CHAPTER 4

THERMODYNAMICS OF DEFORMATION

4.1. Energy Equation

A deforming body, or a given portion of it, can be considered to be a thermodynamic system in continuum mechanics. The first law of thermodynamics relates the mechanical work done on the system and the heat transferred into the system to the change in total energy of the system. The rate at which external surface and body forces are doing work on a body currently occupying the volume V bounded by the surface S is given by Eq. (3.5.6), i.e.,

$$\mathcal{P} = \frac{\mathrm{d}}{\mathrm{d}t} \int_V \frac{1}{2} \rho \, \mathbf{v} \cdot \mathbf{v} \, \mathrm{d}V + \int_V \boldsymbol{\sigma} : \mathbf{D} \, \mathrm{d}V. \tag{4.1.1}$$

Let $\mathbf{q}$ be a vector whose magnitude gives the rate of heat flow by conduction across a unit area normal to $\mathbf{q}$. The direction of $\mathbf{q}$ is the direction of heat flow, so that in time $\mathrm{d}t$ the heat amount $\mathbf{q}\,\mathrm{d}t$ would flow through a unit area normal to $\mathbf{q}$. If the area $\mathrm{d}S$ is oriented so that its normal $\mathbf{n}$ is not in the direction of $\mathbf{q}$, the rate of outward heat flow through $\mathrm{d}S$ is $\mathbf{q} \cdot \mathbf{n} \, \mathrm{d}S$ (Fig. 4.1). Let a scalar r be the rate of heat input per unit mass due to distributed internal heat sources. The total heat input rate into the system is then

$$\mathcal{Q} = -\int_S \mathbf{q} \cdot \mathbf{n} \, \mathrm{d}S + \int_V \rho \, r \, \mathrm{d}V = \int_V (-\boldsymbol{\nabla} \cdot \mathbf{q} + \rho \, r) \, \mathrm{d}V. \tag{4.1.2}$$

According to the first law of thermodynamics there exists a state function of a thermodynamic system, called the total energy of the system $\mathcal{E}_{\mathrm{tot}}$, such that its rate of change is

$$\dot{\mathcal{E}}_{\mathrm{tot}} = \mathcal{P} + \mathcal{Q}. \tag{4.1.3}$$

Neither $\mathcal{P}$ nor $\mathcal{Q}$ is in general the rate of any state function, but their sum is. The total energy of the system consists of the macroscopic kinetic energy

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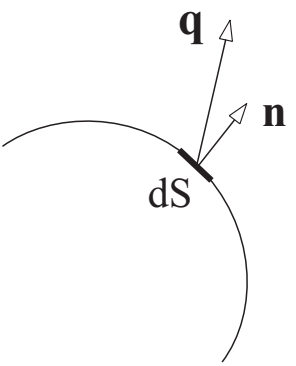

FIGURE 4.1. The heat flow vector $\mathbf{q}$ through the surface element $\mathrm{d}S$ with a unit normal $\mathbf{n}$.

and the internal energy of the system,

$$\mathcal{E}_{\mathrm{tot}} = \frac{\mathrm{d}}{\mathrm{d}t} \int_V \frac{1}{2} \rho \, \mathbf{v} \cdot \mathbf{v} \, \mathrm{d}V + \int_V \rho \, u \, \mathrm{d}V. \tag{4.1.4}$$

The specific internal energy (internal energy per unit mass) is denoted by u. It includes the elastic strain energy and all other forms of energy that do not contribute to macroscopic kinetic energy (e.g., latent strain energy around dislocations, phase-transition energy, energy of random thermal motion of atoms, etc.).

Substituting Eqs. (4.1.1), (4.1.2), and (4.1.4) into Eq. (4.1.3), and having in mind Eq. (3.2.7), gives

$$\int_V (\rho \, \dot{u} - \boldsymbol{\sigma} : \mathbf{D} + \boldsymbol{\nabla} \cdot \mathbf{q} - \rho \, r) \, \mathrm{d}V = 0. \tag{4.1.5}$$

This holds for the whole body and for any part of it, so that locally, at each point, we can write

$$\rho \, \dot{u} = \boldsymbol{\sigma} : \mathbf{D} - \boldsymbol{\nabla} \cdot \mathbf{q} + \rho \, r. \tag{4.1.6}$$

This is the energy equation in the deformed configuration (spatial form of the energy equation).

4.1.1. Material Form of Energy Equation

The corresponding equation written relative to the undeformed configuration is obtained by multiplying Eq. (4.1.6) with $(\det \mathbf{F})$. Since $\rho(\det \mathbf{F}) = \rho^0$,

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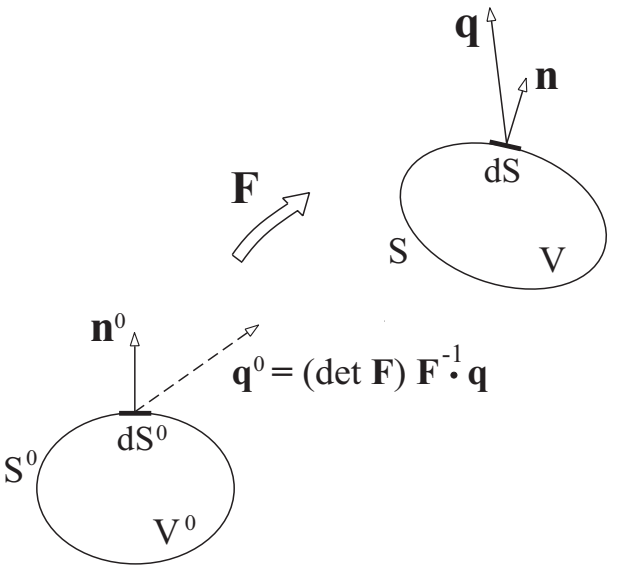

FIGURE 4.2. The nominal rate of the heat flow vector $\mathbf{q}^0$ is related to the heat flow vector $\mathbf{q}$ in the deformed configuration by $\mathbf{q}^0 = (\det \mathbf{F})\mathbf{F}^{-1} \cdot \mathbf{q}$.

and since

$$(\det \mathbf{F})\boldsymbol{\nabla} \cdot \mathbf{q} = \boldsymbol{\nabla}^0 \cdot \left[(\det \mathbf{F})\mathbf{F}^{-1} \cdot \mathbf{q}\right], \tag{4.1.7}$$

by an equation such as (3.3.10), Eq. (4.1.6) becomes

$$\rho^0\, \dot{u} = \mathbf{P} \cdot\cdot\, \dot{\mathbf{F}} - \boldsymbol{\nabla}^0 \cdot \mathbf{q}^0 + \rho^0\, r. \tag{4.1.8}$$

The nominal stress $\mathbf{P}$ is defined by Eq. (3.7.4) ($\mathbf{P} \cdot\cdot\, \dot{\mathbf{F}} = \boldsymbol{\tau} : \mathbf{D}$), and

$$\mathbf{q}^0 = (\det \mathbf{F})\mathbf{F}^{-1} \cdot \mathbf{q} \tag{4.1.9}$$

is the nominal rate of the heat flow vector $\left(\mathbf{q}^0 \cdot \mathbf{n}^0\, \mathrm{d}S^0 = \mathbf{q} \cdot \mathbf{n}\, \mathrm{d}S\right)$; see Fig. 4.2. Equation (4.1.8) is a material form of the energy equation.

