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A FEW THERMODYNAMIC CONSIDERATIONS FOR MATERIALS

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I. INTRODUCTION

A requirement from physical science is that any theory describing material behavior must conform to the general results from Thermodynamics. The purpose of this report is to tie the results given in the file “Classical Thermodynamics” (October 17, 2015, THERMO.DOC¹) to continuum mechanics and to determine any conditions that must be imposed on constitutive equations and corresponding internal energies in order for them to conform to Classical Thermodynamics.

In the case of a continuum mechanics formulation for a particular the system studied is a fixed mass particle. The stresses and strains are considered to be uniform. The first essential part for this study concerns the First Law of Thermodynamics for fixed mass systems which may be expressed as,

$$\rho \cdot \dot{q} = \rho \cdot \dot{E} + \rho \cdot \dot{W}$$

where definitions and a compatible set of units for this equation are,

$$\begin{aligned} \rho \cdot \dot{q} &= \text{time rate of heat flow into the system from its exterior, } \frac{\text{in} - \text{lb}}{\text{slug} - \text{sec}} \\ &= \rho \cdot T \cdot \dot{s} \text{ for a reversible process} \end{aligned}$$

$$\rho \cdot \dot{E} = \text{time rate of change of internal energy, } \frac{\text{in} - \text{lb}}{\text{slug} - \text{sec}}$$

$$\rho \cdot \dot{W} = \text{time rate of work being done by the system on its exterior, } \frac{\text{in} - \text{lb}}{\text{slug} - \text{sec}}$$

$$\rho = \text{mass density, } \frac{\text{slug}}{\text{in}^3}$$

In addition, define,

$$T = \text{absolute temperature, } ^\circ\text{R}$$

$$\rho \cdot \dot{s} = \text{time rate of reversible change of entropy, } \frac{\text{in} - \text{lb}}{\text{slug} - \text{sec} - ^\circ\text{R}}$$

$$\rho \cdot \dot{s}_{\text{TOT}} = \text{time rate of change of total entropy, } \frac{\text{in} - \text{lb}}{\text{slug} - \text{sec} - ^\circ\text{R}}$$

¹ Available from website DR. PAUL PASLAY

To provide some background, briefly consider the elementary case of combined, linear heat transfer and conduction. Let c_v be the specific heat and K the thermal conductivity and define I as,

$$I = \int_{t_0}^t T_{,kk} \cdot dt$$

where $T_{,kk}$ is the Laplacian, t is time and t_0 is a constant reference time. The reversible heat flow rate, \dot{q}_{REV} , is,

$$\dot{q}_{REV} = c_v \cdot \dot{T} + K \cdot \dot{I}$$

Since there is no work done by this system,

$$\dot{W} = 0$$

and the First Law of Thermodynamics is,

$$\dot{q}_{REV} = \dot{E}$$

The two equations for \dot{q}_{REV} show that E is a function of T and I . Then,

$$\dot{E} = \frac{\partial E}{\partial T} \cdot \dot{T} + \frac{\partial E}{\partial I} \cdot \dot{I} = c_v \cdot \dot{T} + K \cdot \dot{I} = c_v \cdot \dot{T} + K \cdot T_{,kk}$$

Consequently,

$$E = c_v \cdot T + K \cdot I$$

and,

$$\dot{s} = \frac{\dot{q}_{REV}}{T} = c_v \cdot \frac{\dot{T}}{T} + K \cdot \frac{T_{,kk}}{T}$$

When a specific constitutive equation is considered, it is often possible to express \dot{W} explicitly. Substituting \dot{W} into the first law and solving for \dot{s} yields an equation whose validity must be determined. The condition that the entropy, s , be a perfect differential (i.e. s is a property dependent only on the state of the material and thus path independent) leads to a condition that must be satisfied by \dot{E} . When this condition is satisfied then the Inequality of Clausius is valid and it becomes a way of expressing the Second Law of Thermodynamics as,

$$\oint ds \geq 0$$

where the equality is only for a reversible cycle.

Several common, elementary, constitutive equations are reviewed in the section below. In each case, the expressions for E , \dot{s} and \dot{s}_{TOT} are determined. In each case, the derivation is given in Cartesian spatial coordinates. These reviews show the kind of restrictions thermodynamics imposes on constitutive equations undergoing changes of *equilibrium states*.

The results below use the common indicial notation for the subscripts i, j, k , and m . A comma preceding subscripts implies partial differentiation with respect to the subscript variable. Additionally, a repeated subscript occurring in a single term implies summation over x, y and z for that term.

Let δ_{ij} be the Kronecker delta defined as,

$$\begin{aligned}\delta_{ij} &= 1 && \text{when } i = j \\ &= 0 && \text{when } i \neq j\end{aligned}$$

then a few examples using indicial notation are,

$$\delta_{ij} \cdot \delta_{ij} = 3$$

$$\sigma_{ij} \cdot \delta_{ij} = \sigma_{kk} = \sigma_{xx} + \sigma_{yy} + \sigma_{zz}$$

$$\sigma_{i,i} = \frac{\partial \sigma_i}{\partial x_i} = \frac{\partial \sigma_x}{\partial x} + \frac{\partial \sigma_y}{\partial y} + \frac{\partial \sigma_z}{\partial z}$$

$$\begin{aligned}\sigma_{VM}^2 &= J_2 = \frac{3}{2} \cdot \left(\sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk} \cdot \delta_{ij} \right) \cdot \left(\sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk} \cdot \delta_{ij} \right) = \frac{3}{2} \cdot \left(\sigma_{ij} \cdot \sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk}^2 \right) \\ &= \sigma_{xx}^2 + \sigma_{yy}^2 + \sigma_{zz}^2 - \sigma_{xx} \cdot \sigma_{yy} - \sigma_{yy} \cdot \sigma_{zz} - \sigma_{zz} \cdot \sigma_{xx} + 3 \cdot \left(\sigma_{xy}^2 + \sigma_{yz}^2 + \sigma_{zx}^2 \right)\end{aligned}$$

II. SELECTED, ILLUSTRATIVE, CONSTITUTIVE EQUATIONS

A. LINEAR THERMOELASTICITY

This constitutive equation relates the strains, e_{ij} , stresses, s_{ij} , and absolute temperature, T , as,

$$\begin{aligned}\sigma_{ij} &= \hat{\lambda} \cdot (e_{kk} - 3 \cdot \alpha \cdot T) \cdot \delta_{ij} + 2 \cdot \hat{G} \cdot (e_{ij} - \alpha \cdot T \cdot \delta_{ij}) \\ &= \hat{\lambda} \cdot e_{kk} \cdot \delta_{ij} + 2 \cdot \hat{G} \cdot e_{ij} - (3 \cdot \hat{\lambda} + 2 \cdot \hat{G}) \cdot \alpha \cdot T \cdot \delta_{ij}\end{aligned}$$

where in terms of the material constants Young's modulus, \hat{E} , and Poisson's ratio, ν ,

$$\hat{\lambda} = \frac{\nu \cdot \hat{E}}{(1 + \nu) \cdot (1 - 2 \cdot \nu)}$$

$$\hat{G} = \frac{\hat{E}}{2 \cdot (1 + \nu)}$$

$$3 \cdot \hat{\lambda} + 2 \cdot \hat{G} = \frac{\hat{E}}{1 - 2 \cdot \nu}$$

$$\hat{E} = \frac{\hat{G} \cdot (3 \cdot \hat{\lambda} + 2 \cdot \hat{G})}{\hat{\lambda}}$$

$$\nu = \frac{\hat{\lambda}}{2 \cdot (\hat{G} + \hat{\lambda})}$$

and the inverse of the constitutive equation is,

$$\begin{aligned}e_{ij} &= \frac{1}{2 \cdot \hat{G}} \cdot \sigma_{ij} + \left[-\frac{\mu}{2 \cdot (1 + \mu) \cdot \hat{G}} \cdot \sigma_{kk} + \alpha \cdot T \right] \cdot \delta_{ij} \\ &= \frac{1}{2 \cdot \hat{G}} \cdot \sigma_{ij} + \left[-\frac{\hat{\lambda}}{2 \cdot \hat{G} \cdot (3 \cdot \hat{\lambda} + 2 \cdot \hat{G})} \cdot \sigma_{kk} + \alpha \cdot T \right] \cdot \delta_{ij}\end{aligned}$$

$$\alpha = \text{thermal coefficient of linear expansion} = \frac{\partial}{\partial T} \left(\frac{1}{\rho} \right), \frac{\text{in}^3}{\text{slug} \cdot ^\circ \text{R}}$$

$$\rho = \text{mass density, a function of } e_{ij} \text{ and } T, \frac{\text{slug}}{\text{in}^3}$$

The parameters $\hat{\lambda}$ and \hat{G} are constants so that, up to this point the internal energy, E , and density, ρ , are functions of e_{ij} and T .

The thermodynamic system under consideration is a particle whose mass is constant. The rate of work per unit volume done by this particle on its exterior is,

$$\dot{W} = -\sigma_{ij} \cdot \dot{e}_{ij}$$

Now assume the internal energy per unit volume is a function of e_{ij} and T so that,

$$\dot{E} = \frac{\partial E}{\partial e_{ij}} \cdot \dot{e}_{ij} + \frac{\partial E}{\partial T} \cdot \dot{T}$$

and the Thermodynamic First Law gives,

$$\dot{q} = \dot{E} + \dot{W} = \left(\frac{\partial E}{\partial e_{ij}} - \sigma_{ij} \right) \cdot \dot{e}_{ij} + \frac{\partial E}{\partial T} \cdot \dot{T}$$

The reversible entropy production rate, \dot{s} , is,

$$\dot{s} = \frac{\dot{q}}{T} = \frac{1}{T} \cdot \left(\frac{\partial E}{\partial e_{ij}} - \sigma_{ij} \right) \cdot \dot{e}_{ij} + \frac{1}{T} \cdot \frac{\partial E}{\partial T} \cdot \dot{T}$$

In order that s be a state function, the following condition must be satisfied,

$$\frac{\partial}{\partial T} \left(\frac{1}{T} \cdot \left(\frac{\partial E}{\partial e_{ij}} - \sigma_{ij} \right) \right) = \frac{\partial}{\partial e_{ij}} \left(\frac{1}{T} \cdot \frac{\partial E}{\partial T} \right)$$

The order of differentiation may be reversed so that,

$$\frac{\partial E}{\partial e_{ij}} = \sigma_{ij} - T \cdot \frac{\partial \sigma_{ij}}{\partial T}$$

When the thermoelasticity constitutive equation given above is substituted into this condition, the result is,

$$\frac{\partial E}{\partial e_{ij}} = \hat{\lambda} \cdot e_{kk} \cdot \delta_{ij} + 2 \cdot \hat{G} \cdot e_{ij}$$

Integration of $\frac{\partial E}{\partial e_{ij}}$ gives,

$$E = \frac{1}{2} \cdot \hat{\lambda} \cdot (e_{kk})^2 + \hat{G} \cdot e_{ij} \cdot e_{ij} + H(T)$$

then,

$$\dot{q} = (3 \cdot \hat{\lambda} + 2 \cdot \hat{G}) \cdot \alpha \cdot T \cdot \dot{e}_{kk} + \frac{\partial H(T)}{\partial T} \cdot \dot{T}$$

$$\dot{s} = (3 \cdot \hat{\lambda} + 2 \cdot \hat{G}) \cdot \alpha \cdot \dot{e}_{kk} + \frac{\partial H(T)}{\partial T} \cdot \frac{\dot{T}}{T}$$

In order to relate $H(T)$ to a physically familiar quantity, note that T is an independent thermodynamic property and when the strain rates are zero the value of \dot{q} is,

$$\dot{q}|_{\dot{e}_{ij}=0} = \frac{\partial H(T)}{\partial T} \cdot \dot{T} \equiv c_v \cdot \dot{T}$$

where c_v is the specific heat at constant volume and assumed to be constant. Then, $H(T)$ may be written as,

$$H(T) = c_v \cdot (T - T_o)$$

where $c_v \cdot T_o$ is a constant of integration. Consequently, E may be written as,

$$E = \frac{1}{2} \cdot \hat{\lambda} \cdot (e_{kk})^2 + \hat{G} \cdot e_{ij} \cdot e_{ij} + c_v \cdot (T - T_o)$$

and,

$$\dot{q} = (3 \cdot \hat{\lambda} + 2 \cdot \hat{G}) \cdot \alpha \cdot T \cdot \dot{e}_{kk} + c_v \cdot \dot{T}$$

$$\dot{s} = (3 \cdot \hat{\lambda} + 2 \cdot \hat{G}) \cdot \alpha \cdot \dot{e}_{kk} + c_v \cdot \frac{\dot{T}}{T}$$

and, since there is no energy dissipation in the material,

$$\dot{s}_{TOT} = \dot{s} = (3 \cdot \hat{\lambda} + 2 \cdot \hat{G}) \cdot \alpha \cdot \dot{e}_{kk} + c_v \cdot \frac{\dot{T}}{T}$$

The temperature, T , is the absolute temperature in the above derivation. When the constitutive equation is used in problem solving, it is common to replace $(T - T_o)$ with a temperature that is not a true thermodynamic temperature (e.g. degrees Celsius).

