21 THERMODYNAMIC FRAMEWORK FOR CONSTITUTIVE MODELING

In this chapter, we will establish the framework for deriving constitutive models that is provided by thermodynamics. In the next chapters, we shall then take full advantage of this framework and demonstrate that we may retrieve a number of theories discussed previously and also establish a number of new constitutive models.

Let us first recall the first and second laws. From (20.21), the first law in its local form is given by

$$\boxed{\rho \dot{u} = \dot{\varepsilon}_{ij}\sigma_{ij} + r - q_{i,i} \quad \textit{first law}}$$

(21.1)

where u is the specific internal energy, q_i is the heat flux vector and r is the heat supply per unit time and unit volume. Moreover, the internal energy u is a state function, i.e. a function that only depends on the current values of the state variables. The state variables are variables that characterize the state of the material and, as previously discussed in Section 20.3, it is not trivial to identify these variables; we shall later return to this important point.

The second law expressed in terms of the local form of the Clausius-Duhem inequality is given by (20.68), i.e.

$$\boxed{\rho \dot{s} - \frac{r}{\theta} + \frac{q_{i,i}}{\theta} - \frac{q_i \theta_{,i}}{\theta^2} \geq 0 \quad \begin{array}{l} \textit{second law} \\ = \textit{Clausius-Duhem inequality} \end{array}}$$

(21.2)

where s is the specific entropy and θ is the absolute temperature. The entropy s is a state function.

The term $q_{i,i} - r$ appearing in (21.2) can be eliminated by means of the first law (21.1) and the Clausius-Duhem inequality then turns into what is called the *dissipation inequality*

> *Dissipation inequality in terms of internal energy u*
>
> $\gamma \geq 0$
>
> *where*
>
> $\gamma \equiv \theta\rho\dot{s} - \rho\dot{u} + \dot{\varepsilon}_{ij}\sigma_{ij} - \dfrac{q_i\theta_{,i}}{\theta}$

(21.3)

where it is emphasized that the internal energy u enters the dissipation inequality. It is recalled that the inequality sign holds for irreversible processes whereas the equality sign holds for reversible processes. The quantity γ defined by (21.3) has the dimension of energy rate per unit volume, i.e. [J/s m^3], and it is zero for reversible processes and positive for irreversible processes; this suggests the terminology of γ being the *dissipation*. Moreover, as emphasized in relation to (20.68), any constitutive model that fulfills (21.3) fulfills all formal requirements enforced by thermodynamics.

In addition to the state functions u and s, it turns out to be convenient to introduce another state function proposed by Helmholtz in 1882, namely *Helmholtz' free energy ψ* per unit mass defined by

> *Helmholtz' free energy*
>
> $\psi = u - s\theta$
>
> ψ *is a state function*

(21.4)

It is evident that the absolute temperature θ can be considered as a state variable, since it certainly is a quantity that - together with other quantities - characterizes the state of the body, cf. definition (20.3). Moreover, since u and s are state functions, it follows from the definition of ψ that it is a state function, cf. (20.5).

From (21.3) and (21.4), we then obtain the following alternative formulation of the dissipation inequality

> *Dissipation inequality in terms of free energy ψ*
>
> $\gamma \geq 0$
>
> *where*
>
> $\gamma \equiv -\rho(\dot{\psi} + s\dot{\theta}) + \dot{\varepsilon}_{ij}\sigma_{ij} - \dfrac{q_i\theta_{,i}}{\theta}$

(21.5)

21.1 Thermo-elastic materials

In Section 20.3, we introduced the concept of state variables and it was noticed that the choice of state variables is not trivial; indeed it depends upon what we

are interested in.

In order to approach this problem, it seems reasonable to consider the simplest possible situation, which certainly is that of a reversible process. In Section 20.6, we found that a reversible process requires infinitely small temperature gradients. Assume therefore that the temperature does not vary over the body and that a reversible process occurs. Intuitively, we would expect that the material then is to respond in an elastic manner and, indeed, our expectations are fulfilled as will appear shortly. Since $\gamma = 0$ and $\theta_{,i} = 0$, (21.5) reduces to

$$\dot{\psi} = -s\dot{\theta} + \frac{1}{\rho}\sigma_{ij}\dot{\varepsilon}_{ij} \tag{21.6}$$

Since the free energy ψ is a state function, the expression above suggests that

$$\boxed{\psi = \psi(\theta, \varepsilon_{ij}) \qquad \textit{thermo-elastic material}} \tag{21.7}$$

Indeed, we obtain

$$\dot{\psi} = \frac{\partial \psi}{\partial \theta}\dot{\theta} + \frac{\partial \psi}{\partial \varepsilon_{ij}}\dot{\varepsilon}_{ij} \tag{21.8}$$

and a comparison with (21.6) supports expression (21.7). Moreover, subtracting (21.8) from (21.6) gives

$$0 = (-s - \frac{\partial \psi}{\partial \theta})\dot{\theta} + (\frac{1}{\rho}\sigma_{ij} - \frac{\partial \psi}{\partial \varepsilon_{ij}})\dot{\varepsilon}_{ij} \tag{21.9}$$

Since we can control the spatially uniform temperature and the strains independently, it is possible to assign arbitrary values to $\dot{\theta}$ and $\dot{\varepsilon}_{ij}$. Expression (21.9) then implies

$$\boxed{s = -\frac{\partial \psi}{\partial \theta}; \quad \sigma_{ij} = \rho\frac{\partial \psi}{\partial \varepsilon_{ij}}} \tag{21.10}$$

Since the entropy s is obtained from ψ by differentiation with respect to the temperature θ, use is made of the phrase that ψ serves as a *potential function* for the entropy. Likewise, the stresses are obtained from ψ by differentiation with respect to the strains and the free energy ψ then serves as a potential function for the stresses.

We found that the quantities θ and ε_{ij} appeared in a natural manner as state variables for the free energy ψ and they are therefore the *natural* or *canonical state variables* for ψ when considering a thermo-elastic material. We might also mention that as both the temperature θ and the strains ε_{ij} can be measured, i.e. observed, θ and ε_{ij} are examples of *observable state variables*; we shall later encounter state variables that are not observable.

To demonstrate that (21.7) and thereby (21.10) define the response of a thermo-elastic material - as already anticipated - let us consider the special case

where $\dot{\theta} = 0$, that is, the temperature does not change with time (we have previously assumed that the temperature does not change with position, i.e. $\theta_{,i} = 0$). Since θ is constant, (21.7) reduces to $\psi = \psi(\theta = \text{constant}, \varepsilon_{ij})$. Moreover, writing $\rho\psi(\theta = \text{constant}, \varepsilon_{ij}) = W(\varepsilon_{ij})$ and observing that the mass density ρ for small strains can be considered as constant, it follows from (21.10) that $\sigma_{ij} = \partial W / \partial\varepsilon_{ij}$. A comparison with (4.5) and (4.8) reveals that we then have identified the strain energy W per unit volume, i.e. we have identified a situation where hyper-elasticity occurs. In conclusion

$$
\boxed{
\begin{array}{l}
\textit{For constant temperature} \\[4pt]
\rho\psi(\theta = constant, \varepsilon_{ij}) = W(\varepsilon_{ij}) = strain\ energy \\[8pt]
\sigma_{ij} = \dfrac{\partial W}{\partial \varepsilon_{ij}} \quad\ \ hyper\text{-}elasticity
\end{array}
}
\tag{21.11}
$$

The requirement of constant temperature is identical with isothermal conditions. Therefore, during isothermal conditions $\rho\psi$ becomes equal to the strain energy W. If the surroundings are kept at a constant temperature, isothermal conditions can be achieved, if the material is loaded so slowly that any temperature difference between the material and the surroundings is allowed to disappear.

The strain energy for elastic materials can be recovered and perform mechanical work. It follows that for isothermal conditions, Helmholtz' free energy ψ is the amount of energy that is 'free' to perform mechanical work.

Let us next consider the case where the temperature is allowed to vary, i.e. $\psi = \psi(\theta, \varepsilon)$. It is expected that this formulation would turn into thermoelasticity and, indeed, this is the situation. Let us expand the free energy $\psi(\theta, \varepsilon_{ij})$ in a Taylor series about the reference state where $\theta = \theta_o$ and $\varepsilon_{ij} = 0$, i.e.

$$
\psi(\theta, \varepsilon_{ij}) = \psi_o + \left(\frac{\partial\psi}{\partial\varepsilon_{ij}}\right)_o \varepsilon_{ij} + \left(\frac{\partial\psi}{\partial\theta}\right)_o (\theta - \theta_o) + \frac{1}{2}\varepsilon_{ij}\left(\frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial\varepsilon_{kl}}\right)_o \varepsilon_{kl}
$$

$$
+ \frac{1}{2}\left(\frac{\partial^2\psi}{\partial\theta^2}\right)_o (\theta - \theta_o)^2 + \left(\frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial\theta}\right)_o (\theta - \theta_o)\varepsilon_{ij}
\tag{21.12}
$$

where the notation $(\ )_o$ indicates that the quantity in question is evaluated at the reference state where $\theta = \theta_o$ and $\varepsilon_{ij} = 0$. From (21.10) and (21.12), it then follows that

$$
\sigma_{ij} = \rho\frac{\partial\psi}{\partial\varepsilon_{ij}} = \rho\left(\frac{\partial\psi}{\partial\varepsilon_{ij}}\right)_o + \rho\left(\frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial\varepsilon_{kl}}\right)_o \varepsilon_{kl} + \rho\left(\frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial\theta}\right)_o (\theta - \theta_o)
$$

Let us assume that no stresses exist at the reference state. It follows that $(\partial\psi/\partial\varepsilon_{ij})_o = 0$ and the expression above reduces to

$$
\sigma_{ij} = D_{ijkl}\varepsilon_{kl} - \beta_{ij}(\theta - \theta_o)
\tag{21.13}
$$

where D_{ijkl} and β_{ij} are defined by

$$D_{ijkl} = \rho\left(\frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial\varepsilon_{kl}}\right)_o ; \quad \beta_{ij} = -\rho\left(\frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial\theta}\right)_o \tag{21.14}$$

Since the elastic stiffness tensor D_{ijkl} is positive definite, cf. (4.24) and (4.25), it is always possible to determine the quantity α_{ij} from the equation

$$D_{ijkl}\alpha_{kl} = \beta_{ij} \tag{21.15}$$

and with C_{ijkl} being the elastic flexibility tensor, we obtain

$$\alpha_{ij} = C_{ijkl}\beta_{kl}$$

From (21.13) and (21.15) follow

$$\sigma_{ij} = D_{ijkl}(\varepsilon_{kl} - \varepsilon_{kl}^o) \quad \text{where} \quad \varepsilon_{ij}^o = \alpha_{ij}(\theta - \theta_o) \tag{21.16}$$

A comparison with (4.62) and (4.64) reveals that we have recovered a description of thermo-elasticity, where ε_{ij}^o becomes the *thermal strains* and α_{ij} the *tensor of thermal expansion coefficients*. If the material is isotropic, then the tensor α_{ij} reduces to $\alpha\delta_{ij}$, where α is the *thermal expansion coefficient*.

According to (21.14), both D_{ijkl} and α_{ij} appearing in (21.16) are constant quantities, but it is easy to obtain a formulation where they may depend upon the temperature. For this purpose and recalling that the term $(\partial\psi/\partial\varepsilon_{ij})_o$ is zero, we may generalize (21.12) and with evident notation postulate

$$\boxed{\begin{aligned} \rho\psi(\theta,\varepsilon_{ij}) &= C + A(\theta)(\theta - \theta_o) + \tfrac{1}{2}B(\theta)(\theta - \theta_o)^2 \\ &+ \tfrac{1}{2}\varepsilon_{ij}D_{ijkl}(\theta)\varepsilon_{kl} - \beta_{ij}(\theta)(\theta - \theta_o)\varepsilon_{ij} \end{aligned}} \tag{21.17}$$

From (21.10), it then follows that

$$\boxed{\begin{aligned} &\textit{Thermo-elasticity with temperature-dependent properties} \\ &\sigma_{ij} = D_{ijkl}(\theta)(\varepsilon_{kl} - \varepsilon_{kl}^o) \quad \text{where} \quad \varepsilon_{ij}^o = \alpha_{ij}(\theta)(\theta - \theta_o) \\ &or \\ &\sigma_{ij} = D_{ijkl}(\theta)\varepsilon_{kl}^e \quad \text{where} \quad \varepsilon_{ij}^e = \varepsilon_{ij} - \varepsilon_{ij}^o \end{aligned}} \tag{21.18}$$

Moreover

$$\boxed{D_{ijkl} = \rho\frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial\varepsilon_{kl}} \quad and \quad \alpha_{ij} = C_{ijkl}\beta_{kl}} \tag{21.19}$$

We have found that thermo-elasticity follows from Helmholtz' free energy taken in the form of $\psi = \psi(\theta,\varepsilon_{ij})$. However, it turns out to be possible to obtain another format for elasticity by specifying the internal energy u. For that purpose, we return to definition (21.4), which after differentiation, becomes

$$\dot{u} = \dot{\psi} + \dot{s}\theta + s\dot{\theta}$$

With (21.4) and (21.6), it follows that

$$\dot{u} = \theta\dot{s} + \frac{1}{\rho}\sigma_{ij}\dot{\varepsilon}_{ij} \tag{21.20}$$

Since the internal energy u is a state function, this expression leads to

$$\boxed{u = u(s, \varepsilon_{ij}) \qquad elasticity} \tag{21.21}$$

Differentiation and comparison with (21.20) yield

$$\boxed{\theta = \frac{\partial u}{\partial s}; \qquad \sigma_{ij} = \rho\frac{\partial u}{\partial \varepsilon_{ij}}} \tag{21.22}$$

In accordance with the terminology discussed previously and since the temperature is obtained from u by differentiation with respect to the entropy, u serves as a potential function for the temperature θ; likewise, u serves as a potential function for the stresses.