The rate of specific internal energy can consequently be written as either of

$$\dot{u} = \frac{1}{\rho}\, \boldsymbol{\sigma} : \mathbf{D} - \frac{1}{\rho}\, \boldsymbol{\nabla} \cdot \mathbf{q} + r = \frac{1}{\rho^0}\, \mathbf{P} \cdot\cdot\, \dot{\mathbf{F}} - \frac{1}{\rho^0}\, \boldsymbol{\nabla}^0 \cdot \mathbf{q}^0 + r. \tag{4.1.10}$$

The stress dependent term,

$$\frac{1}{\rho}\, \boldsymbol{\sigma} : \mathbf{D} = \frac{1}{\rho^0}\, \mathbf{P} \cdot\cdot\, \dot{\mathbf{F}} = \frac{1}{\rho^0}\, \mathbf{T}_{(n)} : \dot{\mathbf{E}}_{(n)} \tag{4.1.11}$$

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is the contribution to the change of internal energy due to the rate of mechanical work, while the remaining terms in Eq. (4.1.10) represent the rate of heat input per unit mass. The stress $\mathbf{T}_{(n)}$ is conjugate to strain $\mathbf{E}_{(n)}$ in the spirit of Eq. (4.1.11), as discussed in Section 3.6.

4.2. Clausius–Duhem Inequality

The first law of thermodynamics is a statement of the energy balance, which applies regardless of the direction in which the energy conversion between work and heat is assumed to occur. The second law of thermodynamics imposes restrictions on possible directions of thermodynamic processes. A state function, called the entropy of the system, is introduced as a measure of microstructural disorder of the system. The entropy can change by interaction of the system with its surroundings through the heat transfer, and by irreversible changes that take place inside the system due to local rearrangements of microstructure caused by deformation. The entropy input rate due to heat transfer is (Truesdell and Noll, 1965; Malvern, 1969)

$$-\int_S \frac{\mathbf{q}\cdot\mathbf{n}}{\theta}\,\mathrm{d}S + \int_V \rho\,\frac{r}{\theta}\,\mathrm{d}V = \int_V \left[-\frac{1}{\rho}\,\boldsymbol{\nabla}\cdot\left(\frac{\mathbf{q}}{\theta}\right) + \frac{r}{\theta}\right]\rho\,\mathrm{d}V, \tag{4.2.1}$$

where $\theta > 0$ is the absolute temperature. The temperature is defined as a measure of the coldness or hotness. It appears in the denominators of the above integrands, because a given heat input causes more disorder (higher entropy change) at lower than at higher temperature (state at lower temperature being less disordered and thus more sensitive to the heat input).

An explicit expression for the rate of entropy change caused by irreversible microstructural changes inside the system depends on the type of deformation and constitution of the material. Denote this part of the rate of entropy change (per unit mass) by γ. The total rate of entropy change of the whole system is then

$$\int_V \rho\,\frac{\mathrm{d}\eta}{\mathrm{d}t}\,\mathrm{d}V = \int_V \left[-\frac{1}{\rho}\,\boldsymbol{\nabla}\cdot\left(\frac{\mathbf{q}}{\theta}\right) + \frac{r}{\theta} + \gamma\right]\rho\,\mathrm{d}V. \tag{4.2.2}$$

Locally, at each point of a deformed body, the rate of specific entropy is

$$\dot{\eta} = -\frac{1}{\rho}\,\boldsymbol{\nabla}\cdot\left(\frac{\mathbf{q}}{\theta}\right) + \frac{r}{\theta} + \gamma. \tag{4.2.3}$$

Since irreversible microstructural changes increase a disorder, they always contribute to an increase of the entropy. Thus, γ is always positive, and is

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referred to as the entropy production rate. The inequality

$$\gamma > 0 \tag{4.2.4}$$

is a statement of the second law of thermodynamics for irreversible processes. Therefore, from Eq. (4.2.3) we can write

$$\dot{\eta} \geq -\frac{1}{\rho}\,\boldsymbol{\nabla}\cdot\left(\frac{\mathbf{q}}{\theta}\right) + \frac{r}{\theta}\,. \tag{4.2.5}$$

The equality sign applies only to reversible processes ($\gamma = 0$). Inequality (4.2.5) is known as the Clausius–Duhem inequality (e.g., Müller, 1985; Ericksen, 1991).

Since

$$\boldsymbol{\nabla}\cdot\left(\frac{\mathbf{q}}{\theta}\right) = \frac{1}{\theta}\,\boldsymbol{\nabla}\cdot\mathbf{q} - \frac{1}{\theta^2}\,\mathbf{q}\cdot\boldsymbol{\nabla}\theta, \tag{4.2.6}$$

the inequality (4.2.5) can be rewritten as

$$\dot{\eta} \geq -\frac{1}{\rho\,\theta}\,\boldsymbol{\nabla}\cdot\mathbf{q} + \frac{r}{\theta} + \frac{1}{\rho\,\theta^2}\,\mathbf{q}\cdot\boldsymbol{\nabla}\theta. \tag{4.2.7}$$

The heat spontaneously flows in the direction from the hot to cold part of the body, so that $\mathbf{q}\cdot\boldsymbol{\nabla}\theta \leq 0$. Since $\theta > 0$, it follows that

$$\frac{1}{\rho\,\theta^2}\,\mathbf{q}\cdot\boldsymbol{\nabla}\theta \leq 0. \tag{4.2.8}$$

Thus, a stronger (more restrictive) form of the Clausius–Duhem inequality is

$$\dot{\eta} \geq -\frac{1}{\rho\,\theta}\,\boldsymbol{\nabla}\cdot\mathbf{q} + \frac{r}{\theta}\,. \tag{4.2.9}$$

Inequality (4.2.9) can alternatively be adopted if the temperature gradients are negligible or equal to zero.

The material forms of the inequalities (4.2.8) and (4.2.9) are

$$\dot{\eta} \geq -\frac{1}{\rho^0\,\theta}\,\boldsymbol{\nabla}^0\cdot\mathbf{q}^0 + \frac{r}{\theta}\,, \tag{4.2.10}$$

and

$$\frac{1}{\rho^0\,\theta^2}\,\mathbf{q}^0\cdot\boldsymbol{\nabla}^0\theta \leq 0. \tag{4.2.11}$$

4.3. Reversible Thermodynamics

If deformation is such that there are no permanent microstructural rearrangements within the material (e.g., thermoelastic deformation), the entropy production rate γ is equal to zero. The rate of entropy change is due

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to heat transfer only, and

$$\theta\dot{\eta} = -\frac{1}{\rho}\,\boldsymbol{\nabla}\cdot\mathbf{q} + r. \tag{4.3.1}$$

The energy equation (4.1.10) in this case becomes

$$\dot{u} = \frac{1}{\rho^0}\,\mathbf{T}_{(n)} : \dot{\mathbf{E}}_{(n)} + \theta\,\dot{\eta}. \tag{4.3.2}$$

Equation (4.3.2) shows that the internal energy is a thermodynamic potential for determining $\mathbf{T}_{(n)}$ and θ, when $\mathbf{E}_{(n)}$ and η are considered to be independent state variables. Indeed, by partial differentiation of

$$u = u\left(\mathbf{E}_{(n)}, \eta\right), \tag{4.3.3}$$

we have

$$\dot{u} = \frac{\partial u}{\partial \mathbf{E}_{(n)}} : \dot{\mathbf{E}}_{(n)} + \frac{\partial u}{\partial \eta}\,\dot{\eta}, \tag{4.3.4}$$

and comparison with Eq. (4.3.2) gives

$$\mathbf{T}_{(n)} = \rho^0\,\frac{\partial u}{\partial \mathbf{E}_{(n)}}\,, \quad \theta = \frac{\partial u}{\partial \eta}\,. \tag{4.3.5}$$

