

## 2.2 Thermoelasticity

In this section, thermoelasticity is considered. By definition, the constitutive relations for such a material depend only on the set of field variables  $\{\mathbf{F}, \theta, \text{Grad}\theta\}$ . This general case will be considered toward the end of this section. Simpler cases, isothermal  $\{\mathbf{F}\}$ , small-strain  $\{\boldsymbol{\varepsilon}\}$ , one-dimensional  $\{\varepsilon\}$ , will be considered first.

In what follows, upper case letters will be used to denote the energy potentials *per unit volume*. As before, lower case denotes *per unit mass* so, for example,  $U = \rho u$  for internal energy.

### 2.2.1 Isothermal Small Strain Elasticity

For isothermal deformations, the basic thermodynamic statement can be written as (see Eqn. 1.6.24)

$$\begin{aligned}\boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} &= \rho \dot{\psi} + \rho \phi \\ &= \dot{\Psi} + \Phi\end{aligned}\tag{2.2.1}$$

where

$$\begin{aligned}\dot{\Psi} &= \rho \dot{\psi} && \text{(rate of change of the free energy per unit volume)} \\ \Phi &= \rho \phi \geq 0 && \text{(dissipation per unit volume)}\end{aligned}$$

In isothermal elasticity<sup>1</sup>,  $\Phi = 0$ , and so one need only specify a free energy function.

#### One-Dimensional Analysis

Consider a simple one-dimensional extension of material. The free energy is a function of kinematic state variables. The only state variable is the single strain  $\varepsilon$  and the only stress is  $\sigma$  and hence

$$\sigma \dot{\varepsilon} = \dot{\Psi}(\varepsilon)\tag{2.2.2}$$

i.e.

$$\sigma \dot{\varepsilon} = \frac{d\Psi(\varepsilon)}{d\varepsilon} \dot{\varepsilon}\tag{2.2.3}$$

so that, since  $\dot{\varepsilon}$  is arbitrary,

$$\sigma = \frac{d\Psi(\varepsilon)}{d\varepsilon}\tag{2.2.4}$$

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<sup>1</sup> this is discussed more rigorously in §2.2.2 below

which agrees with the general relation 1.6.33d. This is the stress-strain (constitutive) equation. In the context of elasticity theory, the Helmholtz free energy function is the elastic strain energy function (Eqn. 2.2.4 is the same as Part I, Eqn. 5.4.9).

The classical linear elastic material corresponds to choosing a simple quadratic free energy function:

$$\Psi(\varepsilon) = \frac{1}{2} E \varepsilon^2 \quad (2.2.5)$$

so

$$\sigma = E \varepsilon, \quad \dot{\sigma} = E \dot{\varepsilon} \quad (2.2.6)$$

A nonlinear example is

$$\begin{aligned} \Psi(\varepsilon) &= E_0 \varepsilon + E_1 \frac{\varepsilon^2}{2} + E_2 \frac{\varepsilon^3}{3} + E_3 \frac{\varepsilon^4}{4} \\ \sigma(\varepsilon) &= E_0 + E_1 \varepsilon + E_2 \varepsilon^2 + E_3 \varepsilon^3 \\ \dot{\sigma} &= (\partial \sigma / \partial \varepsilon) \dot{\varepsilon} \\ &= (E_1 + 2E_2 \varepsilon + 3E_3 \varepsilon^2) \dot{\varepsilon} \end{aligned} \quad (2.2.7)$$

One should ensure that (at least (1))

- (1)  $\sigma(0) = 0$  (zero strain at zero stress) which implies that  $E_0 = 0$
- (2)  $(d\sigma/d\varepsilon)_{\varepsilon=0} \neq 0$  (so one has a non-zero initial modulus)
- (3)  $(d^2\sigma/d\varepsilon^2)_{\varepsilon=0} = 0$  (so that, with (2), the origin is a point of inflection, ensuring similar tensile and compressive strain behaviour)

Note that  $\Psi$  has the dimensions of stress, so that the  $E_i$  also have the dimensions of stress.