B. LINEAR, VISCOUS, COMPRESSIBLE NEWTONIAN FLUID

The constitutive equation for this fluid may be written in terms of the stress, σ_{ij} , the strain, e_{ij} , the deformation rate, \dot{e}_{ij} , and the absolute temperature, T , in the form,

$$\sigma_{ij} = \tilde{\lambda} \cdot \dot{e}_{kk} \cdot \delta_{ij} + 2 \cdot \tilde{\mu} \cdot \dot{e}_{ij} + \tilde{C} \cdot (e_{kk} - 3 \cdot \alpha \cdot T) \cdot \delta_{ij}$$

where,

$$\begin{aligned} \tilde{\lambda} \text{ and } \tilde{\mu} &= \text{volumetric and shear viscosities, constant material properties} \\ \tilde{C} &= \text{elastic compressibility, constant material property} \\ \alpha &= \text{thermal coefficient of linear expansion, a constant} \end{aligned}$$

This case of a fluid introduces new considerations to the determination of the internal energy and the entropy functions. The presence of a viscosity implies that there is a dissipation of energy *within* the material element owing to flow. When the system is dissipative the entropy function cannot be derived using the constitutive equation in the same way as given in the case of the thermoelastic material. By assuming that E is a function of e_{ij} , \dot{e}_{ij} and T and proceeding in the same way as the thermoelastic material derivation shows there is no entropy function that is a state variable. When dissipation is present it is converted to heat and this must be reflected in the contributions to the First Law of Thermodynamics. From a physical point of view, the total work done by the stresses can be divided into two parts. The first part of the work is that which is required to make the entropy a state variable. The second part of the work is the excess of the total work over the first part. The second part is converted to external heat and is not included in the first law equation for the material particle. This may, in this case, be accomplished by splitting the stress into two parts, σD_{ij} and σS_{ij} . The stress, σD_{ij} , is determined from the part of the constitutive equation causing dissipation while the stress, σS_{ij} , is determined from the part of the constitutive equation contributing to the recoverable elastic strain energy as follows,

$$\begin{aligned} \sigma_{ij} &= \sigma D_{ij} + \sigma S_{ij} \\ \sigma D_{ij} &= \tilde{\lambda} \cdot \dot{e}_{kk} \cdot \delta_{ij} + 2 \cdot \tilde{\mu} \cdot \dot{e}_{ij} \\ \sigma S_{ij} &= \tilde{C} \cdot (e_{kk} - 3 \cdot \alpha \cdot T) \cdot \delta_{ij} \end{aligned}$$

The rate of work per unit volume being done by the system is $-\sigma S_{ij} \cdot \dot{e}_{ij}$. Assume the internal energy is a function of e_{kk} and T so that the First Law of Thermodynamics gives,

$$\dot{q} = \frac{\partial E}{\partial e_{kk}} \cdot \dot{e}_{kk} + \frac{\partial E}{\partial T} \cdot \dot{T} - \sigma S_{ij} \cdot \dot{e}_{ij} = \left(\frac{\partial E}{\partial e_{kk}} \cdot \delta_{ij} - \sigma S_{ij} \right) \cdot \dot{e}_{ij} + \frac{\partial E}{\partial T} \cdot \dot{T}$$

and the entropy production rate, \dot{s} , is

$$\dot{s} = \frac{1}{T} \cdot \left(\frac{\partial E}{\partial \mathbf{e}_{kk}} \cdot \delta_{ij} - \sigma S_{ij} \right) \cdot \dot{\mathbf{e}}_{ij} + \frac{\partial E}{\partial T} \cdot \frac{\dot{T}}{T}$$

In order for the entropy to be a state property,

$$-\frac{1}{T^2} \cdot \left(\frac{\partial E}{\partial \mathbf{e}_{kk}} \cdot \delta_{ij} - \sigma S_{ij} \right) + \frac{1}{T} \cdot \left(\frac{\partial^2 E}{\partial T \partial \mathbf{e}_{kk}} \cdot \delta_{ij} - \frac{\partial \sigma S_{ij}}{\partial T} \right) = \frac{1}{T} \cdot \frac{\partial^2 E}{\partial \mathbf{e}_{ij} \partial T} = \frac{1}{T} \cdot \frac{\partial^2 E}{\partial \mathbf{e}_{kk} \partial T} \cdot \delta_{ij}$$

The order of differentiation for the second derivatives is interchangeable so this equation becomes,

$$T \cdot \frac{\partial \sigma S_{ij}}{\partial T} - \sigma S_{ij} = - \frac{\partial E}{\partial \mathbf{e}_{kk}} \cdot \delta_{ij}$$

When the constitutive equation for σS_{ij} is substituted into the above equation, the result is,

$$\frac{\partial E}{\partial \mathbf{e}_{kk}} = \tilde{C} \cdot \mathbf{e}_{kk}$$

The last equation is integrated to give,

$$E = \frac{1}{2} \cdot \tilde{C} \cdot \mathbf{e}_{kk}^2 + J(T)$$

where $J(T)$ is an arbitrary function of T . When E is substituted into the expressions for heat flow rate and entropy production rate given above, the expressions become,

$$\dot{q} = 3 \cdot \alpha \cdot T \cdot \tilde{C} \cdot \dot{\mathbf{e}}_{kk} + \frac{dJ(T)}{dT} \cdot \dot{T}$$

$$\dot{s} = 3 \cdot \alpha \cdot \tilde{C} \cdot \dot{\mathbf{e}}_{kk} + \frac{dJ(T)}{dT} \cdot \frac{\dot{T}}{T}$$

When $\dot{\mathbf{e}}_{kk} = 0$, the heat flow rate is usually written as $c_v \cdot \dot{T}$ with c_v being the specific heat. In this case,

$$\frac{dJ(T)}{dT} = c_v$$

Since c_v is assumed to be a constant, integration yields,

$$J(T) = c_v \cdot (T - T_O)$$

where $c_v \cdot T_0$ is a constant of integration. To summarize,

$$\dot{q} = 3 \cdot \alpha \cdot T \cdot \tilde{C} \cdot \dot{e}_{kk} + c_v \cdot \dot{T}$$

$$\dot{s} = 3 \cdot \alpha \cdot \tilde{C} \cdot \dot{e}_{kk} + c_v \cdot \frac{\dot{T}}{T}$$

$$E = \frac{1}{2} \cdot \tilde{C} \cdot e_{kk}^2 + c_v \cdot (T - T_0)$$

The value of \dot{q} in these equations is the total heat flow rate for the system and some is generated internally while the remainder is supplied externally to the material element.

The internal heat flow rate, \dot{q}_D , is,

$$\dot{q}_D = \sigma D_{ij} \cdot \dot{e}_{ij} = \left(\bar{\lambda} \cdot \dot{e}_{kk} \cdot \delta_{ij} + 2 \cdot \bar{\mu} \cdot \dot{e}_{ij} \right) \cdot \dot{e}_{ij}$$

Now let the externally supplied heat flow rate be \dot{q}^H so that,

$$\dot{q}^H = \dot{q} + \dot{q}_D$$

and,

$$\dot{q}^H = 3 \cdot \alpha \cdot T \cdot \tilde{C} \cdot \dot{e}_{kk} + c_v \cdot \dot{T} + \bar{\lambda} \cdot \dot{e}_{kk}^2 + 2 \cdot \bar{\mu} \cdot \dot{e}_{ij} \cdot \dot{e}_{ij}$$

and then,

$$\dot{s}_{TOT} = \frac{\dot{q}^H}{T} = 3 \cdot \alpha \cdot \tilde{C} \cdot \dot{e}_{kk} + c_v \cdot \frac{\dot{T}}{T} + \frac{\bar{\lambda}}{T} \cdot \dot{e}_{kk}^2 + \frac{2 \cdot \bar{\mu}}{T} \cdot \dot{e}_{ij} \cdot \dot{e}_{ij}$$

The rate of entropy change for the dissipation, \dot{s}_{DISS} , equals $\dot{s}_{TOT} - \dot{s}$ or,

$$\dot{s}_{DISS} = \frac{\bar{\lambda}}{T} \cdot \dot{e}_{kk}^2 + \frac{2 \cdot \bar{\mu}}{T} \cdot \dot{e}_{ij} \cdot \dot{e}_{ij}$$

C. ELASTIC, PERFECTLY-PLASTIC SOLID

The formulation investigated here is the one appearing in the text, *Theory of Perfectly Plastic Solids*, by William Prager and Philip Hodge, Jr. (John Wiley & Sons, Inc., 1951). The von Mises stress, σ_{VM} , is defined to be,

$$\sigma_{VM} = \frac{\sqrt{3}}{\sqrt{2}} \sqrt{\sigma_{ij} \cdot \sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk}^2} = \frac{\sqrt{3}}{\sqrt{2}} \cdot \sqrt{\left(\sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk} \cdot \delta_{ij}\right) \cdot \left(\sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk} \cdot \delta_{ij}\right)}$$

And all possible stress states must be such that,

$$\sigma_{VM} \leq \sigma_{YP}$$

where σ_{YP} is the yield point of the material in tension, a constant. The strain is split into two parts. The elastic strain, eE_{ij} , is directly related to the stress state while the plastic strain rate, $\dot{e}P_{ij}$, is adjusted to be proportional to the reduced stress, $\sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk} \cdot \delta_{ij}$. The total strain rate is the sum of the elastic strain rate and the plastic strain rate, $\dot{e}E_{ij} + \dot{e}P_{ij}$. The relationship between the stress and the elastic strain is,

$$\sigma_{ij} = \left(\lambda \cdot eE_{kk} - \left(3 \cdot \lambda + 2 \cdot G \right) \cdot \alpha \cdot (T - T_0) \right) \cdot \delta_{ij} + 2 \cdot G \cdot eE_{ij}$$

or after inversion,

$$eE_{ij} = \frac{1}{2 \cdot G} \cdot \sigma_{ij} + \left(- \frac{\mu}{2 \cdot (1 + \mu) \cdot G} \cdot \sigma_{kk} + \alpha \cdot (T - T_0) \right) \cdot \delta_{ij}$$

where the material parameter nomenclature is generally the same nomenclature used for the thermoelastic material considered above. The plastic strain changes over a loading increment when $\sigma_{VM} = \sigma_{YP}$ during the increment. This change is governed by,

$$\dot{e}P_{ij} = \Gamma \cdot \left(\sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk} \cdot \delta_{ij} \right) \quad \text{while } \sigma_{VM} = \sigma_{YP}$$

$$\dot{e}P_{ij} = 0 \quad \text{otherwise}$$

where Γ must be adjusted so that $\sigma_{VM} = \sigma_{YP}$ at the end of the increment. Note that $\dot{e}P_{kk} = 0$ so that the plastic strains contribute nothing to the rate of volume change. The rate of doing external work for the elastic strain is assumed to be recoverable while the rate of doing work for the plastic strain is assumed to be dissipated into a heat flow rate within the material element. Define these as,

$$\dot{W}_E = -\sigma_{ij} \cdot \dot{e}E_{ij} = -\left(\lambda \cdot eE_{kk} - \left(3 \cdot \lambda + 2 \cdot G \right) \cdot \alpha \cdot (T - T_0) \right) \cdot \dot{e}E_{kk} - 2 \cdot G \cdot eE_{ij} \cdot \dot{e}E_{ij}$$

$$\begin{aligned}\dot{W}_P &= -\sigma_{ij} \cdot \dot{e}P_{ij} = -2 \cdot \overset{\cup}{G} \cdot eE_{ij} \cdot \Gamma \cdot \left(\sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk} \cdot \delta_{ij} \right) \\ &= -4 \cdot \overset{\cup}{G}^2 \cdot \Gamma \cdot \left(eE_{ij} \cdot eE_{ij} - \frac{1}{3} \cdot eE_{kk}^2 \right) \quad \text{while } \sigma_{VM} = \sigma_{YP}\end{aligned}$$

$$\dot{W}_P = 0 \quad \text{otherwise}$$

Now assume that the internal energy, E , is a function of the elastic strain, eE_{ij} , and the temperature T . For this material the First Law of Thermodynamics is written as,

$$\dot{q} = \dot{E} + \dot{W}_E$$

so that,

$$\dot{q} = \left(\frac{\partial E}{\partial eE_{ij}} - \left(\overset{\cup}{\lambda} \cdot eE_{kk} - \left(3 \cdot \overset{\cup}{\lambda} + 2 \cdot \overset{\cup}{G} \right) \cdot \alpha \cdot (T - T_O) \right) \cdot \delta_{ij} - 2 \cdot \overset{\cup}{G} \cdot eE_{ij} \right) \cdot \dot{e}E_{ij} + \frac{\partial E}{\partial T} \cdot \dot{T}$$

and,

$$\dot{s} = \frac{1}{T} \cdot \left(\frac{\partial E}{\partial eE_{ij}} - \left(\overset{\cup}{\lambda} \cdot eE_{kk} - \left(3 \cdot \overset{\cup}{\lambda} + 2 \cdot \overset{\cup}{G} \right) \cdot \alpha \cdot (T - T_O) \right) \cdot \delta_{ij} - 2 \cdot \overset{\cup}{G} \cdot eE_{ij} \right) \cdot \dot{e}E_{ij} + \frac{1}{T} \cdot \frac{\partial E}{\partial T} \cdot \dot{T}$$