4.3.1. Thermodynamic Potentials

The Helmholtz free energy is related to internal energy by

$$\psi = u - \theta\,\eta. \tag{4.3.6}$$

By differentiating and incorporating Eq. (4.3.2), the rate of the Helmholtz free energy is

$$\dot{\psi} = \frac{1}{\rho^0}\,\mathbf{T}_{(n)} : \dot{\mathbf{E}}_{(n)} - \eta\,\dot{\theta}. \tag{4.3.7}$$

This indicates that ψ is the portion of internal energy u available for doing work at constant temperature ($\dot{\theta} = 0$). The Helmholtz free energy is a thermodynamic potential for $\mathbf{T}_{(n)}$ and η, when $\mathbf{E}_{(n)}$ and θ are considered to be independent state variables. Indeed, by partial differentiation of

$$\psi = \psi\left(\mathbf{E}_{(n)}, \theta\right), \tag{4.3.8}$$

we have

$$\dot{\psi} = \frac{\partial \psi}{\partial \mathbf{E}_{(n)}} : \dot{\mathbf{E}}_{(n)} + \frac{\partial \psi}{\partial \theta}\,\dot{\theta}, \tag{4.3.9}$$

and comparison with Eq. (4.3.7) gives

$$\mathbf{T}_{(n)} = \rho^0\,\frac{\partial \psi}{\partial \mathbf{E}_{(n)}}\,, \quad \eta = -\frac{\partial \psi}{\partial \theta}\,. \tag{4.3.10}$$

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The Gibbs energy can be defined as a Legendre transform of the Helmholtz free energy, i.e.,

$$\Phi_{(n)}\left(\mathbf{T}_{(n)},\theta\right)=\frac{1}{\rho^0}\,\mathbf{T}_{(n)}:\mathbf{E}_{(n)}-\psi\left(\mathbf{E}_{(n)},\theta\right). \tag{4.3.11}$$

Note that $\Phi_{(n)}$ is not measure invariant, although ψ is, because for a given geometry change, the quantity $\mathbf{T}_{(n)}:\mathbf{E}_{(n)}$ in general depends on the selected strain and stress measures $\mathbf{E}_{(n)}$ and $\mathbf{T}_{(n)}$. Recall that these are conjugate in the sense that $\mathbf{T}_{(n)}:\mathrm{d}\mathbf{E}_{(n)}$ is measure invariant.

By differentiating Eq. (4.3.11) and using (4.3.7), it follows that

$$\dot{\phi}_{(n)}=\frac{\partial\Phi_{(n)}}{\partial\mathbf{T}_{(n)}}:\dot{\mathbf{T}}_{(n)}+\frac{\partial\Phi_{(n)}}{\partial\theta}\,\dot{\theta}=\frac{1}{\rho^0}\,\mathbf{E}_{(n)}:\dot{\mathbf{T}}_{(n)}+\eta\,\dot{\theta}, \tag{4.3.12}$$

so that

$$\mathbf{E}_{(n)}=\rho^0\,\frac{\partial\Phi_{(n)}}{\partial\mathbf{T}_{(n)}},\quad \eta=\frac{\partial\Phi_{(n)}}{\partial\theta}. \tag{4.3.13}$$

Finally, the enthalpy function is introduced by

$$h_{(n)}\left(\mathbf{T}_{(n)},\eta\right)=\frac{1}{\rho^0}\,\mathbf{T}_{(n)}:\mathbf{E}_{(n)}-u_{(n)}\left(\mathbf{E}_{(n)},\eta\right)=\Phi_{(n)}\left(\mathbf{T}_{(n)},\theta\right)-\theta\,\eta. \tag{4.3.14}$$

By either Eq. (4.3.2) or Eq. (4.3.12), the rate of enthalpy is

$$\dot{h}_{(n)}=\frac{\partial h_{(n)}}{\partial\mathbf{T}_{(n)}}:\dot{\mathbf{T}}_{(n)}+\frac{\partial h_{(n)}}{\partial\eta}\,\dot{\eta}=\frac{1}{\rho^0}\,\mathbf{E}_{(n)}:\dot{\mathbf{T}}_{(n)}-\theta\,\dot{\eta}. \tag{4.3.15}$$

This demonstrates that the enthalpy is a portion of the internal energy that can be released as heat when stress $\mathbf{T}_{(n)}$ is held constant. Furthermore, Eq. (4.3.15) yields

$$\mathbf{E}_{(n)}=\rho^0\,\frac{\partial h_{(n)}}{\partial\mathbf{T}_{(n)}},\quad \theta=-\frac{\partial h_{(n)}}{\partial\eta}. \tag{4.3.16}$$

The fourth-order tensors

$$\mathbf{\Lambda}_{(n)}=\frac{\partial\mathbf{T}_{(n)}}{\partial\mathbf{E}_{(n)}}=\frac{\partial^2\left(\rho^0\,\psi\right)}{\partial\mathbf{E}_{(n)}\otimes\partial\mathbf{E}_{(n)}}, \tag{4.3.17}$$

$$\mathbf{M}_{(n)}=\frac{\partial\mathbf{E}_{(n)}}{\partial\mathbf{T}_{(n)}}=\frac{\partial^2\left(\rho^0\,\Phi_{(n)}\right)}{\partial\mathbf{T}_{(n)}\otimes\partial\mathbf{T}_{(n)}} \tag{4.3.18}$$

are the isothermal elastic stiffness and compliance tensors corresponding to the selected pair $\left(\mathbf{E}_{(n)},\mathbf{T}_{(n)}\right)$ of conjugate stress and strain tensors. The two fourth-order tensors are the inverse of each other $\left(\mathbf{M}_{(n)}=\mathbf{\Lambda}_{(n)}^{-1}\right)$, since

$$\frac{\partial\mathbf{T}_{(n)}}{\partial\mathbf{E}_{(n)}}:\frac{\partial\mathbf{E}_{(n)}}{\partial\mathbf{T}_{(n)}}=\boldsymbol{I}^0. \tag{4.3.19}$$

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Being defined as the Hessians of $\rho^0\,\psi$ and $\rho^0\,\Phi_{(n)}$ with respect to $\mathbf{E}_{(n)}$ and $\mathbf{T}_{(n)}$, respectively, the tensors $\mathbf{\Lambda}_{(n)}$ and $\mathbf{M}_{(n)}$ possess reciprocal symmetries

$$\Lambda^{(n)}_{ijkl} = \Lambda^{(n)}_{klij}, \quad M^{(n)}_{ijkl} = M^{(n)}_{klij}. \tag{4.3.20}$$

The adiabatic elastic stiffness and compliance tensors are defined as the Hessians of $\rho^0 u$ and $\rho^0 h_{(n)}$ with respect to $\mathbf{E}_{(n)}$ and $\mathbf{T}_{(n)}$, respectively. The relationship with their isothermal counterparts has been discussed by Truesdell and Toupin (1960), McLellan (1980), and Hill (1981).