In the **rate formulation**:  $\dot{\sigma} = D \dot{\varepsilon}$ ,  $D$  is the **instantaneous elastic modulus** (or **stiffness**)  $d\sigma/d\varepsilon$  or  $d^2\Psi/d\varepsilon^2$ .  $D$  is a constant in the linear model, but is, in general, a function of strain, as in the above example, where  $D = E_1 + 2E_2\varepsilon + 3E_3\varepsilon^2$ .

### Three-dimensional Analysis

Generalising the above to three dimensions, the free energy function is

$$\Psi(\varepsilon_{ij}) \quad \Psi(\boldsymbol{\varepsilon}) \quad (2.2.8)$$

so that the basic thermomechanical identity becomes

$$\sigma_{ij} \dot{\varepsilon}_{ij} = \dot{\Psi}(\varepsilon_{ij}) = \frac{\partial \Psi}{\partial \varepsilon_{ij}} \dot{\varepsilon}_{ij} \quad \boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} = \dot{\Psi}(\boldsymbol{\varepsilon}) = \frac{d\Psi}{d\boldsymbol{\varepsilon}} : \dot{\boldsymbol{\varepsilon}} \quad (2.2.9)$$

Since this again holds for all strain rates one can deduce that

$$\sigma_{ij} = \frac{\partial \Psi}{\partial \varepsilon_{ij}} \quad \boldsymbol{\sigma} = \frac{d\Psi}{d\boldsymbol{\varepsilon}} \quad (2.2.10)$$

Again, for the linear elastic material, the free energy function is assumed to be a quadratic function of the strain:

$$\Psi = \frac{1}{2} D_{ijkl} \varepsilon_{ij} \varepsilon_{kl} \quad \Psi = \frac{1}{2} \boldsymbol{\varepsilon} : \mathbf{D} : \boldsymbol{\varepsilon} \quad (2.2.11)$$

so that

$$\begin{aligned} \sigma_{mn} &= \frac{\partial \Psi}{\partial \varepsilon_{mn}} \\ &= \frac{1}{2} D_{ijkl} \frac{\partial \varepsilon_{ij}}{\partial \varepsilon_{mn}} \varepsilon_{kl} + \frac{1}{2} D_{ijkl} \varepsilon_{ij} \frac{\partial \varepsilon_{kl}}{\partial \varepsilon_{mn}} \\ &= \frac{1}{2} D_{mnlk} \varepsilon_{kl} + \frac{1}{2} D_{ijmn} \varepsilon_{ij} \\ &= D_{mnlk} \varepsilon_{kl} \end{aligned} \quad (2.2.12)$$

provided the fourth order stiffness tensor  $\mathbf{D}$  possesses the major symmetry:

$$D_{ijkl} = D_{klij} \quad (2.2.13)$$

( $\mathbf{D}$  satisfies the minor symmetries  $D_{ijkl} = D_{jikl}$  and  $D_{ijkl} = D_{ijlk}$  by virtue of the symmetry of the stress and strain.)

Eqn. 2.1.12 is the stress-strain equation for an anisotropic linear elastic material. The rate form is formally

$$\dot{\sigma}_{ij} = D_{ijkl} \dot{\varepsilon}_{kl} \quad (2.2.14)$$

For a nonlinear material  $\Psi$  is no longer quadratic, and the instantaneous modulus tensor is a function of the strains.

If one starts by proposing the rate form of the elastic law, with a given modulus function  $\mathbf{D}(\boldsymbol{\varepsilon})$ , then in general one cannot integrate Eqn. 2.2.14 to find a free energy function (although one can achieve this in one-dimension). Such a model is termed **hypoelastic**. A model in which  $\Psi$  does exist is called **hyperelastic**. Hyperelastic models automatically satisfy the laws of thermomechanics, hypoelastic ones do not.