In order for the entropy to be a property,

$$\begin{aligned}& -\frac{1}{T^2} \cdot \left(\frac{\partial E}{\partial eE_{ij}} - \left(\overset{\cup}{\lambda} \cdot eE_{kk} - \left(3 \cdot \overset{\cup}{\lambda} + 2 \cdot \overset{\cup}{G} \right) \cdot \alpha \cdot (T - T_O) \right) \cdot \delta_{ij} - 2 \cdot \overset{\cup}{G} \cdot eE_{ij} \right) + \frac{1}{T} \cdot \left(\frac{\partial^2 E}{\partial T \partial eE_{ij}} + \left(3 \cdot \overset{\cup}{\lambda} + 2 \cdot \overset{\cup}{G} \right) \cdot \alpha \cdot \delta_{ij} \right) \\ &= \frac{1}{T} \cdot \frac{\partial^2 E}{\partial eE_{ij} \partial T}\end{aligned}$$

As usual, the order of differentiation of the second derivatives is assumed interchangeable so that,

$$\frac{\partial E}{\partial eE_{ij}} = \overset{\cup}{\lambda} \cdot eE_{kk} \cdot \delta_{ij} + 2 \cdot \overset{\cup}{G} \cdot eE_{ij} + \left(3 \cdot \overset{\cup}{\lambda} + 2 \cdot \overset{\cup}{G} \right) \cdot \alpha \cdot T_O \cdot \delta_{ij}$$

When this equation is integrated there results,

$$E = \frac{1}{2} \cdot \overset{\cup}{\lambda} \cdot eE_{kk}^2 + \overset{\cup}{G} \cdot eE_{ij} \cdot eE_{ij} + \left(3 \cdot \overset{\cup}{\lambda} + 2 \cdot \overset{\cup}{G} \right) \cdot \alpha \cdot T_O \cdot E_{kk} + K(T)$$

and,

$$\dot{q} = \left(3 \cdot \overset{\cup}{\lambda} + 2 \cdot \overset{\cup}{G} \right) \cdot \alpha \cdot T \cdot \dot{e}E_{kk} + \frac{dK(T)}{dT} \cdot \dot{T}$$

$$\dot{s} = \left(3 \cdot \overset{\square}{\lambda} + 2 \cdot \overset{\square}{G}\right) \cdot \alpha \cdot \dot{E}_{kk} + \frac{1}{T} \cdot \frac{\partial K(T)}{\partial T} \cdot \dot{T}$$

Now define a specific heat at constant volume, c_v , using,

$$\dot{q}|_{\dot{E}_{kk}=0} = c_v \cdot \dot{T}$$

to obtain,

$$c_v = \frac{dK(T)}{dT}$$

where, obviously, c_v is a function of temperature only. The heat flow rate and entropy production rate may be written as,

$$\dot{q} = \left(3 \cdot \overset{\square}{\lambda} + 2 \cdot \overset{\square}{G}\right) \cdot \alpha \cdot T \cdot \dot{E}_{kk} + c_v \cdot \dot{T}$$

$$\dot{s} = \left(3 \cdot \overset{\square}{\lambda} + 2 \cdot \overset{\square}{G}\right) \cdot \alpha \cdot \dot{E}_{kk} + \frac{1}{T} \cdot c_v \cdot \dot{T}$$

Similar to the case for a fluid, the quantity \dot{q} is the total heat flow rate in the material element. The quantity \dot{W}_p is the rate of work for the plastic strain that is converted to a heat flow rate. Let $\overset{\square}{q}$ be the externally supplied heat flow rate so that,

$$\text{If } \sigma_{vM} = \sigma_{vP} :$$

$$\overset{\square}{q} = \dot{q} - \dot{W}_p = \left(3 \cdot \overset{\square}{\lambda} + 2 \cdot \overset{\square}{G}\right) \cdot \alpha \cdot T \cdot \dot{E}_{kk} + c_v \cdot \dot{T} + 4 \cdot \overset{\square}{G}^2 \cdot \Gamma \cdot \left(\mathbf{e}E_{ij} \cdot \mathbf{e}E_{ij} - \frac{1}{3} \cdot \mathbf{e}E_{kk}^2\right)$$

and,

$$\dot{s}_{TOT} = \left(3 \cdot \overset{\square}{\lambda} + 2 \cdot \overset{\square}{G}\right) \cdot \alpha \cdot \dot{E}_{kk} + c_v \cdot \frac{\dot{T}}{T} + \frac{4 \cdot \overset{\square}{G}^2 \cdot \Gamma}{T} \cdot \left(\mathbf{e}E_{ij} \cdot \mathbf{e}E_{ij} - \frac{1}{3} \cdot \mathbf{e}E_{kk}^2\right)$$

$$\dot{s}_{DISS} = \dot{s}_{TOT} - \dot{s} = \frac{4 \cdot \overset{\square}{G}^2 \cdot \Gamma}{T} \cdot \left(\mathbf{e}E_{ij} \cdot \mathbf{e}E_{ij} - \frac{1}{3} \cdot \mathbf{e}E_{kk}^2\right)$$

otherwise:

$$\overset{\square}{q} = \left(3 \cdot \overset{\square}{\lambda} + 2 \cdot \overset{\square}{G}\right) \cdot \alpha \cdot T \cdot \dot{E}_{kk} + c_v \cdot \dot{T}$$

$$\dot{s}_{TOT} = \left(3 \cdot \overset{\square}{\lambda} + 2 \cdot \overset{\square}{G}\right) \cdot \alpha \cdot \dot{E}_{kk} + \frac{1}{T} \cdot c_v \cdot \dot{T}$$

$$\dot{\mathbf{s}}_{\text{DISS}} = \dot{\mathbf{s}}_{\text{TOT}} - \dot{\mathbf{s}} = \mathbf{0}$$

D. INCOMPRESSIBLE BINGHAM MATERIAL.

The most common formulation for this material neglects thermal expansion and elastic behavior of the material and this approximation is adopted here. The specific heat, c_v , is assumed to be constant. This material has a yield point stress that must be exceeded before the material can deform. When the yield stress is exceeded, the material flows similar to a fluid but with the flow rate proportional to the excess of the stress over the yield point stress. Let,

$$\sigma_{VM} = \sqrt{\frac{3}{2} \cdot \sigma_{ij} \cdot \sigma_{ij} - \frac{1}{2} \cdot \sigma_{kk}^2} = \sqrt{\frac{3}{2}} \cdot \sqrt{\sigma_{ij} \cdot \sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk}^2} \equiv \sqrt{3} \cdot \tau_{VM}$$

where σ_{VM} is the von Mises stress in tension and τ_{VM} is the von Mises stress in shear. The yield point stress in shear is the value of the von Mises stress in simple shear that causes yielding of the material. For this material it is common to formulate the constitutive equation in terms of the constant value of τ_{YP} . The constitutive equation for the incompressible Bingham material is.

$$\begin{aligned} 2 \cdot \mu \cdot \dot{e}_{ij} &= \frac{\sigma_{VM} - \sqrt{3} \cdot \tau_{YP}}{\sigma_{VM}} \cdot \left(\sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk} \cdot \delta_{ij} \right) && \text{when } \sigma_{VM} \geq \sqrt{3} \cdot \tau_{YP} \\ 2 \cdot \mu \cdot \dot{e}_{ij} &= 0 && \text{otherwise} \end{aligned}$$

When this material undergoes deformation, the entire rate of work done by the stresses is converted to a heat flow rate. Consequently, in the First Law of Thermodynamics for the material $\dot{W} = 0$. In addition, the internal energy is assumed to be a function of temperature only. Under these conditions, the first law becomes,

$$\dot{q} = \frac{\partial E}{\partial T} \cdot \dot{T}$$

and the entropy production rate is,

$$\dot{s} = \frac{\partial E}{\partial T} \cdot \frac{\dot{T}}{T}$$

Clearly, $\frac{\partial E}{\partial T}$ may be interpreted as the specific heat at constant volume, c_v , and it is assumed to have a constant value so that,

$$E = c_v \cdot (T - T_0)$$

$$\dot{q} = c_v \cdot \dot{T}$$

$$\dot{s} = c_v \cdot \frac{\dot{T}}{T}$$

During deformation, the quantity $-\sigma_{ij} \cdot \dot{\epsilon}_{ij}$ is the heat flow rate internal to the material element and,

$$-\sigma_{ij} \cdot \dot{\epsilon}_{ij} = \frac{\sigma_{VM} - \sqrt{3} \cdot \tau_{YP}}{2 \cdot \mu \cdot \sigma_{VM}} \cdot \left(\sigma_{ij} \cdot \sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk}^2 \right) = \frac{(\sigma_{VM} - \sqrt{3} \cdot \tau_{YP}) \cdot \sigma_{VM}}{3 \cdot \mu}, \quad \sigma_{VM} \geq \sqrt{3} \cdot \tau_{YP}$$

$$= 0, \quad \text{otherwise}$$

so that the externally supplied heat flow rate, \dot{q} , is,

$$\dot{q} = c_v \cdot \dot{T} + \frac{(\sigma_{VM} - \sqrt{3} \cdot \tau_{YP}) \cdot \sigma_{VM}}{3 \cdot \mu}, \quad \sigma_{VM} \geq \sqrt{3} \cdot \tau_{YP}$$

$$\dot{q} = c_v \cdot \dot{T}, \quad \text{otherwise}$$

and,

$$\dot{s}_{TOT} = c_v \cdot \frac{\dot{T}}{T} + \frac{(\sigma_{VM} - \sqrt{3} \cdot \tau_{YP}) \cdot \sigma_{VM}}{3 \cdot \mu \cdot T}, \quad \sigma_{VM} \geq \sqrt{3} \cdot \tau_{YP}$$

$$\dot{s}_{TOT} = c_v \cdot \frac{\dot{T}}{T}, \quad \text{otherwise}$$

Owing to the assumption of incompressibility the mean stress, $\frac{1}{3} \cdot \sigma_{kk}$, is indeterminate from the deformation. A similar situation occurs in the case of any incompressible material.