4.3.2. Specific and Latent Heats

Specific heats at constant strain and stress are defined by

$$C_{E_n} = \theta\,\frac{\partial\bar{\eta}}{\partial\theta}\,, \quad C_{T_n} = \theta\,\frac{\partial\hat{\eta}}{\partial\theta}\,, \tag{4.3.21}$$

where

$$\eta = \bar{\eta}\left(\mathbf{E}_{(n)}, \theta\right) = \hat{\eta}\left(\mathbf{T}_{(n)}, \theta\right). \tag{4.3.22}$$

The latent heats of change of strain and stress are the second-order tensors (e.g., Callen, 1960; Fung, 1965; Kestin, 1979)

$$\boldsymbol{\ell}_{E_n} = \theta\,\frac{\partial\bar{\eta}}{\partial\mathbf{E}_{(n)}}\,, \quad \boldsymbol{\ell}_{T_n} = \theta\,\frac{\partial\hat{\eta}}{\partial\mathbf{T}_{(n)}}\,. \tag{4.3.23}$$

In view of the reciprocal relations

$$\rho^0\,\frac{\partial\bar{\eta}}{\partial\mathbf{E}_{(n)}} = -\frac{\partial\mathbf{T}_{(n)}}{\partial\theta}\,, \quad \rho^0\,\frac{\partial\hat{\eta}}{\partial\mathbf{T}_{(n)}} = -\frac{\partial\mathbf{E}_{(n)}}{\partial\theta}\,, \tag{4.3.24}$$

the latent heats can also be expressed as

$$\boldsymbol{\ell}_{E_n} = -\frac{1}{\rho^0}\,\theta\,\frac{\partial\mathbf{T}_{(n)}}{\partial\theta}\,, \quad \boldsymbol{\ell}_{T_n} = \frac{1}{\rho^0}\,\theta\,\frac{\partial\mathbf{E}_{(n)}}{\partial\theta}\,. \tag{4.3.25}$$

The physical interpretation of the specific and latent heats follows from

$$\mathrm{d}\eta = \frac{\partial\bar{\eta}}{\partial\mathbf{E}_{(n)}} : \mathrm{d}\mathbf{E}_{(n)} + \frac{\partial\bar{\eta}}{\partial\theta}\,\mathrm{d}\theta = \frac{1}{\theta}\left(\boldsymbol{\ell}_{E_n} : \mathrm{d}\mathbf{E}_{(n)} + C_{E_n}\mathrm{d}\theta\right), \tag{4.3.26}$$

$$\mathrm{d}\eta = \frac{\partial\hat{\eta}}{\partial\mathbf{T}_{(n)}} : \mathrm{d}\mathbf{T}_{(n)} + \frac{\partial\bar{\eta}}{\partial\theta}\,\mathrm{d}\theta = \frac{1}{\theta}\left(\boldsymbol{\ell}_{T_n} : \mathrm{d}\mathbf{T}_{(n)} + C_{T_n}\mathrm{d}\theta\right). \tag{4.3.27}$$

Thus, the specific heat at constant strain C_{E_n} (often denoted by C_V) is the heat amount $(\theta\,\mathrm{d}\eta)$ required to increase the temperature of a unit mass for the amount $\mathrm{d}\theta$ at constant strain ($\mathrm{d}\mathbf{E}_{(n)} = 0$). Similar interpretation holds for C_{T_n} (often denoted by C_P). The latent heat $\boldsymbol{\ell}_{E_n}$ is the second-order tensor whose ij component represents the heat amount associated with a

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change of the corresponding strain component by $\mathrm{d}E_{ij}^{(n)}$, at fixed temperature and fixed values of the remaining five strain components. Analogous interpretation applies to $\boldsymbol{\ell}_{T_n}$.

By partial differentiation, we have from Eq. (4.3.22)

$$\frac{\partial \hat{\eta}}{\partial \theta} = \frac{\partial \bar{\eta}}{\partial \theta} + \frac{\partial \bar{\eta}}{\partial \mathbf{E}_{(n)}} : \frac{\partial \mathbf{E}_{(n)}}{\partial \theta} \,. \tag{4.3.28}$$

The multiplication by θ and incorporation of Eqs. (4.3.21)–(4.3.25) gives the relationship

$$C_{T_n} - C_{E_n} = \frac{\rho^0}{\theta}\, \boldsymbol{\ell}_{T_n} : \boldsymbol{\ell}_{E_n}. \tag{4.3.29}$$

Furthermore, since

$$\frac{\partial \hat{\eta}}{\partial \mathbf{T}_{(n)}} = \frac{\partial \bar{\eta}}{\partial \mathbf{E}_{(n)}} : \mathbf{M}_{(n)}, \tag{4.3.30}$$

it follows that

$$\boldsymbol{\ell}_{T_n} = \mathbf{M}_{(n)} : \boldsymbol{\ell}_{E_n}. \tag{4.3.31}$$

When this is inserted into Eq. (4.3.29), we obtain

$$C_{T_n} - C_{E_n} = \frac{\rho^0}{\theta}\, \mathbf{M}_{(n)} : (\boldsymbol{\ell}_{E_n} \otimes \boldsymbol{\ell}_{E_n}). \tag{4.3.32}$$

For positive definite elastic compliance $\mathbf{M}_{(n)}$, it follows that

$$C_{T_n} > C_{E_n}. \tag{4.3.33}$$

The change in temperature caused by adiabatic straining $\mathrm{d}\mathbf{E}_{(n)}$, or adiabatic stressing $\mathrm{d}\mathbf{T}_{(n)}$, is obtained by setting $\mathrm{d}\eta = 0$ in Eqs. (4.3.26) and (4.3.27). This gives

$$\mathrm{d}\theta = -\frac{1}{C_{E_n}}\, \boldsymbol{\ell}_{E_n} : \mathrm{d}\mathbf{E}_{(n)}, \quad \mathrm{d}\theta = -\frac{1}{C_{T_n}}\, \boldsymbol{\ell}_{T_n} : \mathrm{d}\mathbf{T}_{(n)}. \tag{4.3.34}$$

4.4. Irreversible Thermodynamics

For irreversible thermodynamic processes (e.g., processes involving plastic deformation) we shall adopt a thermodynamics with internal state variables (Coleman and Gurtin, 1967; Shapery, 1968; Kestin and Rice, 1970; Rice, 1971,1975). A set of internal (structural) variables is introduced to describe, in some average sense, the essential features of microstructural changes that occurred at the considered place during the deformation process. These variables are denoted by ξ_j $(j = 1, 2, \ldots, n)$. For simplicity, they are assumed to be scalars (extension to include tensorial internal variables is straightforward). Inelastic deformation is considered to be a sequence of constrained

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equilibrium states. These states are created by a conceptual constraining of internal variables at their current values through imposed thermodynamic forces f_j. The thermodynamic forces or constraints are defined such that the power dissipation (temperature times the entropy production rate) due to structural rearrangements can be expressed as

$$\theta\,\gamma = f_j\,\dot{\xi}_j. \tag{4.4.1}$$

The rates of internal variables $\dot{\xi}_j$ are called the fluxes, and the forces f_j are their affinities.