Note that the strain energy must be positive,  $\Psi > 0$ . From 2.2.11, this implies that

$$D_{ijkl} \varepsilon_{ij} \varepsilon_{kl} > 0 \quad \boldsymbol{\varepsilon} : \mathbf{D} : \boldsymbol{\varepsilon} > 0 \quad (2.2.15)$$

for all strain tensors, that is, the stiffness tensor must be positive definite.

## Isotropic Elasticity

The theory of isotropic elasticity with small strains is a special case of that for large strains discussed in Part III, §4.4. The theory discussed there applies here, only now with the left Cauchy Green strain replaced by the small strain tensor. Thus, the free energy function must be a function of a set of three invariants of the strain tensor  $\boldsymbol{\varepsilon}$ ,  $\Psi(E_1, E_2, E_3)$ , which here are taken to be

$$\begin{aligned} E_1 &= \varepsilon_{ii} = \text{tr}\boldsymbol{\varepsilon} \\ E_2 &= \varepsilon_{ij}\varepsilon_{ij} = \text{tr}\boldsymbol{\varepsilon}^2 \\ E_3 &= \varepsilon_{ij}\varepsilon_{jk}\varepsilon_{ki} = \text{tr}\boldsymbol{\varepsilon}^3 \end{aligned} \quad (2.2.16)$$

The stress-strain relation is hence given by:

$$\begin{aligned} \sigma_{ij} &= \frac{\partial\Psi}{\partial\varepsilon_{ij}} \\ &= \frac{\partial\Psi}{\partial E_1} \frac{\partial E_1}{\partial\varepsilon_{ij}} + \frac{\partial\Psi}{\partial E_2} \frac{\partial E_2}{\partial\varepsilon_{ij}} + \frac{\partial\Psi}{\partial E_3} \frac{\partial E_3}{\partial\varepsilon_{ij}} \end{aligned} \quad (2.2.17)$$

It is readily verified that {▲ Problem 1}

$$\begin{aligned} \frac{\partial E_1}{\partial\varepsilon_{ij}} &= \delta_{ij} & \frac{\partial E_1}{\partial\boldsymbol{\varepsilon}} &= \mathbf{I} \\ \frac{\partial E_2}{\partial\varepsilon_{ij}} &= 2\varepsilon_{ij} & \frac{\partial E_2}{\partial\boldsymbol{\varepsilon}} &= 2\boldsymbol{\varepsilon} \\ \frac{\partial E_3}{\partial\varepsilon_{ij}} &= 3\varepsilon_{ik}\varepsilon_{kj} & \frac{\partial E_3}{\partial\boldsymbol{\varepsilon}} &= 3\boldsymbol{\varepsilon}^2 \end{aligned} \quad (2.2.18)$$

so that

$$\boldsymbol{\sigma} = \frac{\partial\Psi}{\partial E_1} \mathbf{I} + 2 \frac{\partial\Psi}{\partial E_2} \boldsymbol{\varepsilon} + 3 \frac{\partial\Psi}{\partial E_3} \boldsymbol{\varepsilon}^2 \quad (2.2.19)$$

which is a quadratic polynomial in the strain tensor. If the free energy function does not depend on the third strain invariant  $E_3$ , the tensor relation is actually linear, though it should be appreciated that the coefficients  $\partial\Psi/\partial E_k$ ,  $k = 1, 2, 3$ , will in general depend in a nonlinear manner on the strain invariants.

The classical linear model is recovered by choosing

$$\Psi = \frac{1}{2} \lambda E_1^2 + \mu E_2 \quad \Psi = \frac{1}{2} \lambda (\text{tr}\boldsymbol{\varepsilon})^2 + \mu \text{tr}\boldsymbol{\varepsilon}^2 \quad (2.2.20)$$

for then

$$\sigma_{ij} = \lambda \varepsilon_{kk} \delta_{ij} + 2\mu \varepsilon_{ij} \quad \boldsymbol{\sigma} = \lambda (\text{tr}\boldsymbol{\varepsilon}) \mathbf{I} + 2\mu \boldsymbol{\varepsilon} \quad (2.2.21)$$