When considering the internal energy u, we found that the quantities s and ε_{ij} appeared in natural manner as the state variables and they are therefore the natural or canonical state variables for u when considering an elastic material. While the state variable ε_{ij} can be measured, i.e. ε_{ij} is an observable state variable, we cannot determine the entropy s directly just by making some kind of measurement and s is therefore an example of a state variable that is not observable.

Another interesting point is that u is the *Legendre transformation* of ψ and, likewise, ψ is the Legendre transformation of u. To illustrate the last property, we accept (21.21) and (21.22). Instead of having s and ε_{ij} as the state variables, we can - without knowing the explicit form of $u(s, \varepsilon_{ij})$ - switch to another description where θ and ε_{ij} serve as state variables. For this purpose, the free energy ψ is defined by (21.4). Differentiation gives

$$\dot{\psi} = \dot{u} - \dot{s}\theta - s\dot{\theta}$$

and use of (21.21) and (21.22) results in

$$\dot{\psi} = -s\dot{\theta} + \frac{1}{\rho}\sigma_{ij}\dot{\varepsilon}_{ij}$$

which, as before, implies $\psi = \psi(\theta, \varepsilon_{ij})$ and thereby also relations (21.10). We may also refer to the similar discussion relating to (4.11).

Two additional state functions are often introduced in thermodynamics. If, instead of the description $u = u(s, \varepsilon_{ij})$, we want a formulation with the state variables s and σ_{ij}, the *enthalpy* h is defined by the Legendre transformation $h = u - \frac{1}{\rho}\sigma_{ij}\varepsilon_{ij}$ and it follows that $h = h(s, \sigma_{ij})$. Likewise, if, instead of $\psi = \psi(\theta, \varepsilon_{ij})$, we want a description with the state variables θ and σ_{ij}, *Gibb's free*

energy ϕ is defined by the Legendre transformation $\phi = \psi - \frac{1}{\rho}\sigma_{ij}\varepsilon_{ij}$ and it follows that $\phi = \phi(\theta, \sigma_{ij})$. Indeed it is easy to show that Gibb's free energy ϕ for θ = constant is equal to $-C$ where C is the complementary energy defined by (4.11). However, for constitutive modeling it suffices in most cases to deal with the state functions already introduced, namely: the entropy s, the internal energy u and Helmholtz' free energy ψ.

It is evident that (21.7) and (21.21) are different descriptions of the same phenomena and just as we have shown that (21.7) corresponds to elasticity, (21.21) must also provide a description of elasticity. To illustrate this point, we recall that a reversible process is considered. If, in addition, it is assumed that the heat supply r is zero and that no temperature gradients exist and thereby that the heat flux vector q_i is zero, then (21.2) implies that $\rho\dot{s} = 0$, i.e. the entropy is constant; this is called an *isentropic process*. From (21.21) and (21.22), it then appears that

$$\boxed{\begin{array}{l} \textit{For constant entropy} \\[4pt] \rho u(s = constant, \varepsilon_{ij}) = W(\varepsilon_{ij}) = \textit{strain energy} \\[6pt] \sigma_{ij} = \dfrac{\partial W}{\partial \varepsilon_{ij}} \quad \textit{hyper-elasticity} \end{array}} \qquad (21.23)$$

It follows that we have identified another situation where hyper-elasticity occurs. The conditions $r = 0$ and $\theta_{,i} = 0$ are equivalent to an adiabatic process (no heat input); this situation can be achieved if the material is loaded very quickly since heat exchange with the surroundings then has no time to take place. Under these conditions, (21.23) shows that a hyper-elastic response can occur. On the other hand, if isothermal conditions are considered, (21.11) shows that a hyper-elastic response can occur. Isothermal conditions can be achieved in practice if the material is loaded very slowly.

To obtain the result that (21.7) or (21.21) describes an elastic behavior, it was assumed that no temperature gradients exist and that a reversible process occurs. Suppose now that temperature gradients may exist and therefore that an irreversible process is allowed. Also for these conditions, we maintain the definitions of elasticity given by (21.7) and (21.21). If (21.7) is adopted and advantage is taken of (21.10), then the dissipation inequality (21.5) reduces to $\gamma = -q_i\theta_{,i}/\theta \geq 0$. Likewise, if (21.21) is adopted and advantage is taken of (21.22), the dissipation inequality (21.3) also reduces to $\gamma = -q_i\theta_{,i}/\theta \geq 0$. It is concluded that

$$\boxed{\begin{array}{l} \textit{For elastic materials, i.e. } \psi = \psi(\theta, \varepsilon_{ij}) \textit{ or } u = u(s, \varepsilon_{ij}), \\[4pt] \textit{the dissipation inequality reduces to} \\[6pt] \gamma = -\dfrac{q_i\theta_{,i}}{\theta} \geq 0 \end{array}} \qquad (21.24)$$

This inequality is often termed *Fourier's inequality*. Since the temperature $\theta > 0$, we obtain that the only restriction on elasticity provided by the second law

is $q_i \theta_{,i} \leq 0$. This restriction simply states that the scalar product of the heat flux vector q_i and the temperature gradient $\theta_{,i}$ is non-positive, i.e. heat flows from warm regions towards cold regions. The statement (21.24) also shows that when elastic materials are considered, the only source to irreversibility is the existence of temperature gradients.

We have found that both $\psi = \psi(\theta, \varepsilon_{ij})$ and $u = u(s, \varepsilon_{ij})$ provide descriptions of elasticity; however, whereas the temperature θ is an observable state variable that we can control and, in practice, assign arbitrary values, this is not the case for the state variable s, which is not observable. This means that we cannot, in practice, create experimental conditions by which the entropy s is assigned arbitrary values. Therefore, even though $\psi = \psi(\theta, \varepsilon_{ij})$ and $u = u(s, \varepsilon_{ij})$, in principle, provide equivalent descriptions of elasticity, it is evident that the format $\psi = \psi(\theta, \varepsilon_{ij})$ is the most convenient. It is no surprise that also for inelastic behavior, a description in terms of the free energy ψ is the most advantageous format. We conclude that

> A description in terms of Helmholtz' free energy ψ is more convenient than a description in terms of the internal energy u

21.2   Inelastic materials - Internal variables

After the detailed discussion of thermo-elasticity and the state variables that characterize thermo-elasticity, it is timely to consider the description of inelastic materials. Let us first note that, in general, we can write

$$\boxed{\varepsilon_{ij} = \varepsilon_{ij}^e + \varepsilon_{ij}^{ie} + \varepsilon_{ij}^o}$$

where ε_{ij}^e are the elastic strains, ε_{ij}^{ie} the *inelastic strains* and ε_{ij}^o are the thermal strains; the inelastic strains may be due to plasticity, creep, viscoplasticity, etc. Moreover, the elastic strains ε_{ij}^e are defined by Hooke's law i.e. $\varepsilon_{ij}^e = C_{ijkl}\sigma_{kl}$ where C_{ijkl} is the elastic flexibility tensor.

When choosing the state variables for inelastic materials, it is evident that the strains must enter in some form. To approach this problem, it is observed that there are cases where an arbitrary inelastic material responds in an elastic manner; for plastic materials this occurs during unloading and for time-dependent materials an elastic response follows if the loading rate is sufficiently fast.

As an example, consider the hardening plasticity response shown in Fig. 21.1. An elastic behavior occurs between point O and point A and an elastic behavior is also present during unloading between point B and point C. If the elasticity between O and A is to be described, the free energy ψ is taken as $\psi = \psi(\theta, \varepsilon_{ij})$, cf. (21.7). However, if the elasticity between B and C is to be described, it follows from Fig. 21.1 that we should now take ψ as $\psi = \psi(\theta, \varepsilon_{ij} - \varepsilon_{ij}^{ie})$ where $\varepsilon_{ij}^{ie} = \varepsilon_{ij}^p$.
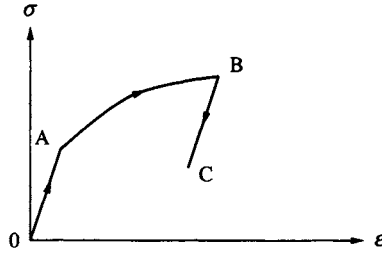
Figure 21.1: Modeling of elastic behavior for hardening plasticity.

This example motivates that while the total strain tensor ε_{ij} is a proper state variable for elasticity, the corresponding state variable for inelastic behavior is $\varepsilon_{ij} - \varepsilon_{ij}^{ie}$, i.e. $\psi = \psi(\theta, \varepsilon_{ij} - \varepsilon_{ij}^{ie})$. It is not surprising that this format is not sufficiently general to model all types of inelasticity and we therefore introduce an additional set of state variables, κ_α, where $\alpha = 1, 2, \cdots$, that characterize the inelastic material. We are then led to the following format

$$\boxed{\psi = \psi(\theta, \varepsilon_{ij} - \varepsilon_{ij}^{ie}, \kappa_\alpha) \quad \textit{inelastic material}} \tag{21.25}$$

The additional set of state variables given by κ_α is also called *internal variables* or *hidden variables*, i.e.

$$\boxed{\kappa_\alpha = \textit{state variables=internal variables= hidden variables}}$$

We do not know the number of internal variables beforehand, and, as indicated, we may have one, two or more internal variables. Moreover, at this point we do not know the type of internal variables, which may be scalars or higher-order tensors. However, we collect all these internal variables into the notation κ_α and use the following definition

$$\boxed{\kappa_\alpha = \textit{internal variables } (\alpha = 1, 2, \dots)}$$

This discussion of internal variables is completely similar to that encountered in plasticity theory, cf. the discussion relating to (9.10) and (9.11).

Of the state variables introduced, the only quantities we can measure directly, without making use of our imagination of how materials behave, are the observable state variables θ and ε_{ij}. Therefore, the internal variables κ_α (and, in principle, also ε_{ij}^{ie}) are not observable state variables and this is the reason for the somewhat peculiar terminology of 'hidden' variables. We will follow the trend in the literature and exclusively use the word internal variables since the terminology of 'hidden' variables may act as a psychological block to acceptance. As an example of an internal variable, we may take the effective plastic strain.

Indeed our choice of internal variables influences the type of inelasticity we can simulate. This aspect will be illustrated in detail in the following chapters.

If we adopt the definition

> *The internal variables κ_α and ε_{ij}^{ie}*
> *change only during inelastic response*

then it is evident that (21.25) is able to describe the situation where the inelastic material responds in an elastic manner, cf. for instance Fig. 21.1. That the format (21.25), in fact, enables us to simulate plasticity, creep, viscoplasticity, etc. is illustrated in the following chapters.

It is a characteristic feature of inelasticity that the material response depends on the previous load history; in that sense the inelastic material possesses a memory. The format (21.25) implies that the load history is monitored through the internal variables κ_α and ε_{ij}^{ie} and this concept is referred to as the *internal variable concept*. This approach was introduced by Onsager (1931a,b), Meixner (1953), Biot (1954) and Ziegler (1958) and later generalized by Coleman and Gurtin (1967) and further explored by Valanis (1968), Lubliner (1972) and Halphen and Nguyen (1975) as well as many others. The review articles by Germain *et al.* (1983) and Reddy and Martin (1994) provide a detailed discussion of the internal variable formalism and contain a number of relevant references.

In this exposition, we will adopt the internal variable approach and only mention that there exists another strategy to represent the memory of the material, the so-called *functional approach*. We may recall that a *functional* can be viewed as a function of a function. As an example, consider the quantity I defined by

$$I(y) = \int_a^b F(x, y(x))dx$$

where $F(x, y)$ and $y = y(x)$ are known functions. Just like the function $y = y(x)$ can be thought of as a rule which assigns a single number $y(x)$ to every number x, then $I(y)$ as defined above assigns a single number $I(y)$ to every function y; in that sense, the quantity $I(y)$ can be viewed as a function of a function and the quantity $I(y)$ is an example of a functional.

For illustration purposes only, assume that we have chosen the functions a and b_{ij}. Consider then the expression

$$\psi = \int_{-\infty}^t \frac{\partial\theta(t')}{\partial t'}a(t - t')dt' + \int_{-\infty}^t \frac{\partial\varepsilon_{ij}(t')}{\partial t'}b_{ij}(t - t')dt'$$

where t denotes the present time and t' is an integration variable. Then the free energy ψ would be a functional of θ and ε_{ij} and ψ would then depend, not only on the present values of θ and ε_{ij}, but also on the history of θ and ε_{ij}.

With this illustration in mind, let us assume that the free energy ψ is given by

$$\boxed{\psi = \mathcal{F}(\theta, \varepsilon_{ij}) \quad \textit{functional approach}} \tag{21.26}$$

where $\mathcal{F}(\theta, \varepsilon_{ij})$ denotes a functional of θ and ε_{ij} i.e. it mimics the entire history of θ and ε_{ij}. The format (21.26) then implies that the free energy ψ not only depends on the current values of θ and ε_{ij}, but also on their histories.

The functional approach illustrated in principle by (21.26) was proposed by Coleman and Noll (1960, 1961) and further explored by Coleman (1964) and it has been used successfully for modeling of viscoelasticity. In general however, when considering, for instance, elasto-plasticity and damage mechanics, the internal variable concept seems to be much more fruitful and following the general trend in the literature, we will here exclusively deal with the internal variable concept.

