invariant to rigid motions in space. Then , σ_{ij} is then given by

$$\sigma_{ij} = 2\rho x_{i\alpha} x_{j\beta} \frac{\partial A}{\partial C_{\alpha\beta}}$$

where ρ is mass density. The entropy density, $s = -\partial A/\partial \vartheta$ and the internal energy density is $E = A + \vartheta s$. Heat flux vector, q_i : Balance of Energy:

$$\rho E = \sigma_{ij} v_{i,j} - q_{i,i}$$

which leads to the entropy production equation

$$\rho\vartheta\dot{s} + q_{i,i} = 0$$

or

$$\rho \dot{s} + \left(\frac{q_i}{\vartheta}\right)_{,i} = \frac{-q_i \vartheta_{,i}}{\vartheta^2}$$

Positive thermal conductivity, $q_i T_{,i} \leq 0$ as in Fourier's law, we have agreement with the second law of thermodynamics. We also observe that for an elastic material, entropy production is the result of heat flow – no viscosity.

Large strain viscoelasticity. For such, we need a constitutive law for history dependence. So we made some assumptions and did some experiments. We came up with the stress depending on the history of strain through a single integral in time. And the strain dependence of the integrand was taken to be relative strain, i.e. $x_{ij}(t,\tau) = x_{i\alpha}X_{\alpha j}$, where the later is the matrix inverse of $x_{i\alpha}$. The concept was that the material wants to return to every configuration that it had in the past as if it were a preferred configuration, but it cannot and so it compromises and gives a weight to each such past configuration, with the more recent counting more than the less recent, (fading memory) and adds the weighted contributions.

The assumption led to the result that from single step stress relaxation results, one could predict the stress history in any other motion. This concept seemed to be verified experimentally as shown by the following data.

Carrying over thermodynamic notions from lin-

ear case:

We assume that there is a scalar function of relative strain and time, t, which we shall call $U(x_{ij}(t,\tau),t)$ with the following properties:

• $U \ge 0$.

•
$$U(\delta_{ij}) = 0$$

•
$$U_* \stackrel{\text{def}}{=} \partial U / \partial t \leq 0.$$

There is a time-temperature superposition constant, $b_T(t)$ so that the effective time to which the material responds is

$$\beta(t) = \int_0^t b_T(\tau) \, d\tau$$

We define a quantity, Σ called *entaxy* which has dimensions of entropy, by

$$\Sigma = \int_{-\infty}^{t} U(x_{ij}(t,\tau),\beta(t) - \beta(\tau))b_T(\tau) d\tau$$

The Helmholtz free energy is given by an expression of the form

$$A = \Phi(\upsilon, \vartheta) + \Sigma$$

where $v = 1/\rho$ is the specific volume and Φ is some given function.

The stress is given by

$$\sigma_{ij} = \rho x_{i\alpha} \frac{\partial A}{\partial x_{j\alpha}}(t)$$

where one can use any reference configuration, X_{α} .

uptohere2 for the balance of energy, one winds up with

$$\rho\vartheta\dot{s} + q_{i,i} = -\rho\vartheta\int_{-\infty}^t U_*b_T(t)b_T(\tau)\,d\tau$$

which gives positive entropy production and, along with positive thermal conductivity, agreement with the second law. As in the linear case, this is a non-equilibrium theory. It can be shown that if $\sigma > 0$ abd no motion is occuring and temperature is not changing, then $\Sigma \downarrow 0$. The only possibility of nothing changing is when $\Sigma = 0$. So Σ is the seat of the non-equilibrium behavior. Furthermore, when $\Sigma = 0$, it can be shown that there is no shear stress. This is a fluid theory in the sense that it cannot support a shear stress in thermodynamic equilibrium. In concluding, let us summarize some features of this theory.

- It is a theory of non-equilibrium thermodynamic behavior.
- It is a fluid theory in the sense that shear stresses are not supported in thermodynamic equilibrium.
- It obeys the first and second laws of thermodynamics.
- Internal energy depends only on temperature. This means that in and isothermal stress relaxation, no heat is flowing. It is just losing its ability to remove energy from its surroundings and return it as heat.

Conclusions

- Linear viscoelasticity can be fit into a nonequilibrium thermodynamic theory by choice of an appropriate Helmholtz free energy.
- Agreement with the second law of thermodynamics occurs as a result of fading memory of the past and positive thermal conductivity.
- These notions can be carried over to a theory of finite strain by an appropriate formulation.
- If stress is taken as proportional to temperature, the finite strain theory presented here has in common with ideal gases or ideal rubbers that work put in is, after temperature equilibration with its surroundings, stored in its surroundings. (in the room)
- In this case, during a stress relaxation, for the theoretical substance described here no

heat is flowing. The substance is merely losing its ability to remove heat from the room and return it as work.

• There is no difficulty in including time-temperature superposition effects.