## The Gibbs Function and the Complementary Energy

From section 1.3, the Helmholtz free energy and the Gibbs energy functions are related by a Legendre transformation. Formally, consider again the one-dimensional stress-strain relation 2.2.4:

$$\sigma = \frac{d\Psi(\varepsilon)}{d\varepsilon} \quad (2.2.22)$$

To invert this expression and express the strain as a function of stress, first partially integrate the equation with respect to strain to obtain

$$\sigma\varepsilon = \Psi(\varepsilon) + C(\sigma) \quad (2.2.23)$$

where  $C(\sigma)$  is an arbitrary function of integration, dependent only on stress. Differentiating with respect to  $\sigma$  leads to

$$\varepsilon = \frac{dC(\sigma)}{d\sigma} \quad (2.2.24)$$

which is the inverse of the original equation. From Table 1.3.1, it is clear that the function  $C$  is the negative of the Gibbs energy function (per unit volume). In this context,  $C$  is the complementary energy discussed in Part I, §5.4. One says that the free energy is the **dual** of the complementary energy, and *vice versa*.

For example, if

$$\Psi = K\varepsilon^3, \quad \sigma = 3K\varepsilon^2 \quad (2.2.25)$$

then {▲ Problem 2}

$$C(\sigma) = 2K(\sigma/3K)^{3/2}. \quad (2.2.26)$$

This theory readily extends to the general three dimensional situation. The original stress strain equation is given by 2.2.10 so that

$$\sigma_{ij}\varepsilon_{ij} = \Psi(\varepsilon_{ij}) + C(\sigma_{ij}) \quad \boldsymbol{\sigma} : \boldsymbol{\varepsilon} = \Psi(\boldsymbol{\varepsilon}) + C(\boldsymbol{\sigma}) \quad (2.2.27)$$

and the strains are now

$$\varepsilon_{ij} = \frac{dC(\sigma_{ij})}{d\sigma_{ij}}, \quad \boldsymbol{\varepsilon} = \frac{dC(\boldsymbol{\sigma})}{d\boldsymbol{\sigma}} \quad (2.2.28)$$

For the linear material,  $\Psi = \frac{1}{2}\boldsymbol{\varepsilon} : \mathbf{D} : \boldsymbol{\varepsilon}$ ,  $\boldsymbol{\varepsilon} = \mathbf{D}^{-1} : \boldsymbol{\sigma}$  and the dual Complementary function is  $C = \frac{1}{2}\boldsymbol{\sigma} : \mathbf{D}^{-1} : \boldsymbol{\sigma}$ . The fact that  $\mathbf{D}$  in the linear case is positive definite ensures that it is invertible. The inverse  $\mathbf{D}^{-1}$  is called the **elastic flexibility tensor C** (see 2.2.11):

$$C = \frac{1}{2} C_{ijkl} \sigma_{ij} \sigma_{kl} \quad C = \frac{1}{2} \boldsymbol{\sigma} : \mathbf{C} : \boldsymbol{\sigma} \quad (2.2.29)$$

## 2.2.2 Large Strain Thermoelasticity

In the general large strain thermoelastic case, the constitutive relations are of the form

$$\begin{aligned} \boldsymbol{\sigma} &= \boldsymbol{\sigma}(\mathbf{F}, \theta, \nabla \theta) \\ \mathbf{q} &= \mathbf{q}(\mathbf{F}, \theta, \nabla \theta) \\ u &= u(\mathbf{F}, \theta, \nabla \theta) \\ \psi &= \psi(\mathbf{F}, \theta, \nabla \theta) \\ s &= s(\mathbf{F}, \theta, \nabla \theta) \end{aligned} \quad (2.2.30)$$

Here, for convenience, the material gradient of 2.1.13 has been replaced with the spatial gradient  $\nabla \theta$  (through  $\nabla \theta = \mathbf{F}^{-1} \text{Grad} \theta$ ).