With these remarks, let us return to the general expression for the free energy ψ given by (21.25), i.e.

$$\psi = \psi(\theta, \varepsilon_{ij} - \varepsilon_{ij}^{ie}, \kappa_\alpha) \tag{21.27}$$

Since θ, $\varepsilon_{ij} - \varepsilon_{ij}^{ie}$ and κ_α are assumed to be the state variables that determine the state, it is only a small restriction to also assume that the stress state σ_{ij} and the entropy s depend on the same state variables, i.e.

$$\sigma_{ij} = \sigma_{ij}(\theta, \varepsilon_{ij} - \varepsilon_{ij}^{ie}, \kappa_\alpha); \qquad s = s(\theta, \varepsilon_{ij} - \varepsilon_{ij}^{ie}, \kappa_\alpha) \tag{21.28}$$

These expressions also represent another viewpoint, namely the *axiom of equipresence*. It states that at the onset, all relations for the material are considered as relations that contain the same list of variables until the contrary is deduced, see for instance Eringen (1975a) and Truesdell and Toupin (1960). However, even though the word 'axiom' is commonly used in the literature, it seems to us to be somewhat too strong a statement and to quote Eringen (1975a) "it is rather a precautionary measure that is valid in all proper scientific methods".

Insertion of (21.27) into the dissipation inequality (21.5) gives

$$\gamma \equiv (\sigma_{ij} - \rho\frac{\partial\psi}{\partial\varepsilon_{ij}})\dot{\varepsilon}_{ij} - \rho(s + \frac{\partial\psi}{\partial\theta})\dot{\theta} + \rho\frac{\partial\psi}{\partial\varepsilon_{ij}}\dot{\varepsilon}_{ij}^{ie} - \rho\frac{\partial\psi}{\partial\kappa_\alpha}\dot{\kappa}_\alpha - \frac{q_i\theta_{,i}}{\theta} \geq 0 \tag{21.29}$$

According to (21.27) and (21.28) all terms in (21.29) except the term $q_i\theta_{,i}/\theta$ are independent of the temperature gradient $\theta_{,i}$. Since we can choose the temperature gradient $\theta_{,i}$ arbitrarily, it is concluded that (21.29) implies that

$$\boxed{\begin{aligned} &\gamma \equiv \gamma_{mech} + \gamma_{ther} \geq 0 \\[4pt] &\textit{where} \\[4pt] &\gamma_{mech} \equiv (\sigma_{ij} - \rho\frac{\partial\psi}{\partial\varepsilon_{ij}})\dot{\varepsilon}_{ij} - \rho(s + \frac{\partial\psi}{\partial\theta})\dot{\theta} + \rho\frac{\partial\psi}{\partial\varepsilon_{ij}}\dot{\varepsilon}_{ij}^{ie} - \rho\frac{\partial\psi}{\partial\kappa_\alpha}\dot{\kappa}_\alpha \geq 0 \\[4pt] &\gamma_{ther} \equiv -\frac{q_i\theta_{,i}}{\theta} \geq 0 \end{aligned}} \tag{21.30}$$

That is, the non-negative dissipation γ can be split into two parts: the non-negative quantity γ_{mech} and the non-negative quantity γ_{ther}. It is evident that γ_{mech} refers to the irreversibility, i.e. the dissipation, of the material as such and it is therefore called the *mechanical dissipation*; in the literature it is often called the *intrinsic* or *internal dissipation*. Likewise, γ_{ther} refers to the irreversibility, i.e. the dissipation, relating to the existence of temperature gradients, i.e. heat flow, and it is therefore called the *thermal dissipation*.

In fact, we have previously discussed in relation to (21.24) the thermal dissipation inequality where it was called Fourier's inequality and which simply states that heat must flow from warm regions towards cold regions. We will assume that the constitutive equation for the heat flux vector q_i is such that Fourier's inequality is always fulfilled; indeed we will later evaluate the consequences for *Fourier's law* given by $q_i = -k_{ij}\theta_{,j}$ when this law is to fulfill Fourier's inequality, cf. the discussion relating to (21.59). We therefore have

$$
\boxed{\begin{array}{l}
\textit{The thermal dissipation inequality} = \textit{Fourier's inequality} \\[2mm]
\gamma_{ther} \equiv -\dfrac{q_i\theta_{,i}}{\theta} \geq 0
\end{array}} \tag{21.31}
$$

In order to fulfill (21.30), we are then left with the requirement $\gamma_{mech} \geq 0$. According to (21.30) and the discussion above, we emphasize that reversibility as such requires that both $\gamma_{mech} = 0$ and $\gamma_{ther} = 0$; however, the material responds reversibly if $\gamma_{mech} = 0$. This is readily shown for thermo-elasticity where $\varepsilon_{ij}^{ie} = \kappa_\alpha = 0$ in combination with (21.10) implies $\gamma_{mech} = 0$.

Let us return to the general expression for γ_{mech} given by (21.30). For thermo-elasticity where $\varepsilon_{ij}^{ie} = \kappa_\alpha = 0$, (21.30) reduces to

$$
\gamma_{mech} \equiv \left(\sigma_{ij} - \rho\frac{\partial\psi}{\partial\varepsilon_{ij}}\right)\dot{\varepsilon}_{ij} - \rho\left(s + \frac{\partial\psi}{\partial\theta}\right)\dot{\theta} = 0
$$

It is recalled that ε_{ij} and θ are observable state variables that we can control independently of each other. Therefore, since neither σ_{ij}, s nor ψ depend on $\dot{\varepsilon}_{ij}$ and $\dot{\theta}$ and as $\dot{\varepsilon}_{ij}$ and $\dot{\theta}$ can be chosen arbitrarily, we immediately conclude from the expression above that we must have $\sigma_{ij} = \rho\,\partial\psi/\partial\varepsilon_{ij}$ and $s = -\partial\psi/\partial\theta$, in accordance with (21.10).

In the general case where the variables κ_α and ε_{ij}^{ie} are also present, the implication of $\gamma_{mech} \geq 0$ as given by (21.30) is much more complex. The reason is that even though $\dot{\varepsilon}_{ij}$ and $\dot{\theta}$ still can be chosen arbitrarily and independently of each other, the rates $\dot{\varepsilon}_{ij}^{ie}$ and $\dot{\kappa}_\alpha$ may, in general, depend on $\dot{\varepsilon}_{ij}$ and $\dot{\theta}$ and this complicates the picture considerably.

However, for elasticity we found that $\sigma_{ij} = \rho\,\partial\psi/\partial\varepsilon_{ij}$. It is therefore tempting to assume that (21.30) implies that

$$
\sigma_{ij} = \rho\frac{\partial\psi}{\partial\varepsilon_{ij}} + b_{ij} \tag{21.32}
$$

Since the unknown quantity b_{ij}, at this point, is completely arbitrary there is, in fact, no loss of generality when assuming the format (21.32). In analogy with (21.28), we assume

$$b_{ij} = b_{ij}(\theta, \varepsilon_{ij} - \varepsilon_{ij}^{ie}, \kappa_\alpha) \tag{21.33}$$

For a purely elastic behavior, where $\dot{\varepsilon}_{ij}^{ie} = \dot{\kappa}_\alpha = 0$, we found that (21.30) implies $\sigma_{ij} = \rho \, \partial\psi/\partial\varepsilon_{ij}$. However, even when we have an inelastic material, its response may, in the limit, manifest itself as elasticity; for elasto-plasticity the response approaches elasticity when neutral loading is approached and for creep and viscoplasticity, the response approaches elasticity when the loading rate is sufficiently rapid. In these cases, we have $\dot{\varepsilon}_{ij}^{ie} \to 0$ and $\dot{\kappa}_\alpha \to 0$ and we must then have $\sigma_{ij} = \rho \, \partial\psi/\partial\varepsilon_{ij}$. From (21.32), it is concluded that $b_{ij} \to 0$ must hold when $\dot{\varepsilon}_{ij}^{ie} \to 0$ and $\dot{\kappa}_\alpha \to 0$. However, in view of (21.33) the quantity b_{ij} is independent of $\dot{\varepsilon}_{ij}^{ie}$ and $\dot{\kappa}_\alpha$ and the only manner in which these requirements can be fulfilled is to require that $b_{ij} = 0$, i.e.

$$\sigma_{ij} = \rho \frac{\partial\psi}{\partial\varepsilon_{ij}} \tag{21.34}$$

Likewise, for thermo-elasticity (21.30) implies that $s = -\partial\psi/\partial\theta$, cf. (21.10). In analogy with (21.28) there is no loss of generality to assume that for inelasticity we have

$$s = -\frac{\partial\psi}{\partial\theta} + c$$

where the unknown function c has the form

$$c = c(\theta, \varepsilon_{ij} - \varepsilon_{ij}^{ie}, \kappa_\alpha)$$

Arguing in exactly the same manner as above, we are led to the conclusion that $c = 0$, i.e.

$$s = -\frac{\partial\psi}{\partial\theta} \tag{21.35}$$

The result that (21.34) and (21.35) hold not only for thermo-elasticity but also for general inelasticity is called *Coleman's relations*. They were derived by Coleman and Gurtin (1967) using a method which in the literature is referred to as *Coleman's method*. This method is completely different from the one adopted here. Indeed, it has been argued by Lubliner (1972, 1982) that Coleman's method, in fact, does not provide the unique solution given by (21.34) and (21.35) and that other solutions are possible. Following Lubliner, it is only when the set of possible solutions is evaluated in relation to the elastic response occurring in the limit also for inelastic materials that the solutions (21.34) and (21.35) emerge. The arguments presented here bear similarities to those of

Lubliner, but they are essentially different and the reader may consult the cited works of Lubliner as well as the original method suggested by Coleman and Noll to appreciate the differences.

According to (21.32) and (21.33) the argumentation above was based on the assumption that the stresses only depend on the current state. However, there are cases where the stresses also depend on the rate of some quantities and the Kelvin model, cf. (14.9) and (14.5), provides such an example. To generalize the results above we therefore write

$$\sigma_{ij} = \rho \frac{\partial \psi}{\partial \varepsilon_{ij}} + \sigma_{ij}^{v} \qquad (21.36)$$

where σ_{ij}^{v} is the *viscous stress* that depends on the rate of some quantities, i.e. $\sigma_{ij}^{v} = \sigma_{ij}^{v}(\dot{\varepsilon}_{ij}, \dot{\varepsilon}_{ij}^{ie}, \dot{\kappa}_{\alpha})$ with the property $\sigma_{ij}^{v}(0,0,0) = 0$. As already touched upon, a viscous stress will appear in some viscoelastic formulations whereas it will be zero in all other cases. With the results (21.36) and (21.35) inserted into the mechanical dissipation inequality in (21.30), we are led to the following important conclusions

<div style="border:1px solid">

For inelasticity we have

$$\psi = \psi(\theta, \varepsilon_{ij} - \varepsilon_{ij}^{ie}, \kappa_{\alpha})$$

where

$$\sigma_{ij} = \rho \frac{\partial \psi}{\partial \varepsilon_{ij}} + \sigma_{ij}^{v}; \qquad s = -\frac{\partial \psi}{\partial \theta}$$

and $\sigma_{ij}^{v} = \sigma_{ij}^{v}(\dot{\varepsilon}_{ij}, \dot{\varepsilon}_{ij}^{ie}, \dot{\kappa}_{\alpha})$ denotes the viscous stress. The mechanical dissipation inequality becomes

$$\gamma_{mech} \equiv \sigma_{ij}\dot{\varepsilon}_{ij}^{ie} + \sigma_{ij}^{v}(\dot{\varepsilon}_{ij} - \dot{\varepsilon}_{ij}^{ie}) - K_{\alpha}\dot{\kappa}_{\alpha} \geq 0$$

where the conjugated thermodynamic forces K_{α} are defined by

$$K_{\alpha} \equiv \rho \frac{\partial \psi}{\partial \kappa_{\alpha}}$$

</div>

(21.37)

Note the definition of the *conjugated thermodynamic forces*. From the expression for γ_{mech} which has the unit [Nm/(m^{3}s)], i.e. energy density rate, we see that the stress σ_{ij} is the 'force' that is energy conjugated to the 'flux' $\dot{\varepsilon}_{ij}^{ie}$; in the same fashion the 'thermodynamic force' K_{α} is energy conjugated to the 'flux' $\dot{\kappa}_{\alpha}$ (or rather to $-\dot{\kappa}_{\alpha}$). It is recalled that elasticity occurs when $\gamma_{mech} = 0$ and this is evidently fulfilled when $\sigma_{ij}^{v} = \dot{\varepsilon}_{ij}^{ie} = \dot{\kappa}_{\alpha} = 0$. However, reversibility as such requires that $\gamma_{mech} = 0$ as well as $\gamma_{ther} = 0$, cf. (21.30).

With the main result (21.37), and for simplicity excluding the viscous stress σ_{ij}^{v} the only remaining topic is to choose expressions for $\dot{\varepsilon}_{ij}^{ie}$ and $\dot{\kappa}_{\alpha}$ that fulfill

the mechanical dissipation inequality. Expressions for $\dot{\varepsilon}_{ij}^{ie}$ and $\dot{\kappa}_\alpha$ are called *evolution laws* and we will now enter a discussion of proper choices of these evolution laws.

21.3 Choice of evolution laws - Fulfillment of the mechanical dissipation inequality

Any constitutive relation must fulfill the mechanical dissipation inequality and excluding for the moment those viscoelastic formulations which contain a viscous stress, the mechanical dissipation inequality appears from (21.37) as

$$\gamma_{mech} \equiv \sigma_{ij}\dot{\varepsilon}_{ij}^{ie} - K_\alpha\dot{\kappa}_\alpha \geq 0 \tag{21.38}$$

The question is now how we can choose expressions for the fluxes $\dot{\varepsilon}_{ij}^{ie}$ and $\dot{\kappa}_\alpha$ so that the mechanical dissipation inequality is fulfilled. These expressions for $\dot{\varepsilon}_{ij}^{ie}$ and $\dot{\kappa}_\alpha$ are called *evolution laws* and in this section we will provide a general discussion of various ways to establish such evolution laws.

