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Prague Talk: Viscoelasticity: by Barry Bernstein

It is common to think of certan subtaces as elastic solids and to think of others

as viscous fluids. But today we deal with media which can behave as either one, depending on conditons, and, indeed, in appropriate senses, commonly exhibit behavior which lies in between that of an elastic solid and that of a viscous fluid and which show elastic behavior and viscous fluid behavior in appropriate limiting senses. These are known as viscoelastic substances and include polymers, which are in common use today. Indeed, it can be argued that the substances which are, in fact, viscoelastic comprise very many material. Indeed, if one considers viscoelasticity as giving us a point of view for mathematical description of material behavior, then one might even argue that this point of view is general enough to cover all materials.

In setting theories for material behavior, energetic aspects, i.e. thermodynamic aspects are too often placed in the background or even ignored completely.

What I shall present to you today is a thermodynamic theory of viscoelastic behavior which has had a certain amount of success and of which I am an author. In its full version, it deals with large deformations and material time dependence. And let me repeat that it is a thermodynamic theory: It obeys the laws of thermodynamics, including the second law. It is my contention that a theory of material behavior should address thermodynamics for at least two reasons: 1) The world, if not the universe, operates thermodynaically and so ignoring thermodynamics leave a theory incomplete and 2) There can be many ways to formulate mechanical relationships so that one needs criteria to select from many formulations those which have the best hope of describing reality and thermodynamic restrictions provide one important set of criteria – obeying the first and second laws.

In the case of large strains in a three dimensional world, there are geometric invariance considerations which introduce a complexity which can mask the physical assumptions at first. So, in presenting the theory, I will initially present the theory in a boiled down version which can omit the three dimensional non-linear considerations in order to bring out the physical assumptions. Then, once we have these considerations in mind, we shall see how they fit into the properly invariant three dimensional theory with large strains.

First, we introduce the limited cast of characters that we need for the simplified theory. We have, to begin with, strain,  $\gamma$ , stress,  $\sigma$ , temperature,  $\vartheta$ , and heat flux, Q, which is the rate at which heat is being removed. We also need the rate of deformation,  $\dot{\gamma}$ .

First let us consider the elastic solid. The stress-strain relation takes the form

$$\sigma = \mu \gamma$$

where  $\mu$  is an elastic modulus. We now do the thermodynamics of this simple model: First of all, the elastic modulus can depend on temperature,  $\vartheta$ , and the Helmholtz free energy,  $A(\gamma, \vartheta)$  obeys

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

which results in A taking the form

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

where h is some function of  $\vartheta$ . The entropy, s, satisfies

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

and the internal energy, E, is given by

$$E = F + \vartheta s$$

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.

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

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

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

The production of entropy for an elastic material is due only to heat flow. Contrast this to the viscous fluid, which we shall introduce next.

In the viscous fluid we have a parameter,  $\eta$ , called *viscosity* and the stress is proportional to the rate of strain, or rate of deformation,  $\dot{\gamma}$ .

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

In general,  $\eta$  is a function of the temperature  $\vartheta$ , i.e.  $\eta = \eta(\vartheta)$ , as is the Helmholtz Free energy,  $A = A(\vartheta)$ . The entropy is then given by  $s = -dA/d\vartheta$ ,

and the internal energy is given by  $E = A + \vartheta s$ . The balance of energy is then  $\dot{E} = \sigma \dot{\gamma} - Q$ , which then sorts out as

$$\frac{\dot{A}}{A+\vartheta s} = \frac{dA}{d\vartheta}\dot{\vartheta} + \dot{\vartheta}s + \vartheta\dot{s} = -s\dot{\vartheta} + s\dot{\vartheta} + \vartheta\dot{s}$$
$$= \eta\dot{\gamma}^2 - Q$$

Which sorts out to

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

so that the second law is satisfied. Note that entropy is produced now not only by heat flow, but by viscous flow and is positive if anything happens. In the case of a viscoelastic substance, we have time dependence. This manifests itself as a dependence of the appropriate variables on time history. In particular, there is what is called a *relaxation modulus*,  $G(t, \vartheta)$ , where t is time. The modulus is measured as follows: Start with the material sample at rest and assume that it can be considered as always having been at rest, i.e. It can be assumed that the sample has forgotten its past history. Load the sample to a fixed strain at an experimental time taken as t = 0, i.e. to a given value of  $\gamma$ , and measure the stress as a function of time t. Then  $\sigma/\gamma$ will give G, Generally it is expected, at least at fixed  $\vartheta$ , that G will be a sum or integral of decaying exponentials

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

where the  $\tau_n$  are called the *relaxation times*. The stress in a general deformation history is then given at present time, t, by

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

where we have omitted  $\vartheta$  for simplicity, but we understand that it is still there. consider now the motion given by

$$\gamma = \begin{cases} 0 & \text{if } t < 0\\ \gamma(t) & \text{if } t > 0 \end{cases}$$

Then one gets

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

So, if the modulus is changing slowly, i.e. if  $\dot{G}$  is not large, one can envision a period of time in which  $\dot{G}$  can be neglected and the material will appear to be elastic with elastic modulus  $\mu = G(0)$ . To turn this around, we can say that whatever the decay rate of G, at the initial time t = 0 and for some time afterwards, the material will appear to be elastic — time in which the elastic approximation holds is always there, but it may be long or short depending on the rate  $\dot{G}$ .