The dissipation inequality 1.6.20 is

$$\phi = -s\dot{\theta} - \dot{\psi} + \frac{1}{\rho} \boldsymbol{\sigma} : \mathbf{d} - \frac{1}{\rho\theta} \mathbf{q} \cdot \nabla \theta \geq 0 \quad (2.2.31)$$

Using the relation Part III, 3.7.25,  $\boldsymbol{\sigma} : \mathbf{d} = \boldsymbol{\sigma} \mathbf{F}^{-T} : \dot{\mathbf{F}}$ , this can be expressed as

$$\rho s \dot{\theta} + \rho \dot{\psi} - \boldsymbol{\sigma} \mathbf{F}^{-T} : \dot{\mathbf{F}} + \frac{1}{\theta} \mathbf{q} \cdot \nabla \theta \leq 0 \quad (2.2.32)$$

With

$$\dot{\psi} = \frac{\partial \psi}{\partial \mathbf{F}} : \dot{\mathbf{F}} + \frac{\partial \psi}{\partial \theta} \dot{\theta} + \frac{\partial \psi}{\partial (\nabla \theta)} \cdot \dot{\nabla \theta} \quad (2.2.33)$$

one has

$$\rho \left( s + \frac{\partial \psi}{\partial \theta} \right) \dot{\theta} - \left( \boldsymbol{\sigma} \mathbf{F}^{-T} - \rho \frac{\partial \psi}{\partial \mathbf{F}} \right) : \dot{\mathbf{F}} + \rho \frac{\partial \psi}{\partial (\nabla \theta)} \cdot \dot{\nabla \theta} + \frac{1}{\theta} \mathbf{q} \cdot \nabla \theta \leq 0 \quad (2.2.34)$$

For any given  $\{\mathbf{F}, \theta, \nabla \theta\}$ , this inequality must hold for any arbitrary values of  $\dot{\mathbf{F}}$ ,  $\dot{\theta}$  and  $\dot{\nabla \theta}$ . Thus the coefficients must be zero:

$$s = -\frac{\partial \psi}{\partial \theta}, \quad \boldsymbol{\sigma} = \rho \frac{\partial \psi}{\partial \mathbf{F}} \mathbf{F}^T, \quad \frac{\partial \psi}{\partial (\nabla \theta)} = 0 \quad (2.2.35)$$

The third of these implies that the free energy is independent of the temperature gradient:

$$\psi = \psi(\mathbf{F}, \theta) \quad (2.2.36)$$

and so the entropy and stress are also; further, the internal energy is

$$u = \psi - \theta \frac{\partial \psi}{\partial \theta} \quad (2.2.37)$$

### Stress-Strain Relation

The stress-deformation relation 2.2.35b can be expressed in a number of different ways, for example, in terms of the PK1 stress  $\mathbf{P} = J\boldsymbol{\sigma}\mathbf{F}^{-\text{T}}$  and the PK2 stress  $\mathbf{S} = J\mathbf{F}^{-1}\boldsymbol{\sigma}\mathbf{F}^{-\text{T}}$  (the first of these follows from the symmetry of the Cauchy stress)

$$\begin{aligned} \boldsymbol{\sigma} &= \rho \frac{\partial \psi}{\partial \mathbf{F}} \mathbf{F}^{\text{T}} = \rho \mathbf{F} \left( \frac{\partial \psi}{\partial \mathbf{F}} \right)^{\text{T}} \\ \mathbf{P} &= \rho_0 \frac{\partial \psi}{\partial \mathbf{F}} \\ \mathbf{S} &= \rho_0 \mathbf{F}^{-1} \frac{\partial \psi}{\partial \mathbf{F}} \end{aligned} \quad (2.2.38)$$

Introducing the free energy per unit *reference* volume,  $\Psi$ , these read as

$$\boldsymbol{\sigma} = J^{-1} \frac{\partial \Psi}{\partial \mathbf{F}} \mathbf{F}^{\text{T}}, \quad \mathbf{P} = \frac{\partial \Psi}{\partial \mathbf{F}}, \quad \mathbf{S} = \mathbf{F}^{-1} \frac{\partial \Psi}{\partial \mathbf{F}} \quad (2.2.39)$$