Let us first write the mechanical dissipation inequality in a slightly more convenient form. For this purpose, define the sets A_Θ and $\dot{a}_\Theta$ by

$$\boxed{A_\Theta = \{\sigma_{ij}, K_\alpha\}\,; \quad \dot{a}_\Theta = \{\dot{\varepsilon}_{ij}^{ie}, -\dot{\kappa}_\alpha\}} \tag{21.39}$$

i.e. the set A_Θ comprises all σ_{ij} and K_α components, i.e. all the 'forces', whereas the set $\dot{a}_\Theta$ comprises all $\dot{\varepsilon}_{ij}^{ie}$ and $-\dot{\kappa}_\alpha$ components, i.e. all the 'fluxes'. The minus sign in front of $\dot{\kappa}_\alpha$ turns out to be convenient since the definitions (21.39) allow the mechanical dissipation inequality (21.38) to be written as

$$\boxed{\gamma_{mech} \equiv A_\Theta\dot{a}_\Theta \geq 0} \tag{21.40}$$

Below, we will consider the dissipation inequality in this general form and ignore, for the moment, that in our case the components of A_Θ and $\dot{a}_\Theta$ are given by (21.39). As an illustration of this generality, we may write the thermal dissipation inequality (21.31) as $\gamma_{ther} \equiv A\dot{a}$ where $A = \{\theta_{,i}/\theta\}$ and $\dot{a} = \{-q_i\}$. Since we could equally well have chosen $A = \{\theta_{,i}\}$ and $\dot{a} = \{-q_i/\theta\}$ this aspect illustrates that the definition of forces and fluxes is not unique.

If all forces are zero, it seems reasonable to assume that also all fluxes are zero, i.e.

$$\dot{a}_\Theta = 0 \quad \text{if} \quad A_\Theta = 0 \tag{21.41}$$

Below, we will discuss various approaches for establishment of the evolution laws for $\dot{a}_\Theta$ so that the dissipation inequality (21.40) is fulfilled; for related viewpoints see for instance Halphen and Nguyen (1975), Germain *et al.* (1983), Eve *et al.* (1990) and Nguyen (2000).

21.3.1   Direct approach

It is certainly possible to directly postulate some evolution laws for $\dot{a}_\Theta$ and then *a posteriori*, check that the dissipation inequality (21.40) is fulfilled. The drawback in this approach is that this *a posteriori* check must be performed for each material model and no general information can be derived for a group of material models

> *Direct approach:*
> *Postulate some evolution laws for $\dot{a}_\Theta$. Check a posteriori*
> *that the dissipation inequality is fulfilled*

21.3.2   Onsager approach

The most simple specific expression that can be adopted for the relation between the fluxes and forces is linear, i.e.

$$\dot{a}_\Theta = L_{\Theta Y} A_Y$$

where the coefficient matrix $L_{\Theta Y}$ is taken as constant; this expression certainly fulfills (21.41) and insertion into (21.40) provides

$$\gamma_{mech} \equiv A_\Theta L_{\Theta Y} A_Y > 0 \quad \text{when} \quad A_\Theta \neq 0$$

where $\geq$ has been replaced by $>$ since we are considering irreversible processes. It appears that the coefficient $L_{\Theta Y}$ must be positive definite. Let us furthermore assume that $L_{\Theta Y}$ is symmetric. We are then led to

> *Onsager's relations:*
>
> $\quad \dot{a}_\Theta = L_{\Theta Y} A_Y$
>
> *where*
>
> $\quad L_{\Theta Y} = L_{Y\Theta} \quad and \quad L_{\Theta Y} \quad is\ positive\ definite$ (21.42)

These relations where proposed by Onsager (1931a,b) and the symmetry property $L_{\Theta Y} = L_{Y\Theta}$ is referred to as the *Onsager reciprocal relations*. Onsager arrived at the reciprocal relations by statistical mechanics considerations and they have been widely used in the literature and confirmed experimentally for a number phenomena within heat, diffusion and electricity, see Fung (1965), and in physical chemistry. However, they have also been criticized, cf. for instance Eringen (1975a) and Truesdell (1969), since the definition of forces and fluxes, as already touched upon, is not unique. In our situation, we can safely state that the Onsager relations are not fundamental laws of nature since they cannot be used to describe general plasticity and viscoplasticity; however, the Onsager relations describe with close accuracy a number of other phenomena and in that sense they can be viewed as relevant material descriptions for some fields of applications.

21.3.3   Potential approach

In order to generalize Onsager's linear theory and obtain a nonlinear theory, let us assume that there exists a function ϕ such that

$$\dot{a}_\Theta = \lambda \frac{\partial \phi}{\partial A_\Theta} ; \quad \lambda \geq 0 \qquad \textit{Potential formulation} \qquad (21.43)$$

It is easily shown that this format contains Onsager's linear theory as a special case. In that case, choose the function ϕ as

$$\phi = \frac{1}{2} A_\Theta L_{\Theta Y} A_Y$$

where nothing is said about the symmetry of $L_{\Theta Y}$. Splitting $L_{\Theta Y}$ into its symmetric and antisymmetric parts according to

$$L_{\Theta Y} = L_{\Theta Y}^s + L_{\Theta Y}^a$$

it then follows that

$$\phi = \frac{1}{2} A_\Theta L_{\Theta Y} A_Y = \frac{1}{2} A_\Theta L_{\Theta Y}^s A_Y \qquad (21.44)$$

Choosing $\lambda = 1$ and inserting (21.44) into (21.43) then provide (21.42).

Returning to the general situation, insertion of (21.43) into (21.40) gives

$$\gamma_{mech} \equiv \lambda A_\Theta \frac{\partial \phi}{\partial A_\Theta} \geq 0 \qquad (21.45)$$

The function ϕ is called the *dissipation potential* and it evidently depends on the forces A_Θ, but we may also allow it to depend on some other variables Z_q, i.e.

$$Z_q = \text{some variables } (q = 1, 2, \ldots) \qquad (21.46)$$

We then obtain

$$\phi = \phi(A_\Theta, Z_q)$$

Within the potential approach there are various ways to ensure that (21.45) is fulfilled.

Homogeneous potential function

One route is to assume that ϕ is a homogeneous function of degree n in A_Θ, i.e.

> ϕ *is a homogeneous function of* A_Θ *of degree* n *if*
>
> $\phi(kA_\Theta, Z_q) = k^n\phi(A_\Theta, Z_q)$

As an example, $\phi = (A_1^3 + A_2^3)Z$ is homogeneous of degree 3 since $\phi(kA_\theta, Z_q) = ((kA_1)^3 + (kA_2)^3)Z = k^3(A_1^3 + A_2^3)Z = k^3\phi(A_\Theta, Z_q)$; as another example, ϕ given by (21.44) is homogeneous of degree 2. By Euler's theorem, see for instance Sokolnikoff and Redheffer (1958), it then follows that

$$A_\Theta \frac{\partial\phi}{\partial A_\Theta} = n\phi \qquad\qquad (21.47)$$

From (21.43) and (21.47) we then obtain

> *The evolution laws*
>
> $$\dot{a}_\Theta = \lambda\frac{\partial\phi}{\partial A_\Theta}; \quad \lambda \geq 0$$
>
> *where* $\phi = \phi(A_\Theta, Z_q)$ *and* ϕ *is a homogeneous function of* A_Θ *of degree* n *implies*
>
> $$\gamma_{mech} \equiv \lambda A_\Theta \frac{\partial\phi}{\partial A_\Theta} = \lambda n\phi \geq 0$$
>
> *and is fulfilled if* $\phi \geq 0$

As a relevant example, ideal von Mises plasticity is given by

$$f = F - \sigma_{yo} \quad \text{where} \quad F = \sigma_{eff} = (\frac{3}{2}s_{ij}s_{ij})^{1/2}$$

where f is the yield function, cf. (12.4). For ideal plasticity there are no internal variables, i.e. $\kappa_\alpha = 0$ and thereby no conjugated thermodynamic forces K_α, cf. the definition of K_α given by (21.37). It then follows from (21.39) that $A_\Theta = \{\sigma_{ij}\}$ and $\dot{a}_\Theta = \{\dot{\varepsilon}_{ij}^p\}$. Choose the dissipation function ϕ as

$$\phi(A_\Theta, Z_q) = \phi(\sigma_{ij}) = F = \sigma_{eff}$$

Since F is a homogeneous function of σ_{ij} of degree 1 we have $\sigma_{ij}\partial F/\partial\sigma_{ij} = F = \sigma_{eff}$, i.e. the dissipation inequality becomes $\gamma_{mech} \equiv \lambda A_\Theta\partial\phi/\partial A_\Theta = \lambda\sigma_{ij}\partial F/\partial\sigma_{ij} = \lambda\sigma_{eff} \geq 0$ which certainly is fulfilled. Moreover, the evolution law $\dot{a}_\Theta = \lambda\partial\phi/\partial A_\Theta$ becomes

$$\dot{\varepsilon}_{ij}^p = \lambda\frac{\partial F}{\partial\sigma_{ij}} = \lambda\frac{\partial f}{\partial\sigma_{ij}}$$

which is exactly the associated flow rule.

Convex potential function

We will now present a very powerful approach for establishment of the evolution laws so that the dissipation inequality is fulfilled.

Let us assume that ϕ is a convex function in A_Θ. From Appendix (A.5), it then follows that

$$\phi(A_\Theta^{(2)}, Z_q) - \phi(A_\Theta^{(1)}, Z_q) \geq (\frac{\partial \phi}{\partial A_\Theta})^{(1)}(A_\Theta^{(2)} - A_\Theta^{(1)}) \tag{21.48}$$

where $A_\Theta^{(1)}$ and $A_\Theta^{(2)}$ are two arbitrary sets of A_Θ and $(\ )^{(1)}$ means that the quantity within the parenthesis should be evaluated at the point $A_\Theta^{(1)}$. Choosing $A_\Theta^{(2)} = 0$ we obtain

$$(\frac{\partial \phi}{\partial A_\theta})^{(1)} A_\Theta^{(1)} \geq \phi(A_\Theta^{(1)}, Z_q) - \phi(0, Z_q)$$

Since $A_\Theta^{(1)}$ denotes an arbitrary set of A_Θ, we write this expression as

$$\frac{\partial \phi}{\partial A_\theta} A_\Theta \geq \phi(A_\Theta, Z_q) - \phi(0, Z_q) \tag{21.49}$$

In (21.48), choose next $A_\Theta^{(1)} = 0$ to obtain

$$\phi(A_\Theta^{(2)}, Z_q) - \phi(0, Z_q) \geq (\frac{\partial \phi}{\partial A_\theta})_{A_\Theta=0} A_\theta^{(2)} \tag{21.50}$$

Due to (21.41) and (21.43), we have

$$(\frac{\partial \phi}{\partial A_\Theta})_{A_\Theta=0} = 0$$

and since $A_\Theta^{(2)}$ in (21.50) denotes an arbitrary set of A_Θ, we can write (21.50) as

$$\phi(A_\Theta, Z_q) - \phi(0, Z_q) \geq 0$$

A comparison of this expression with (21.49) shows that

$$A_\Theta \frac{\partial \phi}{\partial A_\Theta} \geq 0$$

i.e. the dissipation inequality is fulfilled. We are then led to the following very powerful conclusion

> *If the dissipation function* $\phi = \phi(A_\Theta, Z_q)$
> *is a convex function of* A_Θ *and if*
>
> $$\phi(A_\Theta, Z_q) - \phi(0, Z_q) \geq 0$$
>
> *then the evolution laws*
>
> $$\dot{a}_\Theta = \lambda \frac{\partial \phi}{\partial A_\Theta}; \quad \lambda \geq 0$$
>
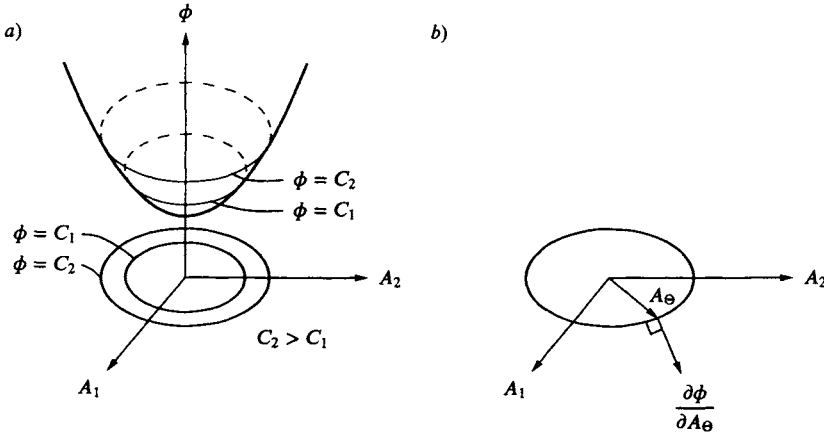> *fulfill the dissipation inequality*

$$(21.51)$$

Figure 21.2: Illustration that the evolution laws $\dot{a}_\Theta = \lambda \partial\phi/\partial A_\Theta$ fulfill the dissipation inequality when ϕ is a convex function.

We observe that the requirement $\phi(A_\Theta, Z_q) - \phi(0, Z_q) \geq 0$ follows from the requirement $(\partial\phi/\partial A_\Theta)_{A_\Theta=0} = 0$ (as well as convexity of ϕ). Moreover, when evaluating the inequality $\phi(A_\Theta, Z_q) - \phi(0, Z_q) \geq 0$, the quantity $\phi(A_\Theta, Z_q)$ should be evaluated at the current state where the evolution law $\dot{a}_\Theta = \lambda \partial\phi/\partial A_\Theta$ is employed. The fundamental result (21.51) is due to Edelen (1972) and the proof given here follows closely that of Eringen (1975a).