If various equilibrium states are considered, each corresponding to the same set of values of internal variables ξ_j, the neighboring states are related by the usual laws of reversible thermodynamics (thermoelasticity), such as Eqs. (4.3.1) and (4.3.2). If neighboring constrained equilibrium states correspond to different values of internal variables, then

$$\theta\,\dot{\eta} = -\frac{1}{\rho}\,\boldsymbol{\nabla}\cdot\mathbf{q} + r + f_j\,\dot{\xi}_j. \tag{4.4.2}$$

Combining this with the energy equation (4.1.10) gives

$$\dot{u} = \frac{1}{\rho^0}\,\mathbf{T}_{(n)} : \dot{\mathbf{E}}_{(n)} + \theta\,\dot{\eta} - f_j\,\dot{\xi}_j. \tag{4.4.3}$$

Thus, the internal energy is a thermodynamic potential for determining $\mathbf{T}_{(n)}$, θ and f_j, when $\mathbf{E}_{(n)}$, η and ξ_j are considered to be independent state variables. Indeed, after partial differentiation of

$$u = u\left(\mathbf{E}_{(n)}, \eta, \boldsymbol{\xi}\right), \tag{4.4.4}$$

the comparison with Eq. (4.4.3) gives

$$\mathbf{T}_{(n)} = \rho^0\,\frac{\partial u}{\partial \mathbf{E}_{(n)}}, \quad \theta = \frac{\partial u}{\partial \eta}, \quad f_j = \frac{\partial u}{\partial \xi_j}. \tag{4.4.5}$$

The internal variables are collectively denoted by $\boldsymbol{\xi}$. The Helmholtz free energy

$$\psi = \psi\left(\mathbf{E}_{(n)}, \theta, \boldsymbol{\xi}\right) \tag{4.4.6}$$

is a thermodynamic potential for determining $\mathbf{T}_{(n)}$, η and f_j, such that

$$\mathbf{T}_{(n)} = \rho^0\,\frac{\partial \psi}{\partial \mathbf{E}_{(n)}}, \quad \eta = -\frac{\partial \psi}{\partial \theta}, \quad f_j = -\frac{\partial \psi}{\partial \xi_j}. \tag{4.4.7}$$

If the Gibbs energy

$$\phi_{(n)} = \phi_{(n)}\left(\mathbf{T}_{(n)}, \theta, \boldsymbol{\xi}\right) \tag{4.4.8}$$

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is used, we have

$$\mathbf{E}_{(n)} = \rho^0 \frac{\partial \Phi_{(n)}}{\partial \mathbf{T}_{(n)}}, \quad \eta = \frac{\partial \Phi_{(n)}}{\partial \theta}, \quad f_j = \frac{\partial \Phi_{(n)}}{\partial \xi_j}. \tag{4.4.9}$$

Note that in Eq. (4.4.7),

$$f_j = \bar{f}_j \left(\mathbf{E}_{(n)}, \theta, \boldsymbol{\xi}\right), \tag{4.4.10}$$

while in Eq. (4.4.9),

$$f_j = \hat{f}_j \left(\mathbf{T}_{(n)}, \theta, \boldsymbol{\xi}\right), \tag{4.4.11}$$

indicating different functional dependences of the respective arguments. Finally, with the enthalpy

$$h_{(n)} = h_{(n)} \left(\mathbf{T}_{(n)}, \eta, \boldsymbol{\xi}\right) \tag{4.4.12}$$

used as a thermodynamic potential, one has

$$\mathbf{E}_{(n)} = \rho^0 \frac{\partial h_{(n)}}{\partial \mathbf{T}_{(n)}}, \quad \theta = -\frac{\partial h_{(n)}}{\partial \eta}, \quad f_j = \frac{\partial h_{(n)}}{\partial \xi_j}. \tag{4.4.13}$$

By taking appropriate cross-derivatives of the previous expressions, we obtain the Maxwell relations. For example,

$$\begin{aligned} \frac{\partial \mathbf{E}_{(n)} \left(\mathbf{T}_{(n)}, \theta, \boldsymbol{\xi}\right)}{\partial \theta} &= \rho^0 \frac{\partial \hat{\eta} \left(\mathbf{T}_{(n)}, \theta, \boldsymbol{\xi}\right)}{\partial \mathbf{T}_{(n)}}, \\ \frac{\partial \mathbf{T}_{(n)} \left(\mathbf{E}_{(n)}, \theta, \boldsymbol{\xi}\right)}{\partial \theta} &= -\rho^0 \frac{\partial \bar{\eta} \left(\mathbf{E}_{(n)}, \theta, \boldsymbol{\xi}\right)}{\partial \mathbf{E}_{(n)}}, \end{aligned} \tag{4.4.14}$$

and

$$\begin{aligned} \frac{\partial \mathbf{E}_{(n)} \left(\mathbf{T}_{(n)}, \theta, \boldsymbol{\xi}\right)}{\partial \xi_j} &= \rho^0 \frac{\partial \hat{f}_j \left(\mathbf{T}_{(n)}, \theta, \boldsymbol{\xi}\right)}{\partial \mathbf{T}_{(n)}}, \\ \frac{\partial \mathbf{T}_{(n)} \left(\mathbf{E}_{(n)}, \theta, \boldsymbol{\xi}\right)}{\partial \xi_j} &= -\rho^0 \frac{\partial \bar{f}_j \left(\mathbf{E}_{(n)}, \theta, \boldsymbol{\xi}\right)}{\partial \mathbf{E}_{(n)}}. \end{aligned} \tag{4.4.15}$$

4.4.1. Evolution of Internal Variables

The selection of appropriate internal variables is a difficult task, which depends on the material constitution and the type of deformation. Once internal variables are selected, it is necessary to construct evolution equations that govern their change during the deformation. For example, if the fluxes are assumed to be linearly dependent on the affinities, we may write

$$\dot{\xi}_j = \Lambda_{ij} f_j. \tag{4.4.16}$$

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The coefficients obey the Onsager reciprocity relations if $\Lambda_{ij} = \Lambda_{ji}$ (e.g., Ziegler, 1983; Germain, Nguyen, and Suquet, 1983).

For some materials and the range of deformation, it may be appropriate to assume that at a given temperature θ and the pattern of internal rearrangements $\boldsymbol{\xi}$, each flux depends only on its own affinity, i.e.,

$$\dot{\xi}_j = \text{function}\,(f_j, \theta, \boldsymbol{\xi})\,. \tag{4.4.17}$$

The flux dependence on the stress $\mathbf{T}_{(n)}$ comes only through the fact that $f_j = \hat{f}_j\left(\mathbf{T}_{(n)}, \theta, \boldsymbol{\xi}\right)$. This type of evolution equation is often adopted in metal plasticity, where it is assumed that the crystallographic slip on each slip system is governed by the resolved shear stress on that system (or, at the dislocation level, the motion of each dislocation segment is governed by the Peach–Koehler force on that segment; Rice, 1971).

4.4.2. Gibbs Conditions of Thermodynamic Equilibrium

The system is in a thermodynamic equilibrium if its state variables do not spontaneously change with time. Thus, among all neighboring states with the same internal energy (in the sense of variational calculus), the equilibrium state is one with the highest entropy. This follows from the laws of thermodynamics. If no external work was done on the system nor heat was transferred to the system, so that its internal energy is constant, any spontaneous change from equilibrium would be accompanied by an increase in the entropy (by the second law). Since there is no spontaneous change from the equilibrium, among all neighboring states with the same internal energy, entropy is at maximum in the state of thermodynamic equilibrium (Fung, 1965).