Note that we have made no assumption about  $G(\infty)$ . We get an approximate elastic interval of time no matter what  $G(\infty)$  is. To get fluid behavior, we need to assume that  $G(\infty) = 0$ , i.e. that relaxation is eventually complete. Doing so, we find that after an integration by parts gives

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

so that if G is replaced by a delta function, we recover the viscous fluid with viscosity being the area under the curve of the relaxation modulus. If the rate at which the relaxation modulus decays with time is fast enough, we will see apparent viscous fluid behavior. Since the fluid point of view is unifying, we adopt it.

Now let us turn to the energies. We take as our Helmholtz free energy

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

where h is some given function of  $\vartheta$ , and proceed as before. The algebra is a bit more complex than before, but the steps are essentially the same. We come out with the following where we have kept the dot to mean the derivative with respect to present time t:

$$s = \frac{1}{2} \int \frac{\partial}{\partial \vartheta} \dot{G}(t - \tau, \vartheta) [\gamma(t) - \gamma(\tau)]^2 d\tau - h'(\vartheta)$$
  

$$E = A + \vartheta s$$
  

$$\dot{E} = \sigma \dot{\gamma} + \vartheta \dot{s} - \frac{1}{2} \int_{-\infty}^t \ddot{G}(t - \tau, \vartheta) [\gamma(t0 - \gamma(\tau))]^2 d\tau$$

After putting this into the energy balance equation, we get, after simplifying,

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

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

Now let us look at a special case, namely when G is proportional to temperature, in analogy to the perfect gas or ideal rubber. Write

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

Then the internal energy becomes

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

So, as in an ideal gas, the internal energy is a function of temperature alone. 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? Go back for a moment to an ideal gas. Suppose that it is originally at room temperature and that it is compressed and then allowed to remain at rest in contact with its isothermal surroundings which we call the room. During rapid compression, the work put in goes into internal energy. It gets hot. Then it cools to the room temperature: at which time the internal energy, depending only on temperature, returns to its original value. When the pressure is released, energy is recovered in the form of work. Where does it come from? It initially comes from internal energy, the lowering of which causes the gas to cool. Then the cooled gas returns to room temperature by removing energy from the room in the form of heat flow.

What is different about our material? As it relaxes, no energy is flowing. But it is losing its ability to give back work and then remove the energy from the room in the form of heat flow.

One other comment may be of interest. Note that if we define  $\Sigma$  by

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

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,  $\Sigma$  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  $\Sigma$  is changing. Equilibrium is possible only if  $\Sigma = 0$ . So we are dealing with thermodynamic non-equilibrium. We proposed that  $\Sigma$ be called *entaxy*, i.e. internal form.

One more refinement should be mentioned, namely time-temperature superposition. The time seen by the material is that on a temperature dependent clock. The higher the temperature, the faster the relaxation. Let  $b_T(\tau)$  be the time read by the material clock at laboratory time and let

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

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. The next task is to carry over our these ideas to a 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  $X_{\alpha}$ ,  $\alpha = 1, 2, 3$ , varies over a given material region in the reference configuration and that  $x_i = x_i(X_{\alpha}, t)$  maps the material point  $X_{\alpha}$  into the spatial point  $x_i$  at time t. The deformation tensor is given by

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

For elastic behavior, the reference configuration is conveniently taken to be a stress-free configuration, if one exists and the Helmholtz free energy is then a function of the deformation gradient with respect to the stress-free configuration. The Helmholtz free energy, being a scalar, depends on the deformation gradient through its right Cauchy-Green tensor

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

which is the part of the deformation which is invariant to rigid motions in space. The stress,  $\sigma_{ij}$  is then given by

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

where  $\rho$  is mass density. The entropy density is, as before,  $s = -\partial A/\partial \vartheta$  and the internal energy density is  $E = A + \vartheta s$ . For heat transfer, we introduce the heat flux vector,  $q_i$ : The integral of  $q_i$  over a volume is the rate at which heat leaves the volume. So we now balance energy by setting the rate of change of internal energy equal to the work rate plus the rate of heat added. After some algebra, one arrives at the entropy production equation

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

which then can be written

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

So as long as heat flows against the temperature gradient, 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.

But we need to get to 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.

In fairness, I must add that we also want the predictions to hold when the strain is reversed. This turned out not to hold for the original materials tested, but recently there have been some results on branched polymers for which the strain reversal seems to hold.

Since most of the thermodynamic notions have already been developed in the linear case, let us end by stating how they carry over to the non-linear situation.

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,  $\Sigma$  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

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

where  $v = 1/\rho$  is the specific volume and  $\Phi$  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,  $X_{\alpha}$ . 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  $\Sigma$  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.