If A_Θ merely consists of two components, a simple graphical illustration of (21.51) is possible. Since ϕ is a convex function and as $(\partial\phi/\partial A_\Theta)_{A_\Theta=0} = 0$, it follows that ϕ has a minimum at $A_\Theta = 0$, cf. Fig. 21.2a). Moreover, the vector $\partial\phi/\partial A_\Theta$ is normal to the contour curves of ϕ in the A_Θ-space and $\partial\phi/\partial A_\Theta$ is directed outwards (towards increasing values of ϕ). That the scalar product $A_\Theta \partial\phi/\partial A_\Theta$ and thereby the dissipation inequality is non-negative are then evident from Fig. 21.2b)

Let us for the moment choose $\lambda = 1$; then the evolution laws become

$$\dot{a}_\Theta = \frac{\partial\phi}{\partial A_\Theta} \tag{21.52}$$

Define the *pseudo-dissipation function* ϕ^* by

$$\phi^* = \phi - \dot{a}_\Theta A_\Theta$$

It follows that

$$\dot{\phi}^* = \frac{\partial\phi}{\partial A_\Theta}\dot{A}_\Theta + \frac{\partial\phi}{\partial Z_q}\dot{Z}_q - \ddot{a}_\Theta A_\Theta - \dot{a}_\Theta \dot{A}_\Theta$$

which with the result (21.52) reduces to

$$\dot{\phi}^* = -A_\Theta \ddot{a}_\Theta + \frac{\partial \phi}{\partial Z_q} \dot{Z}_q$$

It follows that

$$\phi^* = \phi^*(\dot{a}_\Theta, Z_q) \quad \text{and} \quad A_\Theta = -\frac{\partial \phi^*}{\partial \dot{a}_\Theta}; \quad \frac{\partial \phi^*}{\partial Z_q} = \frac{\partial \phi}{\partial Z_q} \qquad (21.53)$$

Whereas (21.52) determines the fluxes by means of the forces, (21.53b) expresses the forces in terms of the fluxes. In recognition of the previous discussion following (21.22), it is evident that ϕ^* is the Legendre transformation of ϕ. We also note that what we have here termed the dissipation function is called by some authors the pseudo-dissipation function and *visa versa*, cf. Lemaitre and Chaboche (1990) and Maugin (1992); however, since the function ϕ turns out to be the one that is most convenient to work with for constitutive modeling, our choice of terminology seems justified.

Returning to the essential result (21.51) and focusing on plasticity/viscoplasticity, let us choose the dissipation function $\phi(A_\Theta, Z_q)$ where $A_\Theta = \{\sigma_{ij}, K_\alpha\}$ as the potential function $g(\sigma_{ij}; K_\alpha)$ previously introduced for nonassociated plasticity and viscoplasticity. Since $A_\Theta = \{\sigma_{ij}, K_\alpha\}$ and $\dot{a}_\Theta = \{\dot{\varepsilon}_{ij}^p, -\dot{\kappa}_\alpha\}$, the evolution laws given by (21.51) become

$$\boxed{\begin{array}{l} \textit{Potential function approach} \\[4pt] \dot{\varepsilon}_{ij}^p = \lambda \dfrac{\partial g}{\partial \sigma_{ij}}; \quad \dot{\kappa}_\alpha = -\lambda \dfrac{\partial g}{\partial K_\alpha} \end{array}} \qquad (21.54)$$

which corresponds exactly to the evolution laws postulated for plasticity in Chapter 10. Now however, we know exactly from (21.51) what requirements must be posed on the potential function g in order that these evolution laws be physically meaningful. Replacing λ by the Λ or $<\Phi(f)>/\eta$ we obtain the evolution equations for creep and Perzyna viscoplasticity, respectively, cf. (15.24) and (15.36).

Recalling that associated plasticity is obtained if the potential function g is chosen as the yield function f, we will now establish associated plasticity by a completely different approach.

The approach to use the convex function ϕ as a dissipation function and derive the evolution equations by (21.54) was pioneered by Halphen and Nguyen (1975). According to their notation, a material with these evolution equations is termed a *generalized standard material*.

Postulate of maximum dissipation

For plasticity, the dissipation inequality (21.37) reads

$$\gamma_{mech} \equiv \sigma_{ij}\dot{\varepsilon}_{ij}^p - K_\alpha \dot{\kappa}_\alpha \geq 0$$

where the yield function f fulfills $f \leq 0$. In accordance with (10.7) and (10.8), it seems natural to choose the thermodynamic forces K_α as the hardening parameters, i.e.

$$f(\sigma_{ij}, K_\alpha) \leq 0$$

The key point is to ensure that $\gamma_{mech} \geq 0$. It then seems natural to investigate the case where γ_{mech} takes the maximal possible value, i.e. we adopt *the postulate of maximum dissipation*; in that case we evidently ensure that $\gamma_{mech} \geq 0$. Maximization of γ_{mech} is equivalent to minimization of $-\gamma_{mech}$. We are then led to the following problem

> *Postulate of maximum dissipation:*
>
> *For given fluxes $\dot{\varepsilon}_{ij}^p$ and $\dot{\kappa}_\alpha$, find those stresses σ_{ij} and conjugated forces K_α that minimize $-\gamma_{mech}$ under the constraint that $f(\sigma_{ij}, K_\alpha) \leq 0$*   (21.55)

In accordance with the Appendix A, this problem is a minimization problem with a constraint in terms of an inequality. Following (A.16), we define the Lagrange function $\mathcal{L}(\sigma_{ij}, K_\alpha, \lambda)$ by

$$\mathcal{L}(\sigma_{ij}, K_\alpha, \lambda) = -\gamma_{mech} + \lambda f = -\sigma_{ij}\dot{\varepsilon}_{ij}^p + K_\alpha \dot{\kappa}_\alpha + \lambda f(\sigma_{ij}, K_\alpha)$$

where λ is a *Lagrange multiplier* and f is assumed to be a convex function of σ_{ij} and K_α. In accordance with (A.17), it follows that $\partial\mathcal{L}/\partial\sigma_{ij} = -\dot{\varepsilon}_{ij}^p + \lambda\partial f/\partial\sigma_{ij} = 0$ and $\partial\mathcal{L}/\partial K_\alpha = \dot{\kappa}_\alpha + \lambda\partial f/\partial K_\alpha = 0$. From (A.17) and (A.15) we then obtain the following *Kuhn-Tucker relations*

> *For plasticity theory where $f(\sigma_{ij}, K_\alpha) \leq 0$ and f is assumed to be a convex function of σ_{ij} and K_α, the postulate of maximum dissipation leads to the associated evolution equations*
>
> $$\dot{\varepsilon}_{ij}^p = \lambda\frac{\partial f}{\partial\sigma_{ij}}; \quad \dot{\kappa}_\alpha = -\lambda\frac{\partial f}{\partial K_\alpha}$$
>
> *as well as*
>
> $$\lambda \geq 0$$
>
> $$\lambda = 0 \quad \text{for elastic behavior}$$
>
> *and*
>
> $$\lambda f = 0$$ (21.56)

It appears that the postulate of maximum dissipation for plasticity leads to associated plasticity, cf. Chapter 10, and that we certainly ensure that the mechanical dissipation inequality is fulfilled. Moreover, the quantity λ, which was

originally introduced as a Lagrange multiplier, turns out to be the plastic multiplier.

The postulate of maximum dissipation is not a principle in the sense of being a law of nature even though some literature tends to suggest that; instead, it may be viewed simply as a means to fulfill the dissipation inequality. However, it may be possible to appeal to some kind of physics behind this postulate. We found in (20.62) and (20.63) that at thermodynamic equilibrium where no mechanical work input and no heat input are supplied, then the entropy is maximum. On the other hand, it seems reasonable to assume that the process to achieve that state is characterized by maximum entropy production and thereby maximum dissipation. However, this is an assumption - a postulate - and not a strict result; if it were a law of nature, nonassociated plasticity would not exist.

Another route of argumentation relates to (9.41) where the postulate of maximum dissipation was also encountered and where it was shown to lead to the associated flow rule $\dot{\varepsilon}_{ij}^p = \lambda \partial f / \partial \sigma_{ij}$. We shall provide a further discussion of this aspect in the following chapter.

It is of significant interest that the postulate of maximum dissipation without any further assumptions by the Kuhn-Tucker relations leads to the conclusion that $\lambda \geq 0$ when $f = 0$ and $\lambda = 0$ when $f < 0$. Previously, in Chapter 10 we had to assume λ as being non-negative.

In this section, we have discussed various ways of establishing evolution laws that fulfill the mechanical dissipation inequality. The main results are (21.51), which for plasticity and viscoplasticity lead to the nonassociated evolution laws given by (21.54), and the postulate of maximum dissipation (21.55), which for plasticity leads to the associated evolution laws (21.56). We will later return to these results and further explore their implications. However, in the present chapter we will return to a discussion of the ramifications of the first law of thermodynamics, which deserves some attention.

21.4   Heat equation

We have shown that fulfillment of the second law of thermodynamics implies the main result given by (21.31) and (21.37). In particular, we observe the restrictions for constitutive modeling given by $\gamma_{ther} \geq 0$ and $\gamma_{mech} \geq 0$. On the other hand, the first law of thermodynamics places no restrictions on constitutive modeling; it simply turns into the *heat equation*, which determines the temperature distribution within the body.

Before attention is given to a derivation of the heat equation, we return to the thermal dissipation inequality (21.31), i.e. *Fourier's inequality*, which may also be written as

$$-q_i \theta_{,i} \geq 0 \tag{21.57}$$

As discussed in Section 20.6, any temperature gradient gives rise to irreversibility and (21.57) can therefore be expressed as

$$-q_i\theta_{,i} > 0 \quad \text{when} \quad \theta_{,i} \neq 0 \tag{21.58}$$

This inequality simply states that heat flows from hot regions towards cold regions.

The reason for heat flow is the existence of a temperature gradient and the simplest constitutive equation that relates the heat flux vector q_i and the temperature gradient $\theta_{,i}$ is a linear relation. This leads to *Fourier's law*, which dates back to 1822, and which reads

$$\boxed{q_i = -k_{ij}\theta_{,j} \quad \text{Fourier's law}} \tag{21.59}$$

where k_{ij} denotes the *tensor of thermal conductivities*. Referring to (21.42), we may consider Fourier's law as an application of the Onsager relations. We will now discuss the pertinent properties of k_{ij} so that inequality (21.58) is fulfilled.

In general, we may assume that k_{ij} depends on the same variables as the free energy ψ, i.e.

$$k_{ij} = k_{ij}(\theta, \varepsilon_{kl} - \varepsilon_{kl}^{ie}, \kappa_\alpha)$$

In practice, however, the tensor k_{ij} is often assumed to be constant or to depend on the temperature θ alone. Insertion of (21.59) into (21.58) yields

$$\theta_{,i}k_{ij}\theta_{,j} > 0 \quad \text{when} \quad \theta_{,i} \neq 0 \tag{21.60}$$

In general, k_{ij} may be split into a symmetric part k_{ij}^s and an antisymmetric part k_{ij}^a according to

$$k_{ij} = k_{ij}^s + k_{ij}^a$$

where

$$k_{ij}^s = \frac{1}{2}(k_{ij} + k_{ji}); \quad k_{ij}^a = \frac{1}{2}(k_{ij} - k_{ji})$$

Then (21.60) becomes

$$\theta_{,i}k_{ij}^s\theta_{,j} > 0 \quad \text{when} \quad \theta_{,i} \neq 0$$

and it follows that the symmetric part k_{ij}^s is positive definite.

This conclusion follows from the second law. However, from the first law and following Truesdell (1969), it turns out to be possible to evaluate the antisymmetric part k_{ij}^a. Referring to the first law (21.1), the heat flux vector q_i only appears in the form of the divergence given by $q_{i,i}$. Using (21.59), we obtain

$$q_{i,i} = -\frac{\partial k_{ij}}{\partial x_i}\theta_{,j} - k_{ij}\theta_{,ij} = -\frac{\partial k_{ij}}{\partial x_i}\theta_{,j} - k_{ij}^s\theta_{,ij} \tag{21.61}$$

where advantage was taken of $k^a_{ij}\theta_{,ij} = -k^a_{ji}\theta_{,ij} = -k^a_{ij}\theta_{,ji} = -k^a_{ij}\theta_{,ij}$, i.e. $k^a_{ij}\theta_{,ij} = 0$. For a homogeneous material, the thermal conductivity tensor k_{ij} does not change with position, i.e. $\partial k_{ij}/\partial x_i = 0$. In that case (21.61) reduces to

$$q_{i,i} = -k^s_{ij}\theta_{,ij}$$

i.e. for homogeneous materials, it is only the symmetric part k^s_{ij} of k_{ij} that influences the divergence $q_{i,i}$. It seems hard to accept that the principal properties of k_{ij} (symmetric or not) are to depend on whether the material is taken in a homogeneous form or in an inhomogeneous form. It therefore seems fully acceptable to assume that k_{ij} is always symmetric and this is in accordance with general experimental evidence. We are then led to the following conclusions

$$\boxed{k_{ij} \text{ is symmetric and positive definite}} \qquad (21.62)$$

We observe that both (21.59) and (21.62) are in agreement with the Onsager relations (21.42). For isotropic materials, k_{ij} reduces to $k_{ij} = k\delta_{ij}$, with k being the *thermal conductivity* and (21.62) implies that $k > 0$, as expected. With Fourier's law and the conclusions above, the inequality $\gamma_{ther} \geq 0$ is always fulfilled, as already anticipated in (21.31). Therefore, the requirements imposed by the second law have been reduced to fulfillment of the mechanical dissipation inequality $\gamma_{mech} \geq 0$ alone.