In the case of material symmetries, they take reduced forms as discussed in Part III, Chapter 4. For example, for isotropic materials the Cauchy stress is a function of the left Cauchy-Green strain only:

$$\boldsymbol{\sigma} = 2J^{-1} \frac{\partial \Psi}{\partial \mathbf{b}} \mathbf{b} \quad (2.2.40)$$

### Gibbs Relations

One also has the useful **Gibbs relations** {▲ Problem 3}

$$\begin{aligned}
\dot{\psi} &= \frac{1}{\rho_0} \mathbf{P} : \dot{\mathbf{F}} - s \dot{\theta} \\
\dot{u} &= \frac{1}{\rho_0} \mathbf{P} : \dot{\mathbf{F}} + \theta \dot{s} \\
\dot{h} &= -\frac{1}{\rho_0} \mathbf{F} : \dot{\mathbf{P}} + \theta \dot{s} \\
\dot{g} &= -\frac{1}{\rho_0} \mathbf{F} : \dot{\mathbf{P}} - s \dot{\theta}
\end{aligned} \tag{2.2.41}$$

### Isothermal Elasticity

For isothermal materials, the free energy becomes the strain energy  $W$  per unit reference volume, e.g. in terms of the PK1 stress, the stress and stress power can be expressed as

$$\mathbf{P} = \frac{\partial W(\mathbf{F})}{\partial \mathbf{F}}, \quad \dot{W} = \frac{\partial W(\mathbf{F})}{\partial \mathbf{F}} : \dot{\mathbf{F}} = \mathbf{P} : \dot{\mathbf{F}} \tag{2.2.42}$$

Since there are no temperature gradients, the entropy inequality 2.2.34 becomes an equality and any process is completely reversible. For a reversible process, the dissipation is  $\phi = \theta \dot{s} = 0$  and so, as mentioned in §1.6.4, such a process is also isentropic.

### Adiabatic Elasticity

For adiabatic conditions, the heat flux is zero, so again the entropy inequality 2.2.34 becomes an equality and any process is reversible and isentropic. Working with the internal energy, from 2.2.41b, with its canonical variables,  $u = u(\mathbf{F}, s)$ , one has

$$\dot{u} = \frac{1}{\rho} \boldsymbol{\sigma} \mathbf{F}^{-T} : \dot{\mathbf{F}} = \frac{1}{\rho_0} \mathbf{P} : \dot{\mathbf{F}} \tag{2.2.43}$$

The internal energy thus becomes the strain energy and one again has 2.2.42.

### Energy Potentials and Canonical Variables

Following on from §1.3, the thermodynamic potentials (per unit reference volume) in terms of canonical variables take the form

$$\Psi = \Psi(\mathbf{F}, \theta), \quad U = U(\mathbf{F}, s), \quad G = G(\mathbf{P}, \theta), \quad H = H(\mathbf{P}, s) \tag{2.2.44}$$

The various relationships for these potentials are given in Table 2.2.1, which is a reproduction of Table 1.3.1 for finite strain reversible processes.

The fourth column contains the Gibbs relations 2.2.41.