The last two equations may be written more compactly using Macaulay brackets² as,

$$\dot{s}_{TOT} = c_v \cdot \frac{\dot{T}}{T} + \left\langle \frac{(\sigma_{VM} - \sqrt{3} \cdot \tau_{YP}) \cdot \sigma_{VM}}{3 \cdot \mu \cdot T} \right\rangle \quad \text{and} \quad \dot{s}_{DISS} = \left\langle \frac{(\sigma_{VM} - \sqrt{3} \cdot \tau_{YP}) \cdot \sigma_{VM}}{3 \cdot \mu \cdot T} \right\rangle$$

Where the added brackets are defined as,

$$\langle x \rangle = x \quad \text{when } x \geq 0 \quad \text{and} \quad \langle x \rangle = 0 \quad \text{otherwise}$$

E. PENG-ROBINSON CUBIC EQUATION OF STATE

² W. H. Macaulay, "Note on the Deflection of Beams", The Messenger of Mathematics, v. 48, p. 129, 1919

This equation is used frequently to represent the state of the material in vapor-liquid equilibrium calculations. No viscous effects are included here. For a specified state (vapor or liquid) the equation contains three constants, R , a and b . It relates the pressure, p , to the specific volume, v , and absolute temperature, T , as follows,

$$p = \frac{R \cdot T}{v - b} - \frac{a}{v^2 + 2 \cdot b \cdot v - b^2}$$

A consistent set of units is,

p	$\frac{\text{lbf}}{\text{in}^2}$	R	$\frac{\text{in}}{^\circ\text{R}}$
T	$^\circ\text{R}$	b	$\frac{\text{in}^3}{\text{lbf}}$
v	$\frac{\text{in}^3}{\text{lbf}}$	a	$\frac{\text{in}^4}{\text{lbf}}$

For this case assume the internal energy is a function of the specific volume and the temperature, $E = E(v, T)$. With

$$\dot{W} = \text{rate of doing work} = p \cdot \dot{v}$$

the First Law of Thermodynamics yields,

$$\dot{q} = \left(\frac{\partial E}{\partial v} + p \right) \cdot \dot{v} + \frac{\partial E}{\partial T} \cdot \dot{T}$$

and then,

$$\dot{s} = \frac{\dot{q}}{T} = \frac{1}{T} \cdot \left(\frac{\partial E}{\partial v} + p \right) \cdot \dot{v} + \frac{\partial E}{\partial T} \cdot \frac{\dot{T}}{T}$$

In order for the entropy to be a state variable,

$$\frac{-1}{T^2} \cdot \left(\frac{\partial E}{\partial v} + p \right) + \frac{1}{T} \cdot \left(\frac{\partial^2 E}{\partial T \partial v} + \frac{\partial p}{\partial T} \right) = \frac{1}{T} \cdot \frac{\partial^2 E}{\partial v \partial T}$$

The second derivatives are independent of the order of differentiation so that,

$$\frac{\partial E}{\partial v} + p - T \cdot \frac{\partial p}{\partial T} = 0$$

When p is eliminated from this equation using the equation of state, the result is,

$$\frac{\partial E}{\partial v} = \frac{a}{v^2 + 2 \cdot b \cdot v - b^2}$$

and integration gives,

$$E = \frac{a}{\sqrt{8 \cdot b^2}} \cdot \ln \left(\frac{2 \cdot v + 2 \cdot b - \sqrt{8 \cdot b^2}}{2 \cdot v + 2 \cdot b + \sqrt{8 \cdot b^2}} \right) + L(T) = \frac{a}{2 \cdot \sqrt{2} \cdot b} \cdot \ln \left(\frac{v + (1 - \sqrt{2}) \cdot b}{v + (1 + \sqrt{2}) \cdot b} \right) + L(T)$$

so that

$$\dot{q} = \frac{R \cdot T}{v - b} \cdot \dot{v} + \frac{dL(T)}{dT} \cdot \dot{T}$$

The multiplier of \dot{T} is the specific heat at constant volume, c_v , so the heat flow rate and entropy production rate become, for constant c_v ,

$$\dot{q} = \frac{R \cdot T}{v - b} \cdot \dot{v} + c_v \cdot \dot{T}$$

$$\dot{s} = \frac{\dot{q}}{T} = \frac{R}{v - b} \cdot \dot{v} + c_v \cdot \frac{\dot{T}}{T}$$

Since there is no energy dissipation for this material,

$$\dot{q} = \dot{q} = \frac{R \cdot T}{v - b} \cdot \dot{v} + c_v \cdot \dot{T}$$

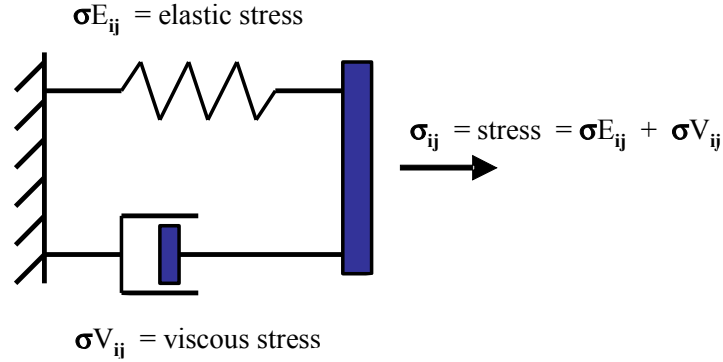
and,

$$\dot{s}_{TOT} = \dot{s} = \frac{R}{v - b} \cdot \dot{v} + c_v \cdot \frac{\dot{T}}{T}$$

Note that, when $a = b = 0$, the Peng-Robinson equation reduces to the ideal gas law. Also note that van der Waals' equation cannot be recovered from the Peng-Robinson equation as a special case.

F. VOIGT MATERIAL (KELVIN-VOIGT MATERIAL)

The sketch below is a conceptual description of this material. Although it is helpful to represent the physical characteristics of the material with this sort of sketch, D. C. Drucker (Second-order Effects in Elasticity. Plasticity and Fluid Dynamics, International Symposium, Haifa, Israel, April 23-27, 1962) has pointed out the limitations of material models based on such sketches.



The contributions to the stress, σE_{ij} , and σV_{ij} , are taken as the classical, linear formulations for thermoelastic and viscous materials. The external work is associated with σE_{ij} only. The work associated with σV_{ij} is dissipated as heat in the material element. The total stress is the sum of the two contributions so,

$$\sigma E_{ij} = \lambda \cdot (e_{kk} - 3 \cdot \alpha \cdot T) \cdot \delta_{ij} + 2 \cdot G \cdot (e_{ij} - \alpha \cdot T \cdot \delta_{ij})$$

$$\sigma V_{ij} = \bar{\lambda} \cdot \dot{e}_{kk} \cdot \delta_{ij} + 2 \cdot \bar{\mu} \cdot \dot{e}_{ij}$$

$$\sigma_{ij} = \sigma E_{ij} + \sigma V_{ij}$$

The internal energy, E , is assumed to be a function of σE_{ij} and T only. The work term is taken as $-\sigma E_{ij} \cdot \dot{e}_{ij}$ and then the First Law of Thermodynamics becomes.

$$\dot{q} = \left(\frac{\partial E}{\partial e_{ij}} - \sigma E_{ij} \right) \cdot \dot{e}_{ij} + \frac{\partial E}{\partial T} \cdot \dot{T}$$

and

$$\dot{s} = \frac{\dot{q}}{T} = \frac{1}{T} \cdot \left(\frac{\partial E}{\partial e_{ij}} - \sigma E_{ij} \right) \cdot \dot{e}_{ij} + \frac{\partial E}{\partial T} \cdot \frac{\dot{T}}{T}$$

The condition that must be satisfied in order that the entropy, s , be a state variable is,

$$\frac{-1}{T^2} \cdot \left(\frac{\partial E}{\partial \mathbf{e}_{ij}} - \sigma E_{ij} \right) + \frac{1}{T} \cdot \left(\frac{\partial^2 E}{\partial T \partial \mathbf{e}_{ij}} - \frac{\partial \sigma E_{ij}}{\partial T} \right) = \frac{1}{T} \cdot \frac{\partial^2 E}{\partial \mathbf{e}_{ij} \partial T}$$

The order of differentiation for the second derivatives may be interchanged so this condition becomes,

$$\frac{\partial E}{\partial \mathbf{e}_{ij}} = \sigma E_{ij} - T \cdot \frac{\partial \sigma E_{ij}}{\partial T}$$

When the constitutive equation for the elastic part of the strain is substituted into this condition, the result is,

$$\frac{\partial E}{\partial \mathbf{e}_{ij}} = \lambda \cdot \mathbf{e}_{kk} \cdot \delta_{ij} + 2 \cdot G \cdot \mathbf{e}_{ij}$$

and integration gives,

$$E = \frac{1}{2} \cdot \lambda \cdot \mathbf{e}_{kk}^2 + G \cdot \mathbf{e}_{ij} \cdot \mathbf{e}_{ij} + M(T)$$

with $M(T)$ being an arbitrary function of temperature. Recognizing that the specific heat at constant volume, c_v , is related to $M(T)$ through,

$$\frac{dM(T)}{dT} = c_v$$

yields,

$$\dot{q} = (3 \cdot \lambda + 2 \cdot G) \cdot \alpha \cdot T \cdot \dot{\mathbf{e}}_{kk} + c_v \cdot \dot{T}$$

$$\dot{s} = (3 \cdot \lambda + 2 \cdot G) \cdot \alpha \cdot \dot{\mathbf{e}}_{kk} + c_v \cdot \frac{\dot{T}}{T}$$

Since the internally generated heat flow rate is $-\sigma V_{ij} \cdot \dot{\mathbf{e}}_{ij}$, the external heat flow rate, \dot{q}^E , is given by,

$$\begin{aligned} \dot{q}^E &= \dot{q} + \sigma V_{ij} \cdot \dot{\mathbf{e}}_{ij} = \dot{q} + \bar{\lambda} \cdot \dot{\mathbf{e}}_{kk}^2 + 2 \cdot \bar{\mu} \cdot \dot{\mathbf{e}}_{ij} \cdot \dot{\mathbf{e}}_{ij} \\ &= (3 \cdot \lambda + 2 \cdot G) \cdot \alpha \cdot T \cdot \dot{\mathbf{e}}_{kk} + c_v \cdot \dot{T} + \bar{\lambda} \cdot \dot{\mathbf{e}}_{kk}^2 + 2 \cdot \bar{\mu} \cdot \dot{\mathbf{e}}_{ij} \cdot \dot{\mathbf{e}}_{ij} \end{aligned}$$

and,

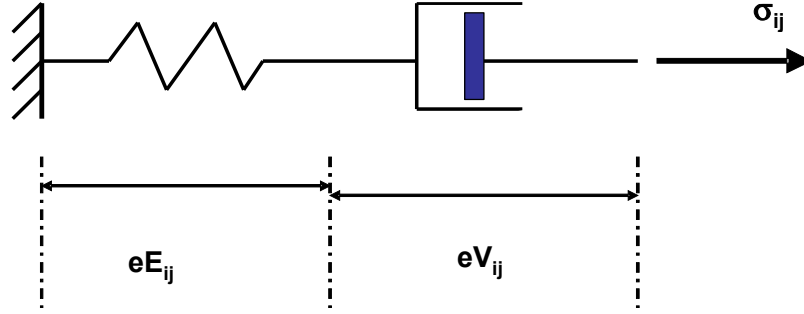
$$\dot{s}_{TOT} = (3 \cdot \lambda + 2 \cdot G) \cdot \alpha \cdot \dot{\mathbf{e}}_{kk} + c_v \cdot \frac{\dot{T}}{T} + \frac{\bar{\lambda}}{T} \cdot \dot{\mathbf{e}}_{kk}^2 + \frac{2 \cdot \bar{\mu}}{T} \cdot \dot{\mathbf{e}}_{ij} \cdot \dot{\mathbf{e}}_{ij}$$

and,

$$\dot{s}_{\text{DISS}} = \dot{s}_{\text{TOT}} - \dot{s} = \frac{\bar{\lambda}}{\text{T}} \cdot \dot{\mathbf{e}}_{\text{kk}}^2 + \frac{2 \cdot \bar{\mu}}{\text{T}} \cdot \dot{\mathbf{e}}_{\text{ij}} \cdot \dot{\mathbf{e}}_{\text{ij}}$$

G. MAXWELL MATERIAL

The sketch below gives a conceptual, physical understanding of the Maxwell material. The strain has separate elastic and viscous components, eE_{ij} and eV_{ij} , that are induced by the total stress, σ_{ij} .