The heat equation will turn out to involve a new material parameter - the *specific heat capacity*. Before attention is turned to solids, and to fully appreciate the difference between various specific heat capacities, it is instructive to first discuss this subject for ideal gases. In fact, for a gas we have already touched upon this subject when we introduced the specific heat capacity c_V at constant volume. According to (20.26), we have

$$\boxed{\begin{array}{l} \textit{Gases:} \\ \textit{The specific heat capacity } c_V \textit{ is the amount of heat that} \\ \textit{must be supplied without change of volume in order to} \\ \textit{increase the temperature of one unit mass one degree} \end{array}} \qquad (21.63)$$

i.e.

$$\delta Q = mc_V d\theta \quad \text{when } V = \text{constant} \qquad (21.64)$$

where m is the mass of the gas in question. For gases, the global form of the first law is given by (20.25), i.e.

$$dU = -p\,dV + \delta Q \qquad (21.65)$$

According to (20.24), we have for ideal gases $U(\theta) = mu(\theta)$, i.e.

$$dU = m\frac{du}{d\theta}d\theta \quad \text{always holds for ideal gases} \qquad (21.66)$$

When V is constant, (21.64) and (21.65) give $dU = mc_V d\theta$ and a comparison with (21.66), which always holds, reveals that

$$dU = mc_V d\theta \quad \text{always holds for ideal gases} \tag{21.67}$$

where $c_V = du/d\theta$, cf. (20.28).

For a gas, let us next define the specific heat capacity c_p by

> *Gases:*
> *The specific heat capacity c_p is the amount of heat that must be supplied without change of pressure in order to increase the temperature of one unit mass one degree* (21.68)

i.e.

$$\delta Q = mc_p d\theta \quad \text{when } p = \text{constant}$$

Insertion of this expression and of (21.67) into (21.65) gives

$$mc_V d\theta = -pdV + mc_p d\theta \tag{21.69}$$

For constant pressure, the ideal gas law $pV = mR\theta$ implies

$$pdV = mRd\theta$$

Insertion into (21.69) results in

$$\boxed{c_p - c_V = R \quad \text{ideal gas}}$$

The specific heat capacity c_p is therefore larger than c_V and the physical reason is that when c_p is measured, heat is supplied, but in order to maintain a constant pressure the gas must expand and thereby perform mechanical work on the surroundings. Therefore when c_p is measured, the heat input is used not only to increase the gas temperature, but also to perform mechanical work on the surroundings. On the other hand, when c_V is measured, the volume is constant and all the heat input goes into an increase of the gas temperature. The difference between c_p and c_V is quite significant for ideal gases and typically, we have $c_p/c_V \approx 1.3 - 1.7$, cf. Schmidt (1963).

Against this background, let us now turn to the specific heat capacities of solid materials. In analogy with (21.63) and (21.68), two definitions are available

> *Solids:*
> *The specific heat capacity c_ε is the amount of heat that must be supplied without change of strains in order to increase the temperature of one unit mass one degree*

and

> *Solids:*
> *The specific heat capacity c_σ is the amount of heat that*
> *must be supplied without change of stresses in order to*
> *increase the temperature of one unit mass one degree*

Evidently, when c_ε or c_σ are measured, the body is assumed to be in a state of homogeneous conditions. By the definitions above, we therefore have

$$\frac{\delta Q}{dt} = mc_\varepsilon \dot{\theta} \qquad \text{when } \varepsilon_{ij} = \text{constant} \tag{21.70}$$

and

$$\frac{\delta Q}{dt} = mc_\sigma \dot{\theta} \qquad \text{when } \sigma_{ij} = \text{constant} \tag{21.71}$$

where m is the mass of the body. Under homogeneous conditions, the first law (21.1) may with (20.12) be written as

$$\rho\dot{u} = \dot{\varepsilon}_{ij}\sigma_{ij} + \frac{1}{V}\frac{\delta Q}{dt}$$

where V is the total volume of the body. Since $m = \rho V$, we obtain

$$\rho\dot{u} = \dot{\varepsilon}_{ij}\sigma_{ij} + \frac{\rho}{m}\frac{\delta Q}{dt}$$

According to (21.4), we have $u = \psi + s\theta$, which leads to

$$\rho(\dot{\psi} + \dot{s}\theta + s\dot{\theta}) = \dot{\varepsilon}_{ij}\sigma_{ij} + \frac{\rho}{m}\frac{\delta Q}{dt} \tag{21.72}$$

For a general inelastic material, the free energy ψ is given by (21.37), i.e.

$$\psi = \psi(\theta, \varepsilon_{ij} - \varepsilon_{ij}^{ie}, \kappa_\alpha)$$

Differentiation and use of the results given in (21.37) then imply

$$\dot{\psi} = -s\dot{\theta} + \frac{\partial\psi}{\partial\varepsilon_{ij}}\dot{\varepsilon}_{ij} - \frac{\partial\psi}{\partial\varepsilon_{ij}}\dot{\varepsilon}_{ij}^{ie} + \frac{\partial\psi}{\partial\kappa_\alpha}\dot{\kappa}_\alpha \tag{21.73}$$

where

$$s = -\frac{\partial\psi}{\partial\theta}$$

It follows that

$$\dot{s} = -\frac{\partial^2\psi}{\partial\theta^2}\dot{\theta} - \frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial\theta}\dot{\varepsilon}_{ij} + \frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial\theta}\dot{\varepsilon}_{ij}^{ie} - \frac{\partial^2\psi}{\partial\kappa_\alpha\partial\theta}\dot{\kappa}_\alpha \tag{21.74}$$

Insertion of this expression and of (21.73) into (21.72) results in

$$
-\rho\theta\frac{\partial^2\psi}{\partial\theta^2}\dot\theta - \rho\theta\frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial\theta}\dot\varepsilon_{ij} + \rho(\theta\frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial\theta} - \frac{\partial\psi}{\partial\varepsilon_{ij}})\dot\varepsilon_{ij}^{ie}
$$

$$
+ (\rho\frac{\partial\psi}{\partial\varepsilon_{ij}} - \sigma_{ij})\dot\varepsilon_{ij} + \rho(\frac{\partial\psi}{\partial\kappa_\alpha} - \theta\frac{\partial^2\psi}{\partial\kappa_\alpha\partial\theta})\dot\kappa_\alpha = \frac{\rho}{m}\frac{\delta Q}{dt} \qquad (21.75)
$$

When the strains are constant, i.e. $\dot\varepsilon_{ij} = 0$, combination of (21.70) and (21.75) gives

$$
-\theta\frac{\partial^2\psi}{\partial\theta^2}\dot\theta + (\theta\frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial\theta} - \frac{\partial\psi}{\partial\varepsilon_{ij}})\dot\varepsilon_{ij}^{ie}
$$

$$
+ (\frac{\partial\psi}{\partial\varepsilon_{ij}} - \frac{\sigma_{ij}}{\rho})\dot\varepsilon_{ij} + (\frac{\partial\psi}{\partial\kappa_\alpha} - \theta\frac{\partial^2\psi}{\partial\kappa_\alpha\partial\theta})\dot\kappa_\alpha = c_\varepsilon\dot\theta \qquad (21.76)
$$

Likewise, if the stresses are constant, combination of (21.71) and (21.75) gives

$$
-\theta\frac{\partial^2\psi}{\partial\theta^2}\dot\theta - \theta\frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial\theta}\dot\varepsilon_{ij} + (\theta\frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial\theta} - \frac{\partial\psi}{\partial\varepsilon_{ij}})\dot\varepsilon_{ij}^{ie}
$$

$$
+ (\frac{\partial\psi}{\partial\varepsilon_{ij}} - \frac{\sigma_{ij}}{\rho})\dot\varepsilon_{ij} + (\frac{\partial\psi}{\partial\kappa_\alpha} - \theta\frac{\partial^2\psi}{\partial\kappa_\alpha\partial\theta})\dot\kappa_\alpha = c_\sigma\dot\theta \qquad (21.77)
$$

where the condition that the stresses are constant remains to be enforced.

It appears that, in principle, both measurements of c_ε and c_σ are dependent on the inelastic processes occurring in the material, as manifested by the presence of the factors $\dot\varepsilon_{ij}^{ie}$ and $\dot\kappa_\alpha$ in (21.76) and (21.77). In practice, however, c_ε and c_σ are measured when the material responds in a thermo-elastic manner. Therefore

> *In practice, c_ε and c_σ are measured during thermo-elastic conditions*

In that case and since the viscous stress now is zero, i.e $\rho\partial\psi/\partial\varepsilon_{ij} = \sigma_{ij}$, (21.76) reduces to

$$
\boxed{c_\varepsilon = -\theta\frac{\partial^2\psi}{\partial\theta^2}} \qquad (21.78)
$$

which in the following we will take as the definition of c_ε. Likewise, (21.77) becomes

$$
-\theta\frac{\partial^2\psi}{\partial\theta^2}\dot\theta - \theta\frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial\theta}\dot\varepsilon_{ij} = c_\sigma\dot\theta \qquad (21.79)
$$

Thermo-elasticity is defined by $\psi = \psi(\theta, \varepsilon_{ij})$ as well as $\sigma_{ij} = \rho\partial\psi/\partial\varepsilon_{ij}$. For constant stresses, it then follows that

$$
\frac{\partial^2\psi}{\partial\theta\partial\varepsilon_{ij}}\dot\theta + \frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial\varepsilon_{kl}}\dot\varepsilon_{kl} = 0
$$

	E [Pa]	ν	α [$\frac{1}{K}$]	ρ [$\frac{\text{kg}}{\text{m}^3}$]
Steel	$2 \cdot 10^{11}$	0.3	$1.1 \cdot 10^{-5}$	$7.8 \cdot 10^3$
Aluminum alloys	$0.7 \cdot 10^{11}$	0.3	$2.3 \cdot 10^{-5}$	$2.7 \cdot 10^3$
Concrete	$0.3 \cdot 10^{11}$	0.15	$1.0 \cdot 10^{-5}$	$2.4 \cdot 10^3$

Table 21.1: Approximative material parameters at room temperature.

Use of (21.19) then gives

$$\dot{\varepsilon}_{ij} = -\rho C_{ijkl}\frac{\partial^2\psi}{\partial\theta\partial\varepsilon_{kl}}\dot{\theta}$$

With this expression and (21.78) inserted into (21.79), we obtain the result

$$c_\sigma - c_\varepsilon = \rho\theta\frac{\partial^2\psi}{\partial\theta\partial\varepsilon_{ij}}C_{ijkl}\frac{\partial^2\psi}{\partial\theta\partial\varepsilon_{kl}} \tag{21.80}$$

Since the flexibility tensor C_{ijkl} is positive definite, we conclude, as expected, that $c_\sigma \geq c_\varepsilon$.

To evaluate (21.80) in more detail, we assume that D_{ijkl} and β_{ij} appearing in (21.17) are temperature independent; we then obtain

$$\frac{\partial^2\psi}{\partial\theta\partial\varepsilon_{ij}} = -\frac{1}{\rho}\beta_{ij} \quad \text{temperature-independent properties}$$

Insertion of this expression and of (21.19) into (21.80) then results in

$$c_\sigma - c_\varepsilon = \frac{\theta}{\rho}\alpha_{ij}D_{ijkl}\alpha_{kl} \quad \textit{temperature-independent properties} \tag{21.81}$$

If we, furthermore, assume isotropy, where D_{ijkl} is given by (4.89), and $\alpha_{ij} = \alpha\delta_{ij}$, where α is the thermal expansion coefficient, (21.81) reduces to

$$c_\sigma - c_\varepsilon = \frac{9K\alpha^2}{\rho}\theta \quad \begin{array}{l}\textit{isotropy} \\ \textit{temperature-independent properties}\end{array} \tag{21.82}$$

where K is the bulk modulus.

Some approximative material parameters are given in Tables 21.1 and 21.2. From the values of Table 21.2 it appears that, at room temperature, the difference between c_σ and c_ε, in practice, is negligible. Moreover, when measuring the

| | $9K\alpha^2/\rho$ | c_σ | $3K\alpha$ | ρc_σ | $\dfrac{c_\sigma - c_\varepsilon}{c_\sigma}$ |
	$[\frac{\text{Nm}}{\text{kgK}^2}]$	$[\frac{\text{Nm}}{\text{kg }K}]$	$[\frac{N}{\text{m}^2 K}]$	$[\frac{N}{\text{m}^2 K}]$	$[\%\,]$
Steel	$2.3 \cdot 10^{-2}$	480	$5.5 \cdot 10^6$	$3.7 \cdot 10^6$	1.4
Aluminum alloys	$10 \cdot 10^{-2}$	960	$5.8 \cdot 10^6$	$2.6 \cdot 10^6$	3.1
Concrete	$0.54 \cdot 10^{-2}$	900	$1.9 \cdot 10^6$	$2.2 \cdot 10^6$	0.2

Table 21.2: Approximative material parameters at room temperature.

specific heat capacity of a solid, the specimen is not exposed to mechanical loading, i.e. $\sigma_{ij} = 0$. In conclusion:

> *In practice, c_σ is the specific heat capacity that is measured. However, the c_σ– and c_ε–values are very close to each other*

(21.83)

Very often the specific heat capacity only varies slowly with temperature; if, therefore, c_ε as given by (21.78) is assumed to be constant, the free energy can be obtained by integration and the result becomes

$$\psi(\theta, \varepsilon_{ij} - \varepsilon_{ij}^{ie}, \kappa_\alpha) = K_1 + c_\varepsilon(\theta - \theta \ln \frac{\theta}{\theta^*})$$
$$+\theta p(\varepsilon_{ij} - \varepsilon_{ij}^{ie}, \kappa_\alpha) + q(\varepsilon_{ij} - \varepsilon_{ij}^{ie}, \kappa_\alpha)$$

where K_1 is an arbitrary constant and θ^* an arbitrary constant temperature whereas p and q denote arbitrary functions. Considering for simplicity thermo-elasticity and by proper choices of the functions p and q, we obtain

$$\psi(\theta, \varepsilon_{ij}) = pK_1 + \rho c_\varepsilon(\theta - \theta \ln \frac{\theta}{\theta^*})$$
$$+ \frac{1}{2}\varepsilon_{ij}D_{ijkl}\varepsilon_{kl} - \beta_{ij}(\theta - \theta_o)\varepsilon_{ij}$$

(21.84)

which holds for thermo-elasticity with constant material parameters; it is evident that formulation (21.17) can be adapted to coincide with the expression above.