Thermo-dynamic	Symbol and	Definition	Rate-form relationship	Maxwell relation
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potential	appropriate variables			
Internal energy	$U(S, \mathbf{F})$		$\dot{U} = \mathbf{P} : \dot{\mathbf{F}} + \theta \dot{S}$	$\theta = \left( \frac{\partial U}{\partial S} \right)_{\mathbf{F}}, \mathbf{P} = \left( \frac{\partial U}{\partial \mathbf{F}} \right)_s$ $\left( \frac{\partial \theta}{\partial \mathbf{F}} \right)_s = \left( \frac{\partial \mathbf{P}}{\partial S} \right)_{\mathbf{F}}$
Enthalpy	$H(S, \mathbf{P})$	$H = U - \mathbf{P} : \mathbf{F}$	$\dot{H} = -\mathbf{F} : \dot{\mathbf{P}} + \theta \dot{S}$	$\theta = \left( \frac{\partial H}{\partial S} \right)_{\mathbf{P}}, \mathbf{F} = -\left( \frac{\partial H}{\partial \mathbf{P}} \right)_s$ $\left( \frac{\partial \theta}{\partial \mathbf{P}} \right)_s = -\left( \frac{\partial \mathbf{F}}{\partial S} \right)_{\mathbf{P}}$
Helmholtz free energy	$\Psi(\theta, \mathbf{F})$	$\Psi = U - \theta S$	$\dot{\Psi} = \mathbf{P} : \dot{\mathbf{F}} - S \dot{\theta}$	$s = -\left( \frac{\partial \Psi}{\partial \theta} \right)_{\mathbf{F}}, \mathbf{P} = \left( \frac{\partial \Psi}{\partial \mathbf{F}} \right)_{\theta}$ $\left( \frac{\partial S}{\partial \mathbf{F}} \right)_{\theta} = -\left( \frac{\partial \mathbf{P}}{\partial \theta} \right)_{\mathbf{F}}$
Gibbs free energy	$G(\theta, \mathbf{P})$	$G = U - \theta S - \mathbf{P} : \mathbf{F}$	$\dot{G} = -\mathbf{F} : \dot{\mathbf{P}} - S \dot{\theta}$	$s = -\left( \frac{\partial G}{\partial \theta} \right)_{\mathbf{P}}, \mathbf{F} = -\left( \frac{\partial G}{\partial \mathbf{P}} \right)_{\theta}$ $\left( \frac{\partial S}{\partial \mathbf{P}} \right)_{\theta} = \left( \frac{\partial \mathbf{F}}{\partial \theta} \right)_{\mathbf{P}}$

Table 2.2.1: Thermodynamic Potentials (per unit reference volume)

### The Gibbs Relation and Classical Thermodynamics

In increment form, the second of the Gibbs relations 2.2.41 can be expressed as

$$ds = \frac{1}{\theta} \left( du - \frac{1}{\rho} \boldsymbol{\sigma} \mathbf{F}^{-\text{T}} : d\mathbf{F} \right) \quad (2.2.45)$$

Consider an elastic (inviscid) fluid, for which by definition the stress is a function of  $\mathbf{F}$  only through the density  $\rho$ :

$$\boldsymbol{\sigma} = -p(\rho, \theta) \mathbf{I} \quad (2.2.46)$$

where  $p$  is the hydrostatic pressure. Using {▲ Problem 4}

$$\frac{\dot{\rho}}{\rho} = -\mathbf{F}^{-\text{T}} : \mathbf{F}, \quad (2.2.47)$$

relation 2.2.45 reduces to the classical thermodynamics Gibbs relation

$$ds = \frac{1}{\theta} \left( du - \frac{p}{\rho^2} d\rho \right) \quad (2.2.48)$$

### Heat Flux

The first law is

$$\begin{aligned}\dot{u} &= \frac{1}{\rho_0} \mathbf{P} : \dot{\mathbf{F}} - \frac{1}{\rho_0} \text{Div} \mathbf{Q} \\ &= \frac{1}{\rho} \boldsymbol{\sigma} : \mathbf{d} - \frac{1}{\rho} \text{div} \mathbf{q}\end{aligned}\quad (2.2.49)$$

Recall that, in this expression, the divergence of the (Cauchy) heat flux represents the heat entering a material element, Eqn. 1.6.4,

$$\frac{\delta Q}{dt} = - \int_v \text{div} \mathbf{q} dv \quad (2.2.50)$$

For a homogeneous material,  $(\delta Q / dt)(1/v) = -\text{div} \mathbf{q}$ .