Alternatively, among all neighboring states with the same entropy, the equilibrium state is one with the lowest internal energy. This again follows from the laws of thermodynamics. With no external work done, the system can change its internal energy only by the heat exchange, and from Eq. (4.4.3) and the second law, $du = -f_j\, d\xi_j < 0$, where $d\xi_j$ designates a virtual change of ξ_j between the two considered neighboring states at the same entropy. Thus, any disturbance from the thermodynamic equilibrium by a spontaneous heat transfer would decrease the internal energy. Since there is

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no spontaneous heat exchange from the equilibrium, among all neighboring states with the same entropy, internal energy is at minimum in the state of thermodynamic equilibrium. It also follows that among all neighboring states with the same temperature, the Helmholtz free energy $\psi = u - \theta\,\eta$ is at minimum in the state of thermodynamic equilibrium.

4.5. Internal Rearrangements without Explicit State Variables

For some inelastic deformation processes it may be more appropriate to assume that there is a set of variables ξ_j that describe internal rearrangements of the material, but that these are not state variables (in the sense that thermodynamic potentials are not point functions of ξ_j), but instead depend on their path history (Rice, 1971). Denoting symbolically by $\mathcal{H}$ the pattern of internal rearrangements, i.e., the set of internal variables ξ_j including the path history by which they were achieved, the Helmholtz free energy can be written as

$$\psi = \psi\left(\mathbf{E}_{(n)}, \theta, \mathcal{H}\right). \tag{4.5.1}$$

At any given state of deformation, an infinitesimal change of $\mathcal{H}$ is assumed to be fully described by a set of scalar infinitesimals $d\xi_j$, such that the change in ψ due to $\mathrm{d}\mathbf{E}_{(n)}$, $\mathrm{d}\theta$ and $d\xi_j$ is, to first order,

$$\mathrm{d}\psi = \frac{\partial\psi}{\partial\mathbf{E}_{(n)}} : \mathrm{d}\mathbf{E}_{(n)} + \frac{\partial\psi}{\partial\theta}\,\mathrm{d}\theta - f_j\,d\xi_j. \tag{4.5.2}$$

It is not necessary that any variable ξ_j exists such that $d\xi_j$ represents an infinitesimal change of ξ_j (the use of an italic d in $d\xi_j$ is meant to indicate this). The stress response and the entropy are

$$\mathbf{T}_{(n)} = \rho^0\,\frac{\partial\psi}{\partial\mathbf{E}_{(n)}}\,, \quad \eta = -\frac{\partial\psi}{\partial\theta}\,, \tag{4.5.3}$$

evaluated from ψ at fixed values of $\mathcal{H}$. The thermodynamic forces f_j are associated with infinitesimals $d\xi_j$, so that irreversible (inelastic) change of the free energy, due to change in $\mathcal{H}$ alone, is given by

$$\begin{aligned} \mathrm{d}^{\mathrm{i}}\psi &= \psi\left(\mathbf{E}_{(n)}, \theta, \mathcal{H} + d\mathcal{H}\right) - \psi\left(\mathbf{E}_{(n)}, \theta, \mathcal{H}\right) \\ &= -f_j\,d\xi_j = -\bar{f}_j\left(\mathbf{E}_{(n)}, \theta, \mathcal{H}\right) d\xi_j. \end{aligned} \tag{4.5.4}$$

Higher-order terms, such as $(1/2)df_j\,d\xi_j$, associated with an infinitesimal change of f_j during the variations $d\xi_j$, are neglected.

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From Eqs. (4.5.3) and (4.5.4), the inelastic part of the stress increment can be defined by (Hill and Rice, 1973)

$$\begin{aligned} \mathrm{d}^{\mathrm{i}}\mathbf{T}_{(n)} &= \mathbf{T}_{(n)}\left(\mathbf{E}_{(n)}, \theta, \mathcal{H} + d\mathcal{H}\right) - \mathbf{T}_{(n)}\left(\mathbf{E}_{(n)}, \theta, \mathcal{H}\right) \\ &= \rho^0 \frac{\partial}{\partial \mathbf{E}_{(n)}}\left(\mathrm{d}^{\mathrm{i}}\psi\right) = -\rho^0 \frac{\partial \bar{f}_j\left(\mathbf{E}_{(n)}, \theta, \mathcal{H}\right)}{\partial \mathbf{E}_{(n)}}\, d\xi_j. \end{aligned} \tag{4.5.5}$$

The gradient of $\mathrm{d}^{\mathrm{i}}\psi$ with respect to $\mathbf{E}_{(n)}$ is evaluated at fixed values of θ, $\mathcal{H}$ and $d\mathcal{H}$. The entropy change due to infinitesimal change of $\mathcal{H}$ alone is determined from

$$\bar{\mathrm{d}}^{\mathrm{i}}\eta = -\frac{\partial}{\partial \theta}\left(\mathrm{d}^{\mathrm{i}}\psi\right) = \frac{\partial \bar{f}_j\left(\mathbf{E}_{(n)}, \theta, \mathcal{H}\right)}{\partial \theta}\, d\xi_j. \tag{4.5.6}$$

Considering the functions $\mathbf{T}_{(n)}\left(\mathbf{E}_{(n)}, \theta, \mathcal{H}\right)$ and $\bar{\eta}\left(\mathbf{E}_{(n)}, \theta, \mathcal{H}\right)$, we can also write

$$\mathrm{d}^{\mathrm{i}}\mathbf{T}_{(n)} = \mathrm{d}\mathbf{T}_{(n)} - \frac{\partial \mathbf{T}_{(n)}}{\partial \mathbf{E}_{(n)}} : \mathrm{d}\mathbf{E}_{(n)} - \frac{\partial \mathbf{T}_{(n)}}{\partial \theta}\,\mathrm{d}\theta, \tag{4.5.7}$$

$$\bar{\mathrm{d}}^{\mathrm{i}}\eta = \mathrm{d}\eta - \frac{\partial \bar{\eta}}{\partial \mathbf{E}_{(n)}} : \mathrm{d}\mathbf{E}_{(n)} - \frac{\partial \bar{\eta}}{\partial \theta}\,\mathrm{d}\theta. \tag{4.5.8}$$

Dually, the change of Gibbs energy due to $\mathrm{d}\mathbf{T}_{(n)}$, $\mathrm{d}\theta$ and $d\xi_j$ is

$$\mathrm{d}\Phi_{(n)} = \frac{\partial \Phi_{(n)}}{\partial \mathbf{T}_{(n)}} : \mathrm{d}\mathbf{T}_{(n)} + \frac{\partial \Phi_{(n)}}{\partial \theta}\,\mathrm{d}\theta + f_j\, d\xi_j. \tag{4.5.9}$$

The strain response and the entropy are

$$\mathbf{E}_{(n)} = \rho^0 \frac{\partial \Phi_{(n)}}{\partial \mathbf{T}_{(n)}}, \quad \eta = \frac{\partial \Phi_{(n)}}{\partial \theta}, \tag{4.5.10}$$

evaluated from $\Phi_{(n)}$ at fixed values of $\mathcal{H}$. The inelastic change of Gibbs energy, due to change in $\mathcal{H}$ alone, is

$$\begin{aligned} \mathrm{d}^{\mathrm{i}}\Phi_{(n)} &= \Phi_{(n)}\left(\mathbf{T}_{(n)}, \theta, \mathcal{H} + d\mathcal{H}\right) - \Phi_{(n)}\left(\mathbf{T}_{(n)}, \theta, \mathcal{H}\right) \\ &= f_j\, d\xi_j = \hat{f}_j\left(\mathbf{T}_{(n)}, \theta, \mathcal{H}\right) d\xi_j. \end{aligned} \tag{4.5.11}$$