With this discussion of the specific heat capacity, we now finally turn to a derivation of the heat equation from the first law. From the first law (21.1) and (21.4), we have

$$\rho(\dot{\psi} + \dot{s}\theta + s\dot{\theta}) = \dot{\varepsilon}_{ij}\sigma_{ij} + r - q_{i,i}$$

(21.85)

With $\dot{\psi}$ and $\dot{s}$ given by (21.73) and (21.74) respectively, insertion of these ex-

pressions into (21.85) results in

$$-\rho\theta\frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial\theta}\dot{\varepsilon}_{ij} + \rho(\theta\frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial\theta} - \frac{\partial\psi}{\partial\varepsilon_{ij}})\dot{\varepsilon}_{ij}^{ie} + (\rho\frac{\partial\psi}{\partial\varepsilon_{ij}} - \sigma_{ij})\dot{\varepsilon}_{ij}$$

$$+ \rho(\frac{\partial\psi}{\partial\kappa_\alpha} - \theta\frac{\partial^2\psi}{\partial\theta\partial\kappa_\alpha})\dot{\kappa}_\alpha - \rho\theta\frac{\partial^2\psi}{\partial\theta^2}\dot{\theta} = r - q_{i,i}$$

With c_ε defined by (21.78) and the heat flux vector q_i given by Fourier's law (21.59), we finally obtain

$$\boxed{\begin{array}{l} \textit{Coupled heat equation} \\[4pt] \rho c_\varepsilon\dot{\theta} = (k_{ij}\theta_{,j})_{,i} + r \\[4pt] \qquad + \rho\theta\frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial\theta}(\dot{\varepsilon}_{ij} - \dot{\varepsilon}_{ij}^{ie}) + \rho\frac{\partial\psi}{\partial\varepsilon_{ij}}\dot{\varepsilon}_{ij}^{ie} \\[4pt] \qquad + (\sigma_{ij} - \rho\frac{\partial\psi}{\partial\varepsilon_{ij}})\dot{\varepsilon}_{ij} - \rho(\frac{\partial\psi}{\partial\kappa_\alpha} - \theta\frac{\partial^2\psi}{\partial\theta\partial\kappa_\alpha})\dot{\kappa}_\alpha \end{array}} \tag{21.86}$$

It appears that determination of the temperature distribution within the body is coupled not only to the strain rate $\dot{\varepsilon}_{ij}$, but also to the inelastic rates $\dot{\varepsilon}_{ij}^{ie}$ and $\dot{\kappa}_\alpha$. Therefore (21.86) comprises a coupled problem and it can only be solved if the equations for $\dot{\varepsilon}_{ij}$, $\dot{\varepsilon}_{ij}^{ie}$ and $\dot{\kappa}_\alpha$ are solved simultaneously.

Let us consider a different format of the coupled heat equation which is based on the entropy. Taking advantage of (21.73) in (21.85) leads to

$$\boxed{\begin{array}{l} \textit{Coupled heat equation} \\[4pt] \rho\theta\dot{s} = \gamma_{mech} + r - q_{i,i} \\[4pt] \textit{where} \\[4pt] \gamma_{mech} = \rho\frac{\partial\psi}{\partial\varepsilon_{ij}}\dot{\varepsilon}_{ij}^{ie} + (\sigma_{ij} - \rho\frac{\partial\psi}{\partial\varepsilon_{ij}})\dot{\varepsilon}_{ij} - \rho\frac{\partial\psi}{\partial\kappa_\alpha}\dot{\kappa}_\alpha \end{array}} \tag{21.87}$$

This neat alternative formulation of the heat equation is occasionally preferred in numerical computations; in the following, however, we choose to work with the temperature instead of its conjugated quantity, the entropy.

It may be of interest to evaluate (21.86) for thermo-elastic behavior. In that case $\dot{\varepsilon}_{ij}^{ie} = \dot{\kappa}_\alpha = 0$, $\sigma_{ij} = \rho\partial\psi/\partial\varepsilon_{ij}$ and we obtain

$$\boxed{\begin{array}{l} \textit{Coupled heat equation for thermo-elasticity} \\[4pt] \rho c_\varepsilon\dot{\theta} = (k_{ij}\theta_{,j})_{,i} + r + \rho\theta\frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial\theta}\dot{\varepsilon}_{ij} \end{array}} \tag{21.88}$$

and the solution of this equation is still coupled to the development of $\dot{\varepsilon}_{ij}$. If, furthermore, both D_{ijkl} and β_{ij} in (21.17) and (21.19) are assumed to be independent of the temperature, we have

$$\rho \frac{\partial^2 \psi}{\partial \varepsilon_{ij} \partial \theta} = -\beta_{ij} = -D_{ijkl}\alpha_{kl}$$

and (21.88) turns into

$$\rho c_\varepsilon \dot{\theta} = (k_{ij}\theta_{,j})_{,i} + r - \theta \dot{\varepsilon}_{ij} D_{ijkl}\alpha_{kl}$$

If, in addition, isotropy is assumed this expression reduces to

> *Coupled heat equation for isotropic thermo-elasticity*
> *and temperature-independent values of E, ν and α*
>
> $\rho c_\varepsilon \dot{\theta} = (k\theta_{,i})_{,i} + r - 3K\alpha\theta\dot{\varepsilon}_{ii}$ (21.89)

where, for isotropy, we have $k_{ij} = k\delta_{ij}$ with k being the thermal conductivity. It appears that it is only the volumetric part of the strain rate that contributes to the coupling between strains and temperature. This coupled heat equation for thermo-elasticity was derived by Duhamel already in 1837.

Expression (21.89) may be used to determine the thermo-elastic response for specimens subjected to a homogeneous stress state and loaded either during isothermal or adiabatic conditions. Since an isotropic material is considered, (21.18) reduces to

$$s_{ij} = 2Ge_{ij}; \qquad \sigma_{kk} = 3K[\varepsilon_{kk} - 3\alpha(\theta - \theta_o)] \qquad (21.90)$$

Let the surroundings of the specimen be kept at a constant temperature. The isothermal condition is then obtained by applying the forces on the specimen so slowly that any temperature difference between the specimen and the surroundings is allowed to disappear. The mechanical loading is obtained by prescribing the stresses; since $\theta = \theta_o$ (21.90) gives

$$\varepsilon_{kk} = \frac{\sigma_{kk}}{3K} \qquad (21.91)$$

Consider next the adiabatic condition where no heat input occurs which is obtained by the conditions $r = 0$ and $\theta_{,i} = 0$. This situation can be achieved if the specimen is loaded very quickly since heat exchange with the surroundings then has no time to take place. In that case (21.89) provides

$$\dot{\theta} = -\frac{3K\alpha}{\rho c_\varepsilon}\theta\dot{\varepsilon}_{kk} \qquad (21.92)$$

Recalling that (21.89) was derived on condition that the material parameters are temperature independent, integration of the expression above gives

$$\ln \frac{\theta}{\theta_o} = -\frac{3K\alpha}{\rho c_\varepsilon}\varepsilon_{kk} \qquad (21.93)$$

We shall later see that the temperature change is very small and we may then write

$$\theta = \theta_o + \Delta\theta \quad \text{where} \quad |\Delta\theta| \ll 1$$

Under these conditions, a Taylor expansion gives

$$\ln\frac{\theta}{\theta_o} = \ln(1 + \frac{\Delta\theta}{\theta_o}) \approx \frac{\Delta\theta}{\theta_o} = \frac{\theta - \theta_o}{\theta_o} \approx \frac{\theta - \theta_o}{\theta}$$

and then (21.93) becomes

$$\theta - \theta_o = -\frac{3K\alpha}{\rho c_\varepsilon}\theta\varepsilon_{kk} \tag{21.94}$$

Insertion into (21.90) provides

$$\varepsilon_{kk} = \frac{\sigma_{kk}}{3K(1 + \frac{9K\alpha^2\theta}{\rho c_\varepsilon})} \tag{21.95}$$

which can be written as

$$\varepsilon_{kk} = \frac{\sigma_{kk}}{3K_{ad}} \quad \text{where} \quad K_{ad} = K(1 + \frac{9K\alpha^2\theta}{\rho c_\varepsilon}) \tag{21.96}$$

where K_{ad} is the apparent bulk modulus during adiabatic loading. During isothermal loading we have (21.91), i.e. $K_{iso} = K$ and (21.96b) may then be written as

$$\boxed{\frac{K_{ad}}{K_{iso}} = 1 + \frac{9K\alpha^2\theta}{\rho c_\varepsilon}}$$

where $K_{iso} = K$. It appears that the material behaves in a stiffer manner during adiabatic loading than during isothermal loading. However, this effect is most often extremely small and for steel we find from Table 21.2 - and recalling that $c_\sigma \approx c_\varepsilon$ - that at room temperature, we have $K_{ad}/K_{iso} \approx 1.014$.

Let us return to (21.94) and demonstrate that the temperature change for thermo-elastic materials during adiabatic conditions is indeed very small. Combination of (21.94) and (21.95) and taking advantage of (21.82) give

$$\theta - \theta_o = -\frac{\alpha\theta\sigma_{kk}}{\rho c_\sigma}$$

Since $\theta - \theta_o$ is very small, we have $\theta \approx \theta_o$, i.e.

$$\boxed{\begin{array}{l}\textit{Kelvin's expression for thermo-elasticity}\\[2mm] \theta - \theta_o = -\dfrac{\alpha\theta_o\sigma_{kk}}{\rho c_\sigma}\end{array}} \tag{21.97}$$

This expression was established by Lord Kelvin already in 1855 and it is called the *Kelvin effect*. For hydrostatic tension, it implies a fall in temperature whereas hydrostatic compression gives rise to a temperature increase and it may be considered as the counterpart to the same phenomenon for gases. However, this effect is very modest. As an example, consider uniaxial loading where $\sigma_{kk} = \sigma$; referring to Tables 21.1 and 21.2, we find for steel at room temperature that a sudden application of a tensile stress of 200 MPa results in a temperature drop of about $0.17\,^\circ C$.

We have demonstrated that straining of a thermo-elastic material in itself only influences the temperature to a very modest degree. In general however, when thermo-elastic behavior is considered the material is not only exposed to mechanical loading, but also to significant temperature loadings that, in turn, influence the stress and strain state, and the problem of coupling effects then becomes more complex. In order to evaluate the coupling effect apparent from (21.89) in such cases, we rewrite this expression according to

$$\rho c_\varepsilon \dot{\theta}(1 + M) = (k\theta_{,i})_{,i} + r \tag{21.98}$$

where the coupling term M is given by

$$M = \frac{9K\alpha^2\theta}{\rho c_\varepsilon} \frac{\dot{\varepsilon}_{ii}}{3\alpha\dot{\theta}}$$

The term $\dot{\varepsilon}_{ii}/(3\alpha\dot{\theta})$ is a natural quantity, since it is the ratio of the total volumetric strain rate to the volumetric thermal strain rate. We can ignore the coupling effect if $M \ll 1$, i.e.

$$\frac{\dot{\varepsilon}_{ii}}{3\alpha\dot{\theta}} \ll \frac{\rho c_\varepsilon}{9K\alpha^2\theta}$$

According to Table 21.2, at room temperature the term $\rho c_\varepsilon/(9K\alpha^2\theta)$ is 71, 33 and 569 for steel, aluminum and concrete, respectively. We can safely replace these restrictions by a stronger condition and - traditionally - one chooses $\dot{\varepsilon}_{ii}/(3\alpha\dot{\theta}) \ll 20$; in that case the coupling term M in (21.98) can be ignored. In conclusion

$$\boxed{\begin{array}{l} \textit{If } \frac{\dot{\varepsilon}_{ii}}{3\alpha\dot{\theta}} \ll 20 \textit{ then} \\[4pt] \textit{the uncoupled heat equation} \\[4pt] \rho c_\varepsilon = (k\theta_{,i})_{,i} + r \\[4pt] \textit{holds for thermo-elasticity with close accuracy} \end{array}} \tag{21.99}$$

The condition $\dot{\varepsilon}_{ii}/(3\alpha\dot{\theta}) \ll 20$ does not seem to be a severe restriction, since we intuitively expect the total volumetric strain rate $\dot{\varepsilon}_{ii}$ to be of the same order of magnitude as the volumetric thermal strain rate $3\alpha\dot{\theta}$. Indeed - and as already discussed - this restriction turns out to be fulfilled in most cases of practical interest

and the reader is referred to Boley and Weiner (1960) for a further evaluation of this issue.