The analytical model developed here uses classical, linear definitions to relate σ_{ij} , eE_{ij} , eV_{ij} and T as follows,

$$\sigma_{ij} = \lambda \cdot (eE_{kk} - 3 \cdot \alpha \cdot T) \cdot \delta_{ij} + 2 \cdot G \cdot (eE_{ij} - \alpha \cdot T \cdot \delta_{ij})$$

$$\sigma_{ij} = \bar{\lambda} \cdot \dot{e}V_{kk} \cdot \delta_{ij} + 2 \cdot \bar{\mu} \cdot \dot{e}V_{ij}$$

and the total strain rate, \dot{e}_{ij} , is defined as,

$$\dot{e}_{ij} = \dot{e}E_{ij} + \dot{e}V_{ij}$$

The external rate of work is $-\sigma_{ij} \cdot \dot{e}E_{ij}$ while the internal rate of work that is converted to heat flow rate is $-\sigma_{ij} \cdot \dot{e}V_{ij}$.

$$\sigma_{ij} \cdot \dot{e}E_{ij} = \lambda \cdot eE_{kk} \cdot \dot{e}E_{mm} + 2 \cdot G \cdot eE_{ij} \cdot \dot{e}E_{ij} - (3 \cdot \lambda + 2 \cdot G) \cdot \dot{e}E_{kk}$$

$$\sigma_{ij} \cdot \dot{e}V_{ij} = \bar{\lambda} \cdot \dot{e}V_{kk}^2 + 2 \cdot \bar{\mu} \cdot \dot{e}V_{ij} \cdot \dot{e}V_{ij}$$

The internal energy, E , is assumed to be a function of eE_{ij} and T only. The First Law of Thermodynamics for this formulation is,

$$\dot{q} = \left(\frac{\partial E}{\partial eE_{ij}} - \sigma_{ij} \right) \cdot \dot{e}E_{ij} + \frac{\partial E}{\partial T} \cdot \dot{T}$$

and

$$\dot{s} = \frac{\dot{q}}{T} = \frac{1}{T} \cdot \left(\frac{\partial E}{\partial e E_{ij}} - \sigma_{ij} \right) \cdot \dot{e} E_{ij} + \frac{\partial E}{\partial T} \cdot \frac{\dot{T}}{T}$$

The condition that entropy be a state variable is,

$$-\frac{1}{T^2} \cdot \left(\frac{\partial E}{\partial e E_{ij}} - \sigma_{ij} \right) + \frac{1}{T} \cdot \left(\frac{\partial^2 E}{\partial T \partial e E_{ij}} - \frac{\partial \sigma_{ij}}{\partial T} \right) = \frac{1}{T} \cdot \frac{\partial^2 E}{\partial e E_{ij} \partial T}$$

The order of differentiation may be interchanged so this equation becomes,

$$\frac{\partial E}{\partial e E_{ij}} = \sigma_{ij} - T \cdot \frac{\partial \sigma_{ij}}{\partial T}$$

Substitution of the constitutive equation for the elastic part of the strain into this equation gives,

$$\frac{\partial E}{\partial e E_{ij}} = \lambda \cdot e E_{kk} \cdot \delta_{ij} + 2 \cdot G \cdot e E_{ij}$$

and integration leads to,

$$E = \frac{1}{2} \cdot \lambda \cdot e E_{kk}^2 + G \cdot e E_{ij} \cdot e E_{ij} + N(T)$$

The function of integration, $N(T)$, is related to the specific heat at constant volume, c_v , through,

$$c_v = \frac{dN(T)}{dT}$$

so that,

$$\dot{q} = (3 \cdot \lambda + 2 \cdot G) \cdot \alpha \cdot T \cdot \dot{e} E_{kk} + c_v \cdot \dot{T}$$

$$\dot{s} = (3 \cdot \lambda + 2 \cdot G) \cdot \alpha \cdot \dot{e} E_{kk} + c_v \cdot \frac{\dot{T}}{T}$$

The external heat flow rate, \dot{q}^{ext} , is the difference between the total heat flow rate, \dot{q} , and the internal heat flow rate, $-\sigma_{ij} \cdot \dot{e} V_{ij}$, so that,

$$\begin{aligned} \dot{q}^{\text{ext}} &= \dot{q} + \sigma_{ij} \cdot \dot{e} V_{ij} = \dot{q} + \bar{\lambda} \cdot \dot{e} V_{kk}^2 + 2 \cdot \bar{\mu} \cdot \dot{e} V_{ij} \cdot \dot{e} V_{ij} \\ &= (3 \cdot \lambda + 2 \cdot G) \cdot \alpha \cdot T \cdot \dot{e} E_{kk} + c_v \cdot \dot{T} + \bar{\lambda} \cdot \dot{e} V_{kk}^2 + 2 \cdot \bar{\mu} \cdot \dot{e} V_{ij} \cdot \dot{e} V_{ij} \end{aligned}$$

and,

$$\dot{s}_{\text{TOT}} = (3 \cdot \lambda + 2 \cdot G) \cdot \alpha \cdot \dot{E}_{\text{kk}} + c_v \cdot \frac{\dot{T}}{T} + \frac{\bar{\lambda}}{T} \cdot \dot{V}_{\text{kk}}^2 + \frac{2 \cdot \bar{\mu}}{T} \cdot \dot{V}_{\text{ij}} \cdot \dot{V}_{\text{ij}}$$

where,

$$\dot{E}_{\text{kk}} = \frac{\dot{\sigma}_{\text{kk}}}{3 \cdot \lambda + 2 \cdot G} + 3 \cdot \alpha \cdot \dot{T}$$

$$\dot{V}_{\text{kk}}^2 = \frac{\dot{\sigma}_{\text{kk}}^2}{(3 \cdot \bar{\lambda} + 2 \cdot \bar{\mu})^2}$$

$$\begin{aligned} \dot{V}_{\text{ij}} \cdot \dot{V}_{\text{ij}} &= 3 \cdot \left(\frac{\bar{\lambda} \cdot \dot{\sigma}_{\text{kk}}}{2 \cdot \bar{\mu} \cdot (3 \cdot \bar{\lambda} + 2 \cdot \bar{\mu})} \right)^2 - \frac{\bar{\lambda} \cdot \dot{\sigma}_{\text{kk}}^2}{2 \cdot \bar{\mu}^2 \cdot (3 \cdot \bar{\lambda} + 2 \cdot \bar{\mu})} + \frac{\dot{\sigma}_{\text{ij}} \cdot \dot{\sigma}_{\text{ij}}}{4 \cdot \bar{\mu}^2} \\ &= \frac{\dot{\sigma}_{\text{ij}} \cdot \dot{\sigma}_{\text{ij}}}{4 \cdot \bar{\mu}^2} - \frac{\lambda \cdot (3 \cdot \bar{\lambda} + 4 \cdot \bar{\mu}) \cdot \sigma_{\text{kk}}^2}{4 \cdot \bar{\mu}^2 \cdot (3 \cdot \lambda + 2 \cdot \bar{\mu})^2} \end{aligned}$$

$$\bar{\lambda} \cdot \dot{V}_{\text{kk}}^2 + 2 \cdot \bar{\mu} \cdot \dot{V}_{\text{ij}} \cdot \dot{V}_{\text{ij}} = \frac{\dot{\sigma}_{\text{ij}} \cdot \dot{\sigma}_{\text{ij}}}{2 \cdot \bar{\mu}} - \frac{3 \cdot \bar{\lambda}^2 \cdot \dot{\sigma}_{\text{kk}}^2}{4 \cdot \bar{\mu} \cdot (3 \cdot \bar{\lambda} + 2 \cdot \bar{\mu})^2}$$

$$\dot{s}_{\text{TOT}} = (3 \cdot \lambda + 2 \cdot G) \cdot \alpha \cdot \dot{E}_{\text{kk}} + c_v \cdot \frac{\dot{T}}{T} + \frac{\dot{\sigma}_{\text{ij}} \cdot \dot{\sigma}_{\text{ij}}}{2 \cdot \bar{\mu} \cdot T} - \frac{3 \cdot \bar{\lambda}^2 \cdot \dot{\sigma}_{\text{kk}}^2}{4 \cdot \bar{\mu} \cdot (3 \cdot \bar{\lambda} + 2 \cdot \bar{\mu})^2 \cdot T}$$

and,

$$\dot{s}_{\text{DISS}} = \dot{s}_{\text{TOT}} - \dot{s} = \frac{\dot{\sigma}_{\text{ij}} \cdot \dot{\sigma}_{\text{ij}}}{2 \cdot \bar{\mu} \cdot T} - \frac{3 \cdot \bar{\lambda}^2 \cdot \dot{\sigma}_{\text{kk}}^2}{4 \cdot \bar{\mu} \cdot (3 \cdot \bar{\lambda} + 2 \cdot \bar{\mu})^2 \cdot T}$$

III. IRREVERSIBLE THERMODYNAMICS RESULTS FOR SOME COMMON ENGINEERING MATERIAL MODELS UNDERGOING CHANGES IN THERMODYNAMIC EQUILIBRIUM

INTRODUCTION

The definition of a reversible thermodynamic process for a constant, unit mass system is that the rate of change of the system entropy, \dot{s} , during the process is given by,

$$\dot{s} = \dot{s}_{\text{REV}} \equiv \frac{\dot{Q}_{\text{REV}}}{T} \leq \frac{\dot{Q}}{T}$$

where a superposed dot implies rate of change and the system has unit volume,

T = absolute temperature

\dot{s} = actual rate of change of entropy of system

\dot{s}_{REV} = corresponding rate of change of entropy during a reversible process

\dot{Q} = actual rate of heat flow into system

\dot{Q}_{REV} = corresponding rate of heat flow into system undergoing a reversible process

\dot{s} , \dot{s}_{REV} , \dot{Q} and \dot{Q}_{REV} are all per unit volume quantities.

An expression determining \dot{s}_{REV} for a homogenous material with defined properties may be found as described above using the First Law of Thermodynamics for a reversible system as,

$$\dot{s}_{\text{REV}} = \frac{1}{T} \cdot \dot{E} + \frac{1}{T} \cdot \dot{W}_{\text{REV}}$$

where,

\dot{E} = rate of internal energy per unit volume increase of the material per unit mass.
The internal energy, E , is a state variable.

\dot{W}_{REV} = rate of doing work per unit volume by system (with constitutive equation satisfied). Instantaneous constitutive equation satisfaction implies instantaneous equilibrium states. The constitutive equation (equation of state) defines the possible equilibrium states for the material.

The internal energy per unit volume of a homogeneous material is part of the definition of the material. It may be specified, for example, as being a function of strain, e_{ij} , and temperature, T . The specification of the variables defining E are based on the physical understanding of the material being modeled.

The expression for \dot{W}_{REV} may be determined using the constitutive equation for the material. Since the constitutive equation defines only equilibrium states it satisfies the required condition on \dot{W}_{REV} .

When the formulations for \dot{E} and \dot{W}_{REV} are substituted into the above equation for the First Law of Thermodynamics for a reversible system, an equation for \dot{s}_{REV} is found. The validity of this equation may be evaluated using a fundamental postulate of thermodynamics. The postulate is that s_{REV} is a property of the material (not path dependent). For example, when the expressions for \dot{E} and \dot{W}_{REV} are,

$$\begin{aligned}\dot{E} &= \frac{\partial E}{\partial e_{ij}} \cdot \dot{e}_{ij} + \frac{\partial E}{\partial T} \cdot \dot{T} \\ \dot{W}_{REV} &= -\sigma_{ij} \cdot \dot{e}_{ij}\end{aligned}$$

where σ_{ij} is a stress component then,

$$\dot{s}_{REV} = \frac{1}{T} \cdot \left(\frac{\partial E}{\partial e_{ij}} - \sigma_{ij} \right) \cdot \dot{e}_{ij} + \frac{1}{T} \cdot \frac{\partial E}{\partial T} \cdot \dot{T}$$

If s_{REV} is a state property, its differential must be an exact differential and expressible as,

$$\dot{s}_{REV} = \frac{\partial s_{REV}}{\partial e_{ij}} \cdot \dot{e}_{ij} + \frac{\partial s_{REV}}{\partial T} \cdot \dot{T}$$

Comparison of the last two equations shows that,

$$\frac{\partial}{\partial T} \left(\frac{1}{T} \cdot \left(\frac{\partial E}{\partial e_{ij}} - \sigma_{ij} \right) \right) = \frac{\partial}{\partial e_{ij}} \left(\frac{1}{T} \cdot \frac{\partial E}{\partial T} \right)$$

The last equation is a partial differential equation for $E(\sigma_{ij}, T)$. Since the second derivative is independent of the order of differentiation the equation reduces to,

$$\frac{\partial E}{\partial e_{ij}} = \sigma_{ij} - T \cdot \frac{\partial \sigma_{ij}}{\partial T}$$

When the constitutive equation is substituted into the last equation, $\frac{\partial E}{\partial \mathbf{e}_{ij}}$ is found explicitly and E can be determined by integration of this equation. Clearly, the procedure just described requires that \dot{E} , \dot{W}_{REV} and the constitutive equations be compatible so that E may be determined.

