If internal energy is a state function of v, S, ξ, then

$$\frac{de}{dt}=\frac{\partial e}{\partial v}\bigg|_{S,\xi}\frac{dv}{dt}+\frac{\partial e}{\partial S}\bigg|_{v,\xi}\frac{dS}{dt}+\frac{\partial e}{\partial \xi}\bigg|_{v,S}\frac{d\xi}{dt} \tag{4.4}$$

$$\equiv -p_x\frac{dv}{dt}+T\frac{dS}{dt}+\eta\frac{d\xi}{dt}. \tag{4.5}$$

If ξ is a dissipative variable, e may still be a state function of v and S and $\eta\equiv 0$. Eliminating de/dt between equations (4.3) and (4.5) yields

$$T\frac{dS}{dt}=(p_x-p_x^*)\frac{dv}{dt}+(\eta^*-\eta)\frac{d\xi}{dt}+\frac{dq}{dt}. \tag{4.6}$$

Entropy, S, can now be eliminated between equations (4.1) and (4.6):

$$[a^{*2}+(p_x^*-p_x)v\Gamma^*]\frac{d\rho}{dt}=\frac{dp_x^*}{dt}-[\alpha^*+\rho\Gamma^*(\eta^*-\eta)]\frac{d\xi}{dt}-\rho\Gamma^*\frac{dq}{dt}. \tag{4.7}$$

If the system is reversible with $p^*=p$, $\eta^*=\eta$, and if $dq/dt=0$, $\alpha^*=\alpha$, $a^*=a$, equation (4.7) reduces to equation (3.5). The calculation proceeds as before from this point; the difference is that the extra terms of equation (4.7) must be carried in the computation. The extension to include several variables ξ_1, ξ_2, etc. is straightforward.

Examples

(i) *Elastic–plastic relaxing solids.* The work of uniaxial compression can be expressed as

$$dw=vp_x\,d\epsilon_x. \tag{4.8}$$

If elastic and plastic strains are occurring simultaneously, increments in elastic and plastic strain may be assumed to be additive:

$$d\epsilon_x=d\epsilon_x^e+d\epsilon_x^p \tag{4.9}$$

where superscripts e and p stand for elastic and plastic, respectively. It can also be assumed, to a good approximation for many substances, that there is no density change associated with plastic strain:

$$d\Theta=d\Theta^e+d\Theta^p=d\Theta^e=\sum_i d\epsilon_{ii}^e=d\epsilon_x=d\rho/\rho. \tag{4.10}$$

The pressure and strain deviators are, respectively,

$$d\Pi_{ij}=dp_{ij}-\delta_{ij}\,d\bar{p},\qquad de_{ij}=d\epsilon_{ij}-\delta_{ij}\,d\Theta/3,\qquad de_{ij}=de_{ij}^e+de_{ij}^p. \tag{4.11}$$

Take principal axis coordinates with uniaxial compression along the x-axis. Then increments in the work of elastic and plastic deformation are

$$dw_{de}=v\sum_j\Pi_j\,de_j^e\qquad\text{elastic}, \tag{4.12}$$

$$dw_{dp}=v\sum_j\Pi_j\,de_j^p\qquad\text{plastic}. \tag{4.13}$$

It is plausible to assume that stress is supported entirely by the elastic strains. To see this, consider the microscopic behavior of a plastically-deforming material from the point of view of dislocation theory, where plastic deformation is synonymous with motion and generation of dislocations. In most materials dislocations probably move at all stress levels, so there is no such thing as a yield point and there is no truly elastic behavior. But in practice the yield point concept is useful and the yield point itself may be taken to be the point at which large numbers of dislocations are set in motion. The motion of dislocations is inhibited by the existence of energy barriers which must be overcome by combination of stored elastic energy and thermal fluctuations of atoms. So, for example, one may consider a strained, work-hardening solid as one in which many dislocations exist but are momentarily immobilized or 'pinned' by energy barriers. If applied stress is held constant, dislocations may occasionally overcome a barrier and move to the next barrier, thus contributing to the plastic deformation by creep.

If the external stress is increased, local strain energy is increased around the pinning points, more dislocations are moved through pinning points and pass on until they are pinned again. If it is assumed that dislocations move freely between pinning points, the plastic strain which results from their motion requires no part of the applied stresses; i.e. the applied stress is supported entirely by the elastic part of the strain. It does follow, however, that a relaxation process may exist. For example, an increment in stress increases local strain energy around pinning points and increases probability that dislocations will break free of their pinning points and move on until pinned again. However, the probability of a dislocation breaking free is time dependent because it depends on thermal fluctuations as well as strain energy. This means that an increment in stress will produce an immediate elastic strain, and that, as time passes, dislocations escape their pins, move and are repinned, so that a plastic strain develops. Or the original increment in strain is reduced as the pinned dislocations escape from their barriers and the elastic strain is reduced. This concept can be expressed quantitatively in the following way for uniaxial strain in an isotropic solid:

$$\begin{aligned} \mathrm{d}p_x &= \lambda\,\mathrm{d}\Theta + 2\mu\,\mathrm{d}\epsilon_x^{\,e} \\ &= (\lambda + 2\mu)\,\mathrm{d}\epsilon_x - 2\mu\,\mathrm{d}\epsilon_x^{\,p}, \end{aligned} \tag{4.14}$$

when divided by $\mathrm{d}t$ this yields equation (3.18). In terms of stress and strain deviators this translates to

$$\begin{aligned} \dot{\Pi}_j &= 2\mu\dot{e}_j - 2\mu\dot{e}_j^{\,p} \\ &= 2\mu\dot{e}_j - F(S, e) \end{aligned} \tag{4.15}$$

where F is a relaxation function.

Equations (4.14) and (4.15) are both based on the assumption that dislocations move between pinning points without drag. If this is not true, a viscous contribution to the stress appears:

$$\mathrm{d}p_x = (\lambda + 2\mu)\,\mathrm{d}\epsilon_x - 2\mu\,\mathrm{d}\epsilon_x^{\,p} + \eta\,\mathrm{d}\dot{\epsilon}_x^{\,p}$$

$$\dot{\Pi}_j = 2\mu\dot{e}_j - 2\mu\dot{e}_j^{\,p} + 2\eta\ddot{e}_j^{\,p}.$$

For uniaxial strain

$$\Pi_x = 4\tau/3, \qquad \Pi_y = \Pi_z = -2\tau/3,$$

$$e_x = 2\epsilon_x/3, \qquad e_y = e_z = -\epsilon_x/3.$$

Then

$$\mathrm{d}\Pi_x = 4\mathrm{d}\tau/3 = 2\mu\,\mathrm{d}e_x^{\,e},$$

$$\mathrm{d}\Pi_y = -2\mathrm{d}\tau/3 = 2\mu\,\mathrm{d}e_y^{\,e},$$

$$\mathrm{d}\tau = 2\mu\,\mathrm{d}\gamma^e,$$

where

$$\mathrm{d}\gamma^e \equiv \mathrm{d}(e_x^{\,e} - e_y^{\,e})/2 = (\mathrm{d}\epsilon_x^{\,e} - \mathrm{d}\epsilon_y^{\,e})/2.$$