Equations (4.5.4) and (4.5.11) show that

$$\mathrm{d}^{\mathrm{i}}\psi + \mathrm{d}^{\mathrm{i}}\Phi_{(n)} = 0, \tag{4.5.12}$$

within the order of accuracy used in Eqs. (4.5.4) and (4.5.11). The inelastic part of strain increment is

$$\begin{aligned} \mathrm{d}^{\mathrm{i}}\mathbf{E}_{(n)} &= \mathbf{E}_{(n)}\left(\mathbf{T}_{(n)}, \theta, \mathcal{H} + d\mathcal{H}\right) - \mathbf{E}_{(n)}\left(\mathbf{T}_{(n)}, \theta, \mathcal{H}\right) \\ &= \rho^0 \frac{\partial}{\partial \mathbf{T}_{(n)}}\left(\mathrm{d}^{\mathrm{i}}\Phi_{(n)}\right) = \rho^0 \frac{\partial \hat{f}_j\left(\mathbf{T}_{(n)}, \theta, \mathcal{H}\right)}{\partial \mathbf{T}_{(n)}}\, d\xi_j. \end{aligned} \tag{4.5.13}$$

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The change of entropy associated with $d\mathcal{H}$ alone is

$$\hat{\mathrm{d}}^{\mathrm{i}}\eta = \frac{\partial}{\partial\theta}\left(\mathrm{d}^{\mathrm{i}}\Phi_{(n)}\right) = \frac{\partial \hat{f}_j\left(\mathbf{T}_{(n)}, \theta, \mathcal{H}\right)}{\partial\theta}\, d\xi_j, \tag{4.5.14}$$

which is different from the entropy change in Eq. (4.5.6). The difference is discussed in the next section. If the functions $\mathbf{E}_{(n)}\left(\mathbf{T}_{(n)}, \theta, \mathcal{H}\right)$ and $\hat{\eta}\left(\mathbf{E}_{(n)}, \theta, \mathcal{H}\right)$ are considered, we can also write

$$\mathrm{d}^{\mathrm{i}}\mathbf{E}_{(n)} = \mathrm{d}\mathbf{E}_{(n)} - \frac{\partial \mathbf{E}_{(n)}}{\partial \mathbf{T}_{(n)}} : \mathrm{d}\mathbf{T}_{(n)} - \frac{\partial \mathbf{E}_{(n)}}{\partial\theta}\,\mathrm{d}\theta, \tag{4.5.15}$$

$$\hat{\mathrm{d}}^{\mathrm{i}}\eta = \mathrm{d}\eta - \frac{\partial\hat{\eta}}{\partial \mathbf{T}_{(n)}} : \mathrm{d}\mathbf{T}_{(n)} - \frac{\partial\hat{\eta}}{\partial\theta}\,\mathrm{d}\theta. \tag{4.5.16}$$

4.6. Relationship between Inelastic Increments

The relationship between the inelastic increments of stress $\mathrm{d}^{\mathrm{i}}\mathbf{T}_{(n)}$ and strain $\mathrm{d}^{\mathrm{i}}\mathbf{E}_{(n)}$ is easily established from Eqs. (4.5.5) and (4.5.13). Since

$$\mathrm{d}^{\mathrm{i}}\mathbf{T}_{(n)} = -\rho^0\,\frac{\partial \bar{f}_j\left(\mathbf{E}_{(n)}, \theta, \mathcal{H}\right)}{\partial \mathbf{E}_{(n)}}\, d\xi_j = -\rho^0\left[\frac{\partial \hat{f}_j\left(\mathbf{T}_{(n)}, \theta, \mathcal{H}\right)}{\partial \mathbf{T}_{(n)}} : \frac{\partial \mathbf{T}_{(n)}}{\partial \mathbf{E}_{(n)}}\right] d\xi_j, \tag{4.6.1}$$

we have

$$\mathrm{d}^{\mathrm{i}}\mathbf{T}_{(n)} = -\frac{\partial \mathbf{T}_{(n)}}{\partial \mathbf{E}_{(n)}} : \mathrm{d}^{\mathrm{i}}\mathbf{E}_{(n)}. \tag{4.6.2}$$

Therefore,

$$\mathrm{d}^{\mathrm{i}}\mathbf{T}_{(n)} = -\mathbf{\Lambda}_{(n)} : \mathrm{d}^{\mathrm{i}}\mathbf{E}_{(n)}, \quad \mathrm{d}^{\mathrm{i}}\mathbf{E}_{(n)} = -\mathbf{M}_{(n)} : \mathrm{d}^{\mathrm{i}}\mathbf{T}_{(n)}, \tag{4.6.3}$$

where

$$\mathbf{\Lambda}_{(n)} = \frac{\partial \mathbf{T}_{(n)}}{\partial \mathbf{E}_{(n)}} = \rho^0\,\frac{\partial^2\psi\left(\mathbf{E}_{(n)}, \theta, \mathcal{H}\right)}{\partial \mathbf{E}_{(n)} \otimes \partial \mathbf{E}_{(n)}}, \tag{4.6.4}$$

$$\mathbf{M}_{(n)} = \frac{\partial \mathbf{E}_{(n)}}{\partial \mathbf{T}_{(n)}} = \rho^0\,\frac{\partial^2\Phi_{(n)}\left(\mathbf{T}_{(n)}, \theta, \mathcal{H}\right)}{\partial \mathbf{T}_{(n)} \otimes \partial \mathbf{T}_{(n)}} \tag{4.6.5}$$

are the instantaneous elastic stiffness and compliance tensors of the material at a given state of deformation and internal structure.

An alternative proof of Eq. (4.6.3) is instructive. In view of the reciprocal relations such as given by Eqs. (4.4.14), we can rewrite Eqs. (4.5.7) and (4.5.15) as

$$\mathrm{d}^{\mathrm{i}}\mathbf{T}_{(n)} = \mathrm{d}\mathbf{T}_{(n)} - \left(\mathbf{\Lambda}_{(n)} : \mathrm{d}\mathbf{E}_{(n)} - \rho^0\,\frac{\partial\bar{\eta}}{\partial \mathbf{E}_{(n)}}\,\mathrm{d}\theta\right), \tag{4.6.6}$$

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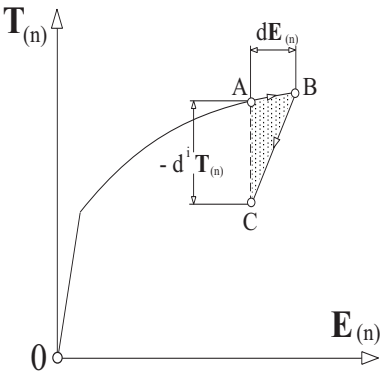

FIGURE 4.3. Schematic representation of an infinitesimal cycle of strain and temperature that involves a change of the pattern of internal rearrangements due to plastic deformation along the segment AB.

$$\mathrm{d}^{\mathrm{i}}\mathbf{E}_{(n)} = \mathrm{d}\mathbf{E}_{(n)} - \left(\mathbf{M}_{(n)} : \mathrm{d}\mathbf{T}_{(n)} + \rho^0 \frac{\partial \hat{\eta}}{\partial \mathbf{T}_{(n)}}\, \mathrm{d}\theta\right). \tag{4.6.7}$$

Taking the inner product of $\mathrm{d}^{\mathrm{i}}\mathbf{E}_{(n)}$ in Eq. (4.6.7) with $\mathbf{\Lambda}_{(n)}$, and having in mind that

$$\mathbf{\Lambda}_{(n)} : \frac{\partial \hat{\eta}}{\partial \mathbf{T}_{(n)}} = \frac{\partial \bar{\eta}}{\partial \mathbf{E}_{(n)}}\,, \tag{4.6.8}$$

yields Eq. (4.6.3).