One extension to the formulation above may be found in the theory of Irreversible Thermodynamics. When this theory is limited to processes that are approximated as being instantaneously in equilibrium (i.e. satisfy the constitutive equations at every instant), the results presented below are obtained using the concept of a dissipative term in the First Law of Thermodynamics. The equations used here for this irreversible process are derived by splitting the heat flow rate into two parts. The first is \dot{Q}_{REV} where it is assumed that the state variable, E , has been determined and \dot{S}_{REV} is determined as described above,

$$\dot{Q}_{REV} = T \cdot \dot{S}_{REV}$$

The second part of the heat flow, \dot{Q}_{DISS} , is defined in terms of the actual rate of change of entropy, \dot{S} as,

$$\dot{Q}_{DISS} = T \cdot (\dot{S} - \dot{S}_{REV}) \equiv T \cdot \dot{S}_{DISS}$$

Consequently, the actual heat flow rate into the system, \dot{Q} , is,

$$\dot{Q} = \dot{Q}_{REV} + \dot{Q}_{DISS} = T \cdot \dot{S}$$

The results reported in the preceding section included the procedures given in this section without introducing the formalities of Irreversible Thermodynamics. The tabulation below summarizes the results of the preceding section. For each of the seven material models studied the following tabulation gives,

1. the constitutive equation
2. the equation for the internal energy, E
3. the reversible rate of change of entropy, \dot{S}_{REV}
4. the total rate of change of entropy, \dot{S}_{TOT}
5. the dissipative rate of change of entropy, \dot{S}_{DISS}

The slight changes in the nomenclature below are obvious. Two of the seven materials in the following tabulation have $\dot{S}_{DISS} = 0$ (linear thermoelasticity and Peng-Robinson). In Irreversible Thermodynamic theory the expressions for \dot{S}_{DISS} are generalized using Onsager's relations that include non-equilibrium states. When the constitutive equations are satisfied at every instant, \dot{S}_{DISS} determines the coefficients for the Onsager relations.

A. LINEAR THERMOELASTICITY

$$\sigma_{ij} = \lambda \cdot (e_{kk} - 3 \cdot \alpha \cdot T) \cdot \delta_{ij} + 2 \cdot G \cdot (e_{ij} - \alpha \cdot T \cdot \delta_{ij})$$

$$E = \frac{1}{2} \cdot \lambda \cdot (e_{kk})^2 + G \cdot e_{ij} \cdot e_{ij} + c_v \cdot (T - T_O)$$

$$\dot{s}_{\text{REV}} = (3 \cdot \lambda + 2 \cdot G) \cdot \alpha \cdot \dot{e}_{kk} + c_v \cdot \frac{\dot{T}}{T}$$

$$\dot{s}_{\text{TOT}} = (3 \cdot \lambda + 2 \cdot G) \cdot \alpha \cdot \dot{e}_{kk} + c_v \cdot \frac{\dot{T}}{T}$$

$$\dot{s}_{\text{DISS}} = 0$$

B. LINEAR, VISCOUS, COMPRESSIBLE NEWTONIAN FLUID

$$\sigma_{ij} = \lambda \cdot \dot{e}_{kk} \cdot \delta_{ij} + 2 \cdot \mu \cdot \dot{e}_{ij} + C \cdot (e_{kk} - 3 \cdot \alpha \cdot T) \cdot \delta_{ij}$$

$$E = \frac{1}{2} \cdot C \cdot (e_{kk})^2 + c_v \cdot (T - T_O)$$

$$\dot{s}_{REV} = 3 \cdot \alpha \cdot C \cdot \dot{e}_{kk} + c_v \cdot \frac{\dot{T}}{T}$$

$$\dot{s}_{TOT} = 3 \cdot \alpha \cdot C \cdot \dot{e}_{kk} + c_v \cdot \frac{\dot{T}}{T} + \frac{\lambda}{T} \cdot (\dot{e}_{kk})^2 + \frac{2 \cdot \mu}{T} \cdot \dot{e}_{ij} \cdot \dot{e}_{ij}$$

$$\dot{s}_{DISS} = \frac{\lambda}{T} \cdot (\dot{e}_{kk})^2 + \frac{2 \cdot \mu}{T} \cdot \dot{e}_{ij} \cdot \dot{e}_{ij}$$

C. ELASTIC, PERFECTLY-PLASTIC SOLID

$$\begin{aligned}\sigma_{VM} &= \sqrt{\frac{3}{2} \cdot \sigma_{ij} \cdot \sigma_{ij} - \frac{1}{2} \cdot \sigma_{kk}^2} \\ &= \sqrt{\frac{3}{2} \cdot \sqrt{\left(\sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk} \cdot \delta_{ij}\right) \cdot \left(\sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk} \cdot \delta_{ij}\right)}} \quad (\Gamma \text{ adjusted to ensure this condition})\end{aligned}$$

$$\dot{e}_{ij} = \dot{e}E_{ij} + \Gamma \cdot \left(\sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk} \cdot \delta_{ij}\right)$$

$$\sigma_{ij} = (\lambda \cdot eE_{kk} - (3 \cdot \lambda + 2 \cdot G) \cdot \alpha \cdot (T - T_O)) \cdot \delta_{ij} + 2 \cdot G \cdot eE_{ij}$$

or

$$eE_{ij} = \frac{\sigma_{ij}}{2 \cdot G} + \left(-\frac{\lambda}{3 \cdot \lambda + 2 \cdot G} \cdot \frac{\sigma_{kk}}{2 \cdot G} + \alpha \cdot (T - T_O) \right) \cdot \delta_{ij}$$

$$E = \frac{1}{2} \cdot \lambda \cdot eE_{kk}^2 + G \cdot eE_{ij} \cdot eE_{ij} + (3 \cdot \lambda + 2 \cdot G) \cdot \alpha \cdot T_O \cdot eE_{kk} + c_v \cdot (T - T_O)$$

$$\dot{s}_{REV} = (3 \cdot \lambda + 2 \cdot G) \cdot \alpha \cdot \dot{e}E_{kk} + c_v \cdot \frac{\dot{T}}{T}$$

$$\dot{s}_{TOT} = (3 \cdot \lambda + 2 \cdot G) \cdot \alpha \cdot \dot{e}E_{kk} + c_v \cdot \frac{\dot{T}}{T} + \frac{4 \cdot G^2 \cdot \Gamma}{T} \cdot \left(eE_{ij} \cdot eE_{ij} - \frac{1}{3} \cdot (eE_{kk})^2 \right)$$

$$\begin{aligned}\dot{s}_{DISS} &= \frac{4 \cdot G^2 \cdot \Gamma}{T} \cdot \left(eE_{ij} \cdot eE_{ij} - \frac{1}{3} \cdot (eE_{kk})^2 \right) \\ &= \frac{\Gamma}{T} \cdot \left(\sigma_{ij} \cdot \sigma_{ij} - \frac{1}{3} \cdot (\sigma_{kk})^2 + \frac{16 \cdot G^2}{3 \cdot \lambda + 2 \cdot G} \cdot \sigma_{kk} \cdot \alpha \cdot T \right) \\ &= \frac{\Gamma}{T} \cdot \left(\frac{2}{3} \cdot \sigma_{VM}^2 + \frac{16 \cdot G^2}{3 \cdot \lambda + 2 \cdot G} \cdot \sigma_{kk} \cdot \alpha \cdot T \right)\end{aligned}$$

D. INCOMPRESSIBLE BINGHAM MATERIAL

$$\sigma_{VM} = \sqrt{\frac{3}{2} \cdot \sigma_{ij} \cdot \sigma_{ij} - \frac{1}{2} \cdot \sigma_{kk}^2} = \sqrt{\frac{3}{2}} \cdot \sqrt{\sigma_{ij} \cdot \sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk}^2} \equiv \sqrt{3} \cdot \tau_{VM}$$

$$2 \cdot \mu \cdot \dot{\epsilon}_{ij} = \frac{\sigma_{VM} - \sqrt{3} \cdot \tau_{YP}}{\sigma_{VM}} \cdot \left(\sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk} \cdot \delta_{ij} \right) \quad \text{when } \sigma_{VM} \geq \sqrt{3} \cdot \tau_{YP}$$

$$2 \cdot \mu \cdot \dot{\epsilon}_{ij} = 0 \quad \text{otherwise}$$

$$E = c_v \cdot (T - T_0)$$

$$\dot{s}_{REV} = c_v \cdot \frac{\dot{T}}{T}$$

$$\dot{s}_{TOT} = c_v \cdot \frac{\dot{T}}{T} + \frac{(\sigma_{VM} - \sqrt{3} \cdot \tau_{YP}) \cdot \sigma_{VM}}{3 \cdot \mu \cdot T} \quad \sigma_{VM} \geq \sqrt{3} \cdot \tau_{YP}$$

$$\dot{s}_{TOT} = c_v \cdot \frac{\dot{T}}{T} \quad \text{otherwise}$$

$$\dot{s}_{DISS} = \frac{(\sigma_{VM} - \sqrt{3} \cdot \tau_{YP}) \cdot \sigma_{VM}}{3 \cdot \mu \cdot T} \quad \sigma_{VM} \geq \sqrt{3} \cdot \tau_{YP}$$

$$\dot{s}_{DISS} = 0 \quad \text{otherwise}$$

E. PENG-ROBINSON CUBIC EQUATION OF STATE

$$p = \frac{R \cdot T}{v - b} - \frac{a}{v^2 + 2 \cdot b \cdot v - b^2}$$

$$E = \frac{a}{2 \cdot \sqrt{2} \cdot b} \cdot \ln \left(\frac{v + (1 - \sqrt{2}) \cdot b}{v + (1 + \sqrt{2}) \cdot b} \right)$$

$$\dot{s}_{\text{REV}} = \frac{R}{v - b} \cdot \dot{v} + c_v \cdot \frac{\dot{T}}{T}$$

$$\dot{s}_{\text{TOT}} = \frac{R}{v - b} \cdot \dot{v} + c_v \cdot \frac{\dot{T}}{T}$$

$$\dot{s}_{\text{DISS}} = 0$$

F. VOIGT MATERIAL (KELVIN-VOIGT MATERIAL)

$$\sigma E_{ij} = \lambda \cdot (\mathbf{e}_{kk} - 3 \cdot \alpha \cdot T) \cdot \delta_{ij} + 2 \cdot G \cdot (\mathbf{e}_{ij} - \alpha \cdot T \cdot \delta_{ij})$$

$$\sigma V_{ij} = \bar{\lambda} \cdot \dot{\mathbf{e}}_{kk} \cdot \delta_{ij} + 2 \cdot \bar{\mu} \cdot \dot{\mathbf{e}}_{ij}$$

$$\sigma_{ij} = \sigma E_{ij} + \sigma V_{ij}$$

$$E = \frac{1}{2} \cdot \lambda \cdot (\mathbf{e}_{kk})^2 + G \cdot \mathbf{e}_{ij} \cdot \mathbf{e}_{ij} + c_v \cdot (T - T_o)$$

$$\dot{s}_{\text{REV}} = (3 \cdot \lambda + 2 \cdot G) \cdot \alpha \cdot \dot{\mathbf{e}}_{kk} + c_v \cdot \frac{\dot{T}}{T}$$

$$\dot{s}_{\text{TOT}} = (3 \cdot \lambda + 2 \cdot G) \cdot \alpha \cdot \dot{\mathbf{e}}_{kk} + c_v \cdot \frac{\dot{T}}{T} + \frac{\bar{\lambda}}{T} \cdot (\dot{\mathbf{e}}_{kk})^2 + \frac{2 \cdot \bar{\mu}}{T} \cdot \dot{\mathbf{e}}_{ij} \cdot \dot{\mathbf{e}}_{ij}$$

$$\dot{s}_{\text{DISS}} = \frac{\bar{\lambda}}{T} \cdot (\dot{\mathbf{e}}_{kk})^2 + \frac{2 \cdot \bar{\mu}}{T} \cdot \dot{\mathbf{e}}_{ij} \cdot \dot{\mathbf{e}}_{ij}$$