After this discussion of thermo-elasticity, we return to the general coupled heat equation given by (21.86). If the loading is performed very quickly, no heat exchange can occur with the surroundings of the body. Moreover, this rapid loading does not allow any heat flow to take place. Disregarding heat flow can be obtained by ignoring the heat flux vector $q_i = -k_{ij}\theta_{,j}$, i.e. by putting $k_{ij}\theta_{,j} = 0$. Likewise, since no heat exchange with the surroundings is possible, we put $r = 0$. These conditions are called *adiabatic heating* and (21.86) then reduces to

$$
\boxed{
\begin{aligned}
&\textit{Adiabatic heating}\\[4pt]
&\rho c_\varepsilon \dot\theta = \sigma_{ij}\dot\varepsilon_{ij}^{ie} + \left(\sigma_{ij} - \rho\frac{\partial\psi}{\partial\varepsilon_{ij}}\right)\dot\varepsilon_{ij}\\[6pt]
&\quad +\rho\theta\frac{\partial^2\psi}{\partial\varepsilon_{ij}\partial\theta}(\dot\varepsilon_{ij} - \dot\varepsilon_{ij}^{ie}) - \rho\left(\frac{\partial\psi}{\partial\kappa_\alpha} - \theta\frac{\partial^2\psi}{\partial\theta\partial\kappa_\alpha}\right)\dot\kappa_\alpha
\end{aligned}
}
\tag{21.100}
$$

For a given stress state σ_{ij} and a given expression for the free energy ψ, then once the quantities $\dot\varepsilon_{ij}$, $\dot\varepsilon_{ij}^{ie}$ and $\dot\kappa_\alpha$ are known, the right-hand side of this expression is known and (21.100) then determines directly the temperature rate $\dot\theta$. That is, the temperature change can be determined without solving any field problem that involves the boundary conditions of the body; instead the problem is solved directly at each point in the body. For isotropic thermo-elasticity with temperature-independent material properties (21.100) reduces to (21.92). It should also be emphasized that (21.100) for an inhomogeneously loaded body allows the development of an inhomogeneous temperature distribution over the body. This inhomogeneous temperature field is allowed to exist since the loading was assumed to be so rapid that heat flow within the body has no time to take place.

It is noted, however, that since $\dot\varepsilon_{ij}$, $\dot\varepsilon_{ij}^{ie}$ and $\dot\kappa_\alpha$, in general, depends on $\dot\theta$, expression (21.100) still defines a coupled problem in the numerical sense (but it is not a coupled boundary value problem). Numerical solution strategies for this problem as well as the general case of the coupled heat equation (21.86) will be discussed later on in Chapter 23.

Expression (21.100) determines the temperature change that results from mechanical loading alone. For thermo-elasticity, we have seen that this effect is very modest, cf. the discussion of (21.97). For inelastic materials, however, the effect may be very significant and we shall return to this aspect in Chapter 23.

With evident notation, (21.100) may be written as

$$\rho c_\varepsilon \dot\theta = \sigma_{ij}\dot\varepsilon_{ij}^{ie} + Y$$

From the experiments of Taylor and Quinney (1934) for steel and metals it is found that

$$
\boxed{\rho c_\varepsilon \dot\theta = \eta\sigma_{ij}\dot\varepsilon_{ij}^{ie} \quad \textit{Adiabatic heating}}
\tag{21.101}
$$

where $\eta \approx 0.90 - 0.95$. It appears that $Y \approx -(0.05 - 0.10)\sigma_{ij}\dot{\varepsilon}_{ij}^{ie}$ and since Y has the dimension of energy rate [Nm/(m³s)], it follows that the material absorbs a certain energy that does not manifest itself in terms of a temperature increase. Instead, this absorbed energy is used to transform the microstructure of the material by phase changes, pile-up of dislocations etc. The absorbed energy therefore transforms into *latent heat* that can be recovered when the material is heated, i.e. annealed, cf. the discussion of Taylor and Quinney (1934) and Bever *et al.* (1973).

In many applications in the literature, the factor η in (21.101) is treated as a material constant. However, if (21.100) is written in the form (21.101) it is evident that η must depend on the evolution laws for $\dot{\kappa}_{\alpha}$ and $\dot{\varepsilon}_{ij}^{ie}$ and on the stresses σ_{ij} and the thermodynamic forces $K_{\alpha}(= \rho\partial\psi/\partial\kappa_{\alpha})$ and - despite the traditional attitude in the literature - it is not surprising that η for a given material will not become a constant. In recent years, there has been an increasing interest for theoretical determination of the η-factor and detailed considerations are presented by Chaboche (1993b), Kamlah and Haupt (1998) and Rosakis *et al.* (2000).

21.5 Properties of state functions at thermodynamical equilibrium

We will now consider a body at a state where no mechanical work input or heat input occur. Following (20.62), the body is then in thermodynamical equilibrium, if no changes of the state variables can occur. In (20.63) and following Gibbs, it was then concluded that when the internal energy is constant, thermodynamic equilibrium exists when the entropy attains a maximum value. We will now express these properties in precise mathematical terms by which we can characterize the properties of the state functions at thermodynamical equilibrium; in particular we want to identify which properties the free energy ψ must possess in order to achieve thermodynamic equilibrium.

According to (21.4), we have

$$u = \psi + s\theta$$

Differentiation with respect to time and use of (21.37) results in

$$\dot{u} = \theta\dot{s} + \frac{\partial\psi}{\partial\varepsilon_{ij}}(\dot{\varepsilon}_{ij} - \dot{\varepsilon}_{ij}^{ie}) + \frac{\partial\psi}{\partial\kappa_{\alpha}}\dot{\kappa}_{\alpha} \qquad (21.102)$$

The internal energy is a state function and the expression above suggests that

$$u = u(s, \varepsilon_{ij} - \varepsilon_{ij}^{ie}, \kappa_{\alpha})$$

Differentiation of the expression and comparison with (21.102) provides

$$\frac{\partial u}{\partial s} = \theta ; \qquad \frac{\partial u}{\partial\varepsilon_{ij}} = \frac{\partial\psi}{\partial\varepsilon_{ij}} ; \qquad \frac{\partial u}{\partial\kappa_{\alpha}} = \frac{\partial\psi}{\partial\kappa_{\alpha}}$$

Since $\theta > 0$, (21.102) may be solved for $\dot{s}$ to obtain

$$\dot{s} = \frac{1}{\theta}\dot{u} - \frac{1}{\theta}\frac{\partial\psi}{\partial\varepsilon_{ij}}(\dot{\varepsilon}_{ij} - \dot{\varepsilon}_{ij}^{ie}) - \frac{1}{\theta}\frac{\partial\psi}{\partial\kappa_{\alpha}}\dot{\kappa}_{\alpha} \qquad (21.103)$$

The entropy s is a state function and we must therefore have

$$s = s(u, \varepsilon_{ij} - \varepsilon_{ij}^{ie}, \kappa_{\alpha})$$

i.e.

$$\dot{s} = \frac{\partial s}{\partial u}\dot{u} + \frac{\partial s}{\partial\varepsilon_{ij}}(\dot{\varepsilon}_{ij} - \dot{\varepsilon}_{ij}^{ie}) + \frac{\partial s}{\partial\kappa_{\alpha}}\dot{\kappa}_{\alpha} \qquad (21.104)$$

A comparison of this expression with (21.103) shows that

$$\frac{\partial s}{\partial u} = \frac{1}{\theta}; \quad \frac{\partial s}{\partial\varepsilon_{ij}} = -\frac{1}{\theta}\frac{\partial\psi}{\partial\varepsilon_{ij}}; \quad \frac{\partial s}{\partial\kappa_{\alpha}} = -\frac{1}{\theta}\frac{\partial\psi}{\partial\kappa_{\alpha}} \qquad (21.105)$$

With these preliminaries we now consider a situation where the internal energy u is constant and where the entropy s attains a maximum value at thermodynamic equilibrium. Therefore $\dot{u} = \dot{s} = 0$ and (21.104) then provides

$$\frac{\partial s}{\partial\varepsilon_{ij}}(\dot{\varepsilon}_{ij} - \dot{\varepsilon}_{ij}^{ie}) + \frac{\partial s}{\partial\kappa_{\alpha}}\dot{\kappa}_{\alpha} = 0 \qquad (21.106)$$

Moreover, following Appendix (A.12) the condition that $s = s(u, \varepsilon_{ij} - \varepsilon_{ij}^{ie}, \kappa_{\alpha})$ for constant u attains a maximum value can be expressed as

$$(\dot{\varepsilon}_{ij} - \dot{\varepsilon}_{ij}^{ie})\frac{\partial^2 s}{\partial\varepsilon_{ij}\partial\varepsilon_{kl}}(\dot{\varepsilon}_{kl} - \dot{\varepsilon}_{kl}^{ie})$$
$$+ 2(\dot{\varepsilon}_{ij} - \dot{\varepsilon}_{ij}^{ie})\frac{\partial^2 s}{\partial\varepsilon_{ij}\partial\kappa_{\alpha}}\dot{\kappa}_{\alpha} + \dot{\kappa}_{\alpha}\frac{\partial^2 s}{\partial\kappa_{\alpha}\partial\kappa_{\beta}}\dot{\kappa}_{\beta} < 0 \qquad (21.107)$$

This is simply to say that the entropy s at thermodynamic equilibrium is a concave function with respect to the variables $\varepsilon_{ij} - \varepsilon_{ij}^{ie}$ and κ_{α}.

Having identified in mathematical terms the properties of the entropy s, we will now identify the corresponding properties for Helmholtz' free energy ψ. Insertion of (21.105b) and (21.105c) into (21.106) and (21.107) gives the results sought for

$$\boxed{\begin{array}{l}\textit{At thermodynamic equilibrium}\\[4pt] \dfrac{\partial\psi}{\partial\varepsilon_{ij}}(\dot{\varepsilon}_{ij} - \dot{\varepsilon}_{ij}^{ie}) + \dfrac{\partial\psi}{\partial\kappa_{\alpha}}\dot{\kappa}_{\alpha} = 0\end{array}} \qquad (21.108)$$

and

$$
\boxed{
\begin{aligned}
&At\ thermodynamic\ equilibrium \\[4pt]
&(\dot{\varepsilon}_{ij} - \dot{\varepsilon}_{ij}^{ie})\frac{\partial^2 \psi}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}}(\dot{\varepsilon}_{kl} - \dot{\varepsilon}_{kl}^{ie}) \\[4pt]
&+ 2(\dot{\varepsilon}_{ij} - \dot{\varepsilon}_{ij}^{ie})\frac{\partial^2 \psi}{\partial \varepsilon_{ij} \partial \kappa_\beta}\dot{\kappa}_\beta + \dot{\kappa}_\alpha \frac{\partial^2 \psi}{\partial \kappa_\alpha \partial \kappa_\beta}\dot{\kappa}_\beta > 0
\end{aligned}
}
\qquad (21.109)
$$

which according to Appendix (A.8) means that Helmholtz' free energy ψ is a convex function with respect to the variables $\varepsilon_{ij} - \varepsilon_{ij}^{ie}$ and κ_α.

From (21.37) we have $s = -\partial \psi / \partial \theta$ and differentiation gives

$$
\dot{s} = -[\frac{\partial^2 \psi}{\partial \theta^2}\dot{\theta} + \frac{\partial^2 \psi}{\partial \theta \partial \varepsilon_{mn}}(\dot{\varepsilon}_{mn} - \dot{\varepsilon}_{mn}^{ie}) + \frac{\partial^2 \psi}{\partial \theta \partial \kappa^\gamma}\dot{\kappa}^\gamma]
$$

and as $\dot{s} = 0$ holds at thermodynamic equilibrium we obtain

$$
\dot{\theta} = -\frac{\theta}{c_\varepsilon}[\frac{\partial^2 \psi}{\partial \theta \partial \varepsilon_{mn}}(\dot{\varepsilon}_{mn} - \dot{\varepsilon}_{mn}^{ie}) + \frac{\partial^2 \psi}{\partial \theta \partial \kappa^\gamma}\dot{\kappa}^\gamma]
$$

However, by using (21.108) in this expression we obtain

$$
\boxed{\dot{\theta} = 0 \quad at\ thermodynamic\ equilibrium}
$$

We will now prove that the free energy ψ not only is a convex function in $\varepsilon_{ij} - \varepsilon_{ij}^{ie}$ and κ_α, but also that it attains a minimum at thermodynamic equilibrium. Since $\psi = \psi(\theta, \varepsilon - \varepsilon_{ij}^{ie}, \kappa_\alpha)$ we obtain with the expression above as well as (21.108)

$$
\boxed{\dot{\psi} = 0 \quad at\ thermodynamic\ equilibrium}
$$

This result combined with (21.109) shows that ψ attains a minimum value at thermodynamic equilibrium. According to (21.78) the specific heat capacity c_ε is defined by $c_\varepsilon = -\theta \partial^2 \psi / \partial \theta^2$ and as $\theta > 0$ and we certainly expect the heat capacity to be positive, we conclude that ψ is a concave function of the absolute temperature θ.

Let us finally specialize to thermo-elasticity, where the internal variables ε_{ij}^{ie} and κ_α do not exist and where (21.109) reduces to

$$
\dot{\varepsilon}_{ij}\frac{\partial^2 \psi}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}}\dot{\varepsilon}_{kl} > 0
\qquad (21.110)
$$

We do not expect any peculiarities connected with thermo-elasticity; therefore, it seems reasonable to expect that thermo-elastic materials are stable in a thermodynamic sense and we therefore expect the expression above to be fulfilled.

Since $\partial^2\psi/\partial\varepsilon_{ij}\partial\varepsilon_{kl} = D_{ijkl}/\rho$, cf. (21.19), we conclude that (21.110) is fulfilled for

$$\boxed{D_{ijkl} \quad \textit{is positive definite}}$$

That the elastic stiffness tensor D_{ijk} is positive definite is precisely what we anticipated already in Chapter 4, cf. (4.24) and (4.25), and for isotropic elasticity this is fulfilled when $E > 0$ and $-1 < \nu < \frac{1}{2}$, cf. (4.96).