The relationship between $\hat{\mathrm{d}}^{\mathrm{i}}\eta$ and $\bar{\mathrm{d}}^{\mathrm{i}}\eta$ can also be established. Since by partial differentiation

$$\frac{\partial \hat{f}_j}{\partial \theta} = \frac{\partial \bar{f}_j}{\partial \theta} + \frac{\partial \bar{f}_j}{\partial \mathbf{E}_{(n)}} : \frac{\partial \mathbf{E}_{(n)}}{\partial \theta}\,, \quad \frac{\partial \bar{f}_j}{\partial \theta} = \frac{\partial \hat{f}_j}{\partial \theta} + \frac{\partial \hat{f}_j}{\partial \mathbf{T}_{(n)}} : \frac{\partial \mathbf{T}_{(n)}}{\partial \theta}\,, \tag{4.6.9}$$

and in view of reciprocal relations, Eqs. (4.5.6) and (4.5.14) give

$$\hat{\mathrm{d}}^{\mathrm{i}}\eta = \bar{\mathrm{d}}^{\mathrm{i}}\eta + \frac{\partial \bar{\eta}}{\partial \mathbf{E}_{(n)}}\, \mathrm{d}^{\mathrm{i}}\mathbf{E}_{(n)}, \quad \bar{\mathrm{d}}^{\mathrm{i}}\eta = \hat{\mathrm{d}}^{\mathrm{i}}\eta + \frac{\partial \hat{\eta}}{\partial \mathbf{T}_{(n)}}\, \mathrm{d}^{\mathrm{i}}\mathbf{T}_{(n)}. \tag{4.6.10}$$

Alternatively, one can use Eqs. (4.5.8) and (4.5.16), and the connections

$$\frac{\partial \hat{\eta}}{\partial \theta} = \frac{\partial \bar{\eta}}{\partial \theta} + \frac{\partial \bar{\eta}}{\partial \mathbf{E}_{(n)}} : \frac{\partial \mathbf{E}_{(n)}}{\partial \theta}\,, \quad \frac{\partial \bar{\eta}}{\partial \theta} = \frac{\partial \hat{\eta}}{\partial \theta} + \frac{\partial \hat{\eta}}{\partial \mathbf{T}_{(n)}} : \frac{\partial \mathbf{T}_{(n)}}{\partial \theta}\,. \tag{4.6.11}$$

In a rate-independent elastoplastic material, the only way to vary $\mathcal{H}$ but not $\mathbf{E}_{(n)}$ and θ is to perform a cycle of $\mathbf{E}_{(n)}$ and θ that includes $d\mathcal{H}$. Consider a cycle that starts at the state $A\left(\mathbf{E}_{(n)}, \theta, \mathcal{H}\right)$, goes through the state $B\left(\mathbf{E}_{(n)} + \mathrm{d}\mathbf{E}_{(n)}, \theta + \mathrm{d}\theta, \mathcal{H} + d\mathcal{H}\right)$, and ends at the state $C\left(\mathbf{E}_{(n)}, \theta, \mathcal{H} + d\mathcal{H}\right)$.

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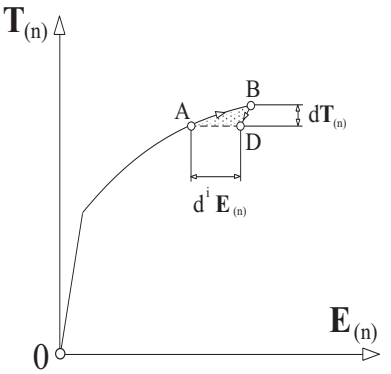

FIGURE 4.4. Schematic representation of an infinitesimal cycle of stress and temperature that involves a change of the pattern of internal rearrangements due to plastic deformation along the segment AB.

The cycle is shown in Fig. 4.3. If the stress and entropy at A were $\mathbf{T}_{(n)}$ and η, in the state B they are $\mathbf{T}_{(n)} + \mathrm{d}\mathbf{T}_{(n)}$ and $\eta + \mathrm{d}\eta$. The change of entropy during the loading from A to B caused by $d\mathcal{H}$ is such that

$$\theta(\mathrm{d}\eta)^{\mathrm{i}} = f_j \, d\xi_j, \tag{4.6.12}$$

by Eq. (4.4.1) for the entropy production rate. After strain and temperature are returned to their values at the beginning of the cycle by elastic unloading, the state C is reached. The stress there is $\mathbf{T}_{(n)} + \mathrm{d}^{\mathrm{i}}\mathbf{T}_{(n)}$, and the entropy is $\eta + \bar{\mathrm{d}}^{\mathrm{i}}\eta$. The stress difference $\mathrm{d}^{\mathrm{i}}\mathbf{T}_{(n)}$ is the stress decrement after the cycle of strain and temperature that includes $d\mathcal{H}$. The entropy difference $\bar{\mathrm{d}}^{\mathrm{i}}\eta$ is different from $(\mathrm{d}\eta)^{\mathrm{i}}$ in Eq. (4.6.12), because the heat input during the unloading from B to C, required to return the temperature to its value before the cycle, is in general different than the heat input during the loading path from A to B.

Alternatively, consider a stress/temperature cycle $A \rightarrow B \rightarrow D$ (Fig. 4.4). In the state D the stress and temperature are returned to their values before the cycle, so that $A\left(\mathbf{T}_{(n)}, \theta, \mathcal{H}\right)$, $B\left(\mathbf{T}_{(n)} + \mathrm{d}\mathbf{T}_{(n)}, \theta + \mathrm{d}\theta, \mathcal{H} + d\mathcal{H}\right)$, and $D\left(\mathbf{T}_{(n)}, \theta, \mathcal{H} + d\mathcal{H}\right)$. The strain and entropy in the state A are $\mathbf{E}_{(n)}$ and η. In the state B they are $\mathbf{E}_{(n)} + \mathrm{d}\mathbf{E}_{(n)}$ and $\eta + \mathrm{d}\eta$. The entropy change from A to B caused by $d\mathcal{H}$ is as in Eq. (4.6.12). After stress and temperature are returned to their values before the cycle by elastic unloading, the state

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D is reached, where the strain is $\mathbf{E}_{(n)} + \mathrm{d}^{\mathrm{i}}\mathbf{E}_{(n)}$, and the entropy $\eta + \hat{\mathrm{d}}^{\mathrm{i}}\eta$. The strain difference $\mathrm{d}^{\mathrm{i}}\mathbf{E}_{(n)}$ is the strain increment after the cycle of stress and temperature that includes $d\mathcal{H}$. The entropy difference $\hat{\mathrm{d}}^{\mathrm{i}}\eta$ is different from $(\mathrm{d}\eta)^{\mathrm{i}}$, because the heat input along the unloading path from B to D is in general different than along the loading path from A to B. The entropy differences $\hat{\mathrm{d}}^{\mathrm{i}}\eta$ and $\bar{\mathrm{d}}^{\mathrm{i}}\eta$ are also different because there is a heat exchange along the unloading portion of the path between D and C, which makes the entropies in the states C and D in general different.

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