G. MAXWELL MATERIAL

$$\sigma_{ij} = \lambda \cdot (\epsilon E_{kk} - 3 \cdot \alpha \cdot T) \cdot \delta_{ij} + 2 \cdot G \cdot (\epsilon E_{ij} - \alpha \cdot T \cdot \delta_{ij})$$

$$\sigma_{ij} = \bar{\lambda} \cdot \dot{\epsilon} V_{kk} \cdot \delta_{ij} + 2 \cdot \bar{\mu} \cdot \dot{\epsilon} V_{ij} \quad \text{or} \quad \dot{\epsilon} V_{ij} = \frac{1}{2 \cdot \bar{\mu}} \cdot \sigma_{ij} - \frac{\bar{\lambda}}{2 \cdot \bar{\mu} \cdot (3 \cdot \bar{\lambda} + 2 \cdot \bar{\mu})} \cdot \sigma_{kk} \cdot \delta_{ij}$$

and the total strain rate, $\dot{\epsilon}_{ij}$, is defined as,

$$\dot{\epsilon}_{ij} = \dot{\epsilon} E_{ij} + \dot{\epsilon} V_{ij}$$

$$E = \frac{1}{2} \cdot \lambda \cdot (\epsilon E_{kk})^2 + G \cdot \epsilon E_{ij} \cdot \epsilon E_{ij} + c_v \cdot (T - T_0)$$

$$\dot{s}_{REV} = (3 \cdot \lambda + 2 \cdot \mu) \cdot \alpha \cdot \dot{\epsilon} E_{kk} + c_v \cdot \frac{\dot{T}}{T}$$

$$\begin{aligned} \dot{s}_{TOT} &= (3 \cdot \lambda + 2 \cdot \mu) \cdot \alpha \cdot \dot{\epsilon} E_{kk} + c_v \cdot \frac{\dot{T}}{T} + \frac{\bar{\lambda}}{T} \cdot (\dot{\epsilon} V_{kk})^2 + \frac{2 \cdot \bar{\mu}}{T} \cdot \dot{\epsilon} V_{ij} \cdot \dot{\epsilon} V_{ij} \\ &= (3 \cdot \lambda + 2 \cdot G) \cdot \alpha \cdot \dot{\epsilon} E_{kk} + c_v \cdot \frac{\dot{T}}{T} + \frac{\dot{\sigma}_{ij} \cdot \dot{\sigma}_{ij}}{2 \cdot \bar{\mu} \cdot T} - \frac{3 \cdot \bar{\lambda}^2 \cdot \dot{\sigma}_{kk}^2}{4 \cdot \bar{\mu} \cdot (3 \cdot \bar{\lambda} + 2 \cdot \bar{\mu})^2 \cdot T} \end{aligned}$$

$$\dot{s}_{DISS} = \frac{\bar{\lambda}}{T} \cdot (\dot{\epsilon} V_{kk})^2 + \frac{2 \cdot \bar{\mu}}{T} \cdot \dot{\epsilon} V_{ij} \cdot \dot{\epsilon} V_{ij} = \frac{\dot{\sigma}_{ij} \cdot \dot{\sigma}_{ij}}{2 \cdot \bar{\mu} \cdot T} - \frac{3 \cdot \bar{\lambda}^2 \cdot \dot{\sigma}_{kk}^2}{4 \cdot \bar{\mu} \cdot (3 \cdot \bar{\lambda} + 2 \cdot \bar{\mu})^2 \cdot T}$$

IV. NON-EQUILIBRIUM THERMODYNAMICS

The subject of Non-Equilibrium Thermodynamics considers thermodynamic systems that are not at all instants in equilibrium (don't satisfy the constitutive equations). The preceding sections have dealt with dissipation resulting from viscous flow and plastic flow. In all of the above cases the entropy dissipation can be expressed in terms of state variables or their time derivatives (σ_{ij} , $\dot{\sigma}_{ij}$ or $\dot{\epsilon}_{ij}$). In this section the more complicated case of predicting behavior when the instantaneous state is not in equilibrium is considered.

The publication most frequently cited in this field is the book *Non-Equilibrium Thermodynamics* by S. R. de Groot and P. Mazur (Dover Publications, 1984). This book presents the classical approach by using the difference between the total entropy rate and the reversible entropy rate as the measure of the non-equilibrium state. In this book the measure is designated by σ , called "entropy production" and, according to the Second Law of Thermodynamics, must be ≥ 0 . For cases considered by de Groot and Mazur the entropy production is restricted to the form,

$$\sigma = \sum_i J_i \cdot X_i$$

where J_i is a flux, X_i is a thermodynamic force and i is summed over all the non-equilibrium influences. The fluxes are assumed to be expressible in the phenomenological equations as,

$$J_i = \sum_j L_{ij} \cdot X_j$$

and the quantities L_{ij} are called the phenomenological coefficients. Eliminating J_i in the two preceding equations gives.

$$\sigma = \sum_i \sum_j L_{ij} \cdot X_i \cdot X_j$$

de Groot and Mazur give numerous examples and show that in many cases, but not all cases, the Onsager Reciprocal Relations are satisfied. The Onsager Reciprocal Relations are,

$$L_{ij} = L_{ji}$$

that is, the phenomenological coefficients are symmetric

The single case studied below has the constitutive equations completely specified. This case is in this category of materials with memory. The behavior of these materials depends on the past loading history. When the loading is removed at a specified time the

material may continue to deform after that time. The paper³ describing the constitutive equation and giving some comparisons with experiments can be described as an incompressible, gelling, Bingham material. The constitutive equations are, using Macaulay brackets,

$$2 \cdot \mu \cdot d_{ij} = \left\langle \frac{\sqrt{J_2} - \tau_{\text{CRIT}}}{\sqrt{J_2}} \right\rangle \cdot \left(\sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk} \cdot \delta_{ij} \right)$$

where,

$$\langle x \rangle = x \text{ if } x > 0; = 0 \text{ otherwise}$$

μ = a viscosity type constant, > 0

d_{ij} = component of deformation rate, in terms of velocity components v_i ,
 $= \frac{1}{2} \cdot (v_{i,j} + v_{j,i})$

σ_{ij} = component of the stress tensor

J_2^2 = second invariant of the reduced stress tensor
 $= \frac{1}{2} \cdot \left(\sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk} \cdot \delta_{ij} \right) \cdot \left(\sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk} \cdot \delta_{ij} \right)$

τ_{CRIT} = yield point in shear at time t , current yield point in shear

$$\begin{aligned} & \int_{\xi=-\infty}^{\xi=t} D_2 \cdot e^{-\alpha \cdot (t-\xi)} \cdot d\xi \\ \tau_1 &= \tau_1 - \frac{\int_{\xi=-\infty}^{\xi=t} D_2 \cdot e^{-\alpha \cdot (t-\xi)} \cdot d\xi}{\beta + \int_{\xi=-\infty}^{\xi=t} D_2 \cdot e^{-\alpha \cdot (t-\xi)} \cdot d\xi} \cdot (\tau_1 - \tau_0) \end{aligned}$$

t = current time

ξ = dummy variable for time

α = time constant, > 0

β = a constant in the equation for τ_{CRIT} , ≥ 0

³ * A. Slibar and P. R. Paslay, "On the Analytical Description of the Flow of Thixotropic Materials", Second-order Effects in Elasticity, Plasticity and Fluid Dynamics, International Symposium, Haifa, Israel, April 23-27, (1962) pp. 314-330. See also H. C. H. Darley and George R. Gray, *Composition and Properties of Drilling and Completion Fluids*, Fifth Edition, Gulf Publishing Company, 1988, pp. 203,204.

$$\begin{aligned} D_2^2 &= \text{second invariant of deformation rate tensor} \\ &= \frac{1}{2} \cdot \mathbf{d}_{ij} \cdot \mathbf{d}_{ij} \end{aligned}$$

$$\tau_1 = \text{fully gelled yield point in shear, } \geq \tau_0$$

$$\tau_0 = \text{minimum achievable yield point in shear, } \geq 0$$

The rate of doing external work by the stresses, \dot{W} , is,

$$\begin{aligned} \dot{W} &= \sigma_{ij} \cdot \mathbf{d}_{ij} = \frac{\sqrt{J_2} - \tau_{\text{CRIT}}}{2 \cdot \mu \cdot \sqrt{J_2}} \cdot \left(\sigma_{ij} \cdot \sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk}^2 \right) = \frac{\sqrt{J_2} - \tau_{\text{CRIT}}}{2 \cdot \mu \cdot \sqrt{J_2}} \cdot J_2 \\ &= \frac{\sqrt{J_2} - \tau_{\text{CRIT}}}{2 \cdot \mu} \cdot \sqrt{J_2} \end{aligned}$$

The specific heat, c_v , is assumed to be constant and the internal energy, E , is assumed to be a function of T only so the reversible rate of heating, \dot{q}_{REV} , is,

$$\dot{q}_{\text{REV}} = \frac{dE}{dT} \cdot \dot{T} = c_v \cdot \dot{T}$$

and,

$$\dot{s}_{\text{REV}} = c_v \cdot \frac{\dot{T}}{T}$$

Then,

$$\dot{q}_{\text{TOT}} = c_v \cdot \dot{T} + \frac{\sqrt{J_2} - \tau_{\text{CRIT}}}{2 \cdot \mu} \cdot \sqrt{J_2}$$

and,

$$\dot{s}_{\text{TOT}} = c_v \cdot \frac{\dot{T}}{T} + \frac{\sqrt{J_2} - \tau_{\text{CRIT}}}{2 \cdot \mu \cdot T} \cdot \sqrt{J_2}$$

so that,

$$\dot{s}_{\text{DISS}} = \dot{s}_{\text{TOT}} - \dot{s}_{\text{REV}} = \frac{\sqrt{J_2} - \tau_{\text{CRIT}}}{2 \cdot \mu \cdot T} \cdot \sqrt{J_2}$$

Similar to the earlier cases for different materials, \dot{s}_{DISS} is non-vanishing when there are viscous influences in the material behavior. In the other cases an equilibrium state (i. e.-

$\dot{s}_{\text{DISS}} = 0$) can be found by setting the deformation rate to zero. On the other hand, the value of τ_{CRIT} is dependent on the past history of the deformation rate so an equilibrium state cannot be established instantaneously.

For this gelling material it is clear that \dot{s}_{DISS} will not vanish when there has been a non-vanishing deformation rate. When a constant, non-vanishing deformation rate is imposed for a long time, \dot{s}_{DISS} for the material will approach a constant value denoted here as the steady state value. To illustrate how a steady state condition may be determined, consider this material in a viscometer that imposes a constant shear deformation rate. Furthermore, idealize this deformation rate as a single non-trivial component, d_{xy} , imposed since $\xi = -\infty$. The value of τ_{CRIT} can be found from D_2 being constant ($= D_0$) and $D_0 = +|d_{xy}|$ to be,

$$\begin{aligned}\tau_{\text{CRIT}} &= \tau_1 - \frac{\int_{\xi=-\infty}^t D_0 \cdot e^{-\alpha(t-\xi)} \cdot d\xi}{\beta + \int_{\xi=-\infty}^t D_0 \cdot e^{-\alpha(t-\xi)} \cdot d\xi} \cdot (\tau_1 - \tau_0) = \tau_1 \cdot \frac{\alpha \cdot \beta}{\alpha \cdot \beta + D_0} + \tau_0 \cdot \frac{D_0}{\alpha \cdot \beta + D_0} \\ &= \tau_1 \cdot \frac{\alpha \cdot \beta}{\alpha \cdot \beta + |d_{xy}|} + \tau_0 \cdot \frac{|d_{xy}|}{\alpha \cdot \beta + |d_{xy}|}\end{aligned}$$

For this deformation rate history the constitutive equations give,

$$\sigma_{xx} = \sigma_{yy} = \sigma_{zz} \quad \text{and} \quad \sigma_{xy}$$

as the only non-trivial stress components. Other than being equal to one another, the normal stresses are indeterminate from the constitutive equations because the material is incompressible. For this steady state the shear stress, σ_{xy} , and all components of the deformation rate are time independent. The x-y constitutive equation becomes,

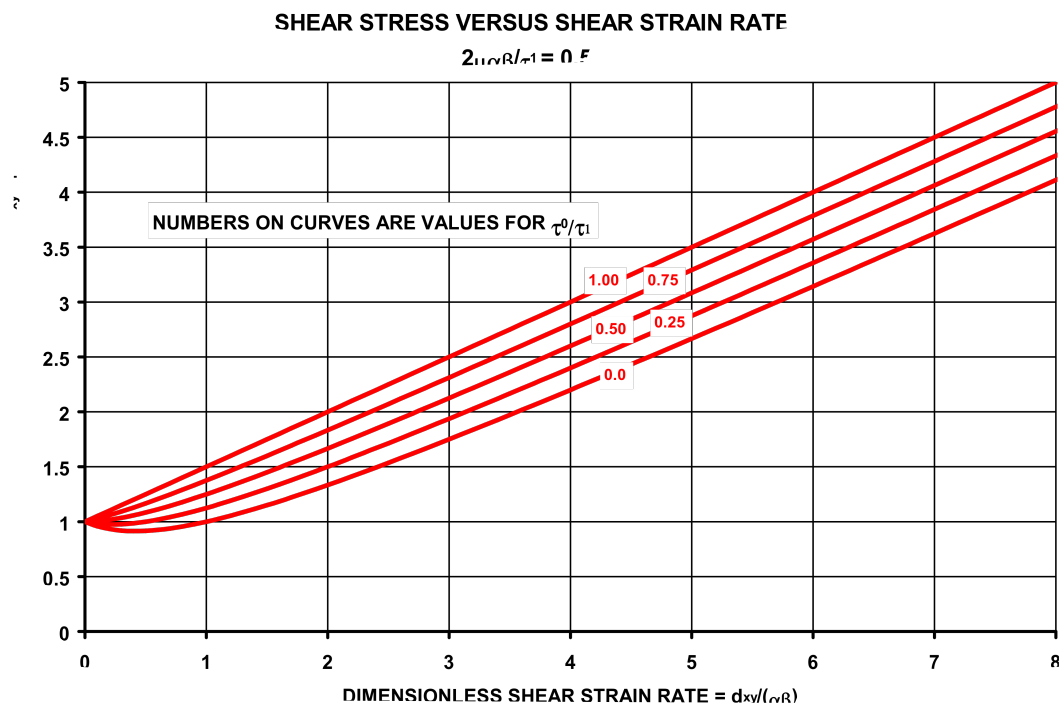
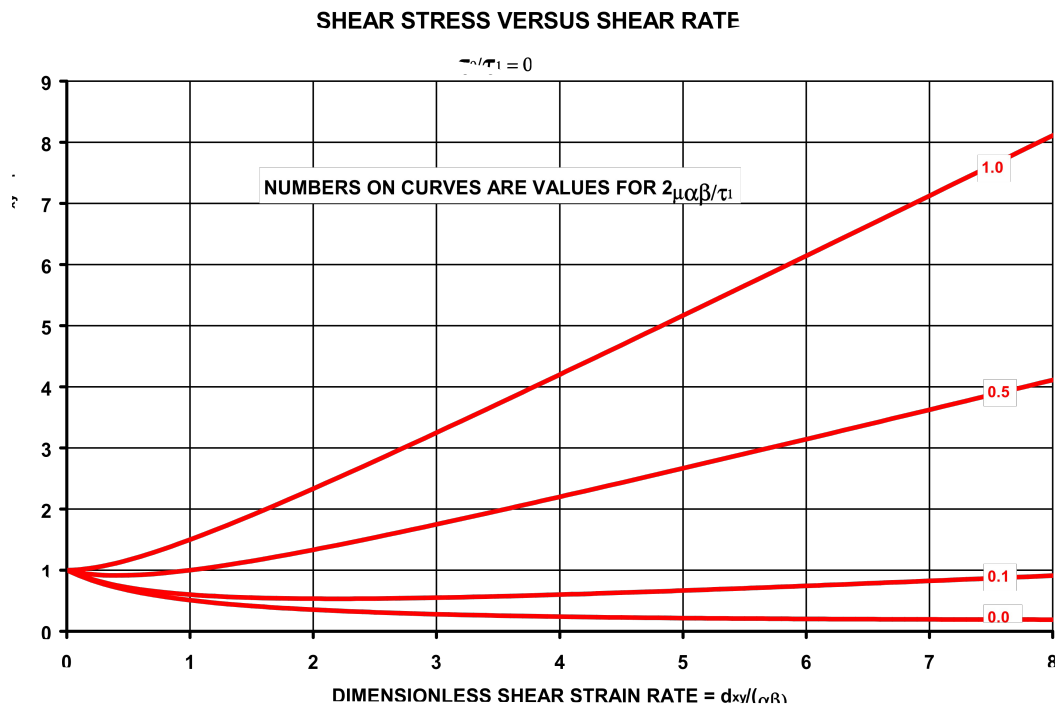
$$|\sigma_{xy}| = \tau_{\text{CRIT}} + 2 \cdot \mu \cdot |d_{xy}| = \tau_1 \cdot \frac{\alpha \cdot \beta}{\alpha \cdot \beta + |d_{xy}|} + \tau_0 \cdot \frac{|d_{xy}|}{\alpha \cdot \beta + |d_{xy}|} + 2 \cdot \mu \cdot |d_{xy}|$$

or,

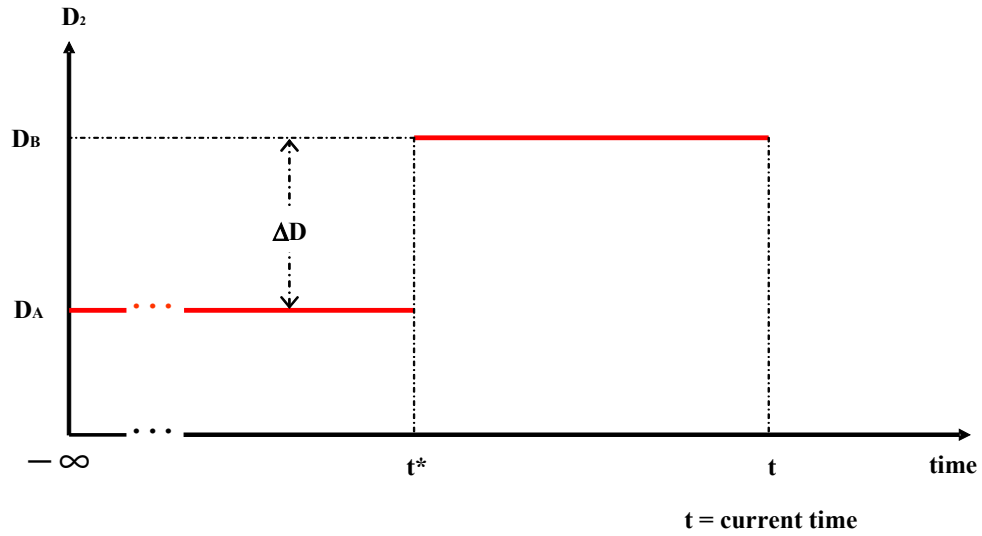
$$\left| \frac{\sigma_{xy}}{\tau_1} \right| = \frac{1}{1 + \frac{|d_{xy}|}{\alpha \cdot \beta}} + \frac{\tau_0}{\tau_1} \cdot \frac{\frac{|d_{xy}|}{\alpha \cdot \beta}}{1 + \frac{|d_{xy}|}{\alpha \cdot \beta}} + \frac{2 \cdot \mu \cdot \alpha \cdot \beta}{\tau_1} \cdot \frac{|d_{xy}|}{\alpha \cdot \beta}, \quad 1 \geq \frac{\tau_0}{\tau_1} \geq 0$$

The two figures below are based on the last equation. The first figure shows the influence of viscosity when $\tau_0 = 0$ and the second shows the influence of $\frac{\tau_0}{\tau_1}$ when

$$\frac{\mu \cdot \alpha \cdot \beta}{\tau_1} = 0.25.$$



A second example illustrating the determination of the variation of \dot{s}_{DISS} with time is presented at this point. For this example, the only non-vanishing component of the deformation rate is $d_{xy} > 0$. The time history for d_{ij} is defined in the sketch below.



The integral determining τ_{CRIT} for $t > t^*$ is,

$$\int_{\xi=-\infty}^{\xi=t} D_2 \cdot e^{-\alpha \cdot (t-\xi)} \cdot d\xi = \int_{\xi=-\infty}^{t^*} D_A \cdot e^{-\alpha \cdot (t-\xi)} \cdot d\xi + \int_{\xi=t^*}^{\xi=t} D_B \cdot e^{-\alpha \cdot (t-\xi)} \cdot d\xi = \frac{1}{\alpha} \cdot [D_B - (D_B - D_A) \cdot e^{-\alpha \cdot (t-t^*)}]$$

so that for $t > t^*$,

$$\tau_{\text{CRIT}} = \tau_1 + \frac{D_B - (D_B - D_A) \cdot e^{-\alpha \cdot (t-t^*)}}{\alpha \cdot \beta + D_B - (D_B - D_A) \cdot e^{-\alpha \cdot (t-t^*)}} \cdot (\tau_1 - \tau_0)$$

and,

$$\sigma_{xy} = \tau_{\text{CRIT}} + 2 \cdot \mu \cdot D_B$$

The last equation, in dimensionless form after eliminating τ_{CRIT} , becomes,

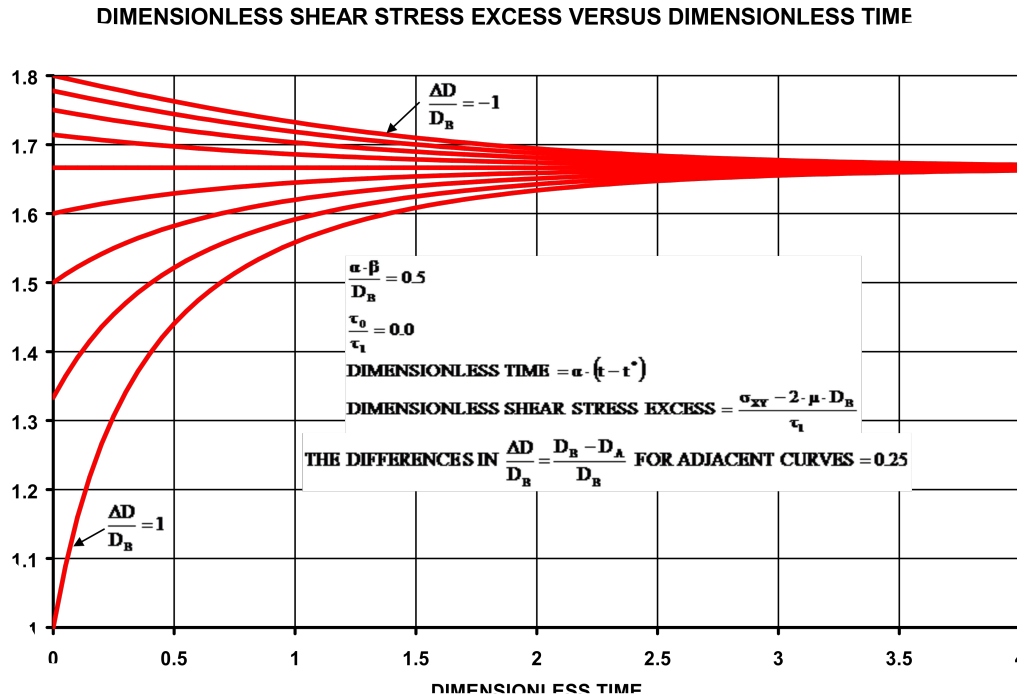
$$\frac{\sigma_{xy}}{\tau_1} = \frac{1 - \frac{\Delta D}{D_B} \cdot e^{-\alpha \cdot (t-t^*)}}{\frac{\alpha \cdot \beta}{D_B} + 1 - \frac{\Delta D}{D_B} \cdot e^{-\alpha \cdot (t-t^*)}} \cdot \left(1 - \frac{\tau_0}{\tau_1} \right) + 1 + \frac{2 \cdot \mu \cdot D_B}{\tau_1}, \quad (t - t^*) > 0$$

The above results may be used to evaluate the rate of dissipative entropy, \dot{s}_{DISS} , when $t > t^*$ as,

$$\dot{s}_{\text{DISS}} = \frac{\sqrt{J_2} - \tau_{\text{CRIT}}}{2 \cdot \mu \cdot T} \cdot \sqrt{J_2} = \frac{\sigma_{xy} - \tau_{\text{CRIT}}}{2 \cdot \mu \cdot T} \cdot \sigma_{xy} = \frac{D_B \cdot \sigma_{xy}}{T}$$

The figure below gives time histories of $\frac{\sigma_{xy} - 2 \cdot \mu \cdot D_B}{\tau_1}$ for different values of $\frac{\Delta D}{D_B}$ when

$$\frac{\alpha \cdot \beta}{D_B} = 0.5 \text{ and } \frac{\tau_0}{\tau_1} = 0.$$



V. OBSERVATIONS CONCERNING NON-EQUILIBRIUM THERMODYNAMICS

The customary presentation and treatment of Non-Equilibrium Thermodynamics is exemplified in de Groot and Mazur's treatise, cited earlier. Examples of many phenomena are presented including thermal conduction, chemical reactions and magnetic fields. A change of state is accompanied by a change of entropy. The excess of this change over the corresponding reversible change is expressed as the sum of products of "thermodynamic forces" and "thermodynamic displacements". A linear relationship between these forces and displacements is postulated in every case. Many phenomena, but not all, are shown to satisfy the Onsager Reciprocal Relations.

In continuum mechanics the typical investigation proceeds differently from the scheme described in de Groot and Mazur's treatise. The common, practical, continuum mechanics investigation begins with a specified, defining constitutive equation and a compatible internal energy. The internal energy is compatible when it and the constitutive equation can be used with the First Law of Thermodynamics to derive an expression for the entropy that is a path independent variable. The preceding section presents a case of a gelling material. The gelling strength, τ_{CRIT} , depends on the past history of an invariant of the deformation rate. The only time an equilibrium state (that is, $\dot{s}_{\text{DISS}} = 0$) is reached, in a practical sense, is when there has been no shearing for a long time. The presence of a practical, steady state behavior is predicted for the gelling material when a constant, non-vanishing deformation rate is maintained for a long time. Two illustrative examples are given above to demonstrate that the special tools of non-equilibrium thermodynamics are not required for a typical continuum mechanics study.