Using 2.2.41b, one has the useful relation between the rate of entropy and the heat flux vector for a thermoelastic material:

$$\theta \dot{s} = - \frac{1}{\rho_0} \text{Div} \mathbf{Q} = - \frac{1}{\rho} \text{div} \mathbf{q} \quad (2.2.51)$$

## Heat Conduction

From 2.2.34, the dissipation inequality reads

$$\mathbf{q}(\mathbf{F}, \theta, \nabla \theta) \cdot \nabla \theta \leq 0 \quad (2.2.52)$$

This is **Fourier's inequality** and merely states that heat flows from a hot region to a cold region. One usually assumes **Fourier's law of heat conduction**:

$$\mathbf{q} = -\mathbf{K}(\mathbf{F}, \theta) \nabla \theta \quad (2.2.53)$$

where  $\mathbf{K}$  is the **thermal conductivity** tensor. This constitutive law is sometimes referred to as **Duhamel's law of heat conduction**, to distinguish it from the case of a thermally isotropic material, for which  $\mathbf{K} = k\mathbf{I}$ , which is then referred to as Fourier's law.

If one considers the left hand side of Eqn. 2.2.52 to be a function of  $\nabla \theta$ , this function attains a maximum (of zero) when  $\nabla \theta = 0$ . Thus

$$\left. \frac{\partial}{\partial \nabla \theta} (\mathbf{q} \cdot \nabla \theta) \right|_{\nabla \theta = 0} = \left( \frac{\partial \mathbf{q}}{\partial \nabla \theta} \right)^T \nabla \theta + \mathbf{q} \Big|_{\nabla \theta = 0} = \mathbf{q}(\mathbf{F}, \theta, \mathbf{0}) = \mathbf{0} \quad (2.2.54)$$

This implies that, without a temperature gradient, there is no heat flow. Since it is a maximum,

$$\frac{\partial^2}{\partial(\nabla\theta)^2}(\mathbf{q} \cdot \nabla\theta) \Big|_{\nabla\theta=0} = \left( \frac{\partial\mathbf{q}}{\partial\nabla\theta} \right)^T + \frac{\partial\mathbf{q}}{\partial\nabla\theta} \quad (2.2.55)$$

must be negative semi-definite. This implies that the symmetric part of the thermal conductivity tensor  $\mathbf{K}$  in 2.2.53 must be positive semi-definite.

Consider next the quantity  $\mathbf{K} : \partial^2\theta / \partial\mathbf{x}^2$ . Since  $\partial(\partial\theta / \partial x_i) / \partial x_j = \partial(\partial\theta / \partial x_j) / \partial x_i$ ,  $\partial^2\theta / \partial\mathbf{x}^2$  is symmetric. Further, the double contraction of a symmetric tensor and a skew tensor is zero. Thus  $\mathbf{K} : \partial^2\theta / \partial\mathbf{x}^2 = \text{sym}\mathbf{K} : \partial^2\theta / \partial\mathbf{x}^2$ . The heat flux appears in the first law only as  $\text{div}\mathbf{q}$ . Evaluating this gives, with Fourier's law,

$$\text{div}\mathbf{q} = \frac{\partial}{\partial x_i} \left( -K_{ij} \frac{\partial\theta}{\partial x_j} \right) = -\frac{\partial K_{ij}}{\partial x_i} \frac{\partial\theta}{\partial x_j} - K_{ij} \frac{\partial^2\theta}{\partial x_i \partial x_j} \quad (2.2.56)$$

For a homogeneous material,  $\partial K_{ij} / \partial x_i = 0$ , and so

$$\text{div}\mathbf{q} = -\text{sym}\mathbf{K} : \frac{\partial^2\theta}{\partial\mathbf{x}^2} \quad (2.2.57)$$

Thus, for homogeneous materials, it is only the symmetric part of the thermal conductivity tensor which enters the energy balance. In fact, it is almost universally accepted that  $\mathbf{K}$  is symmetric, whether the material is homogeneous or not.

### Heat Capacity and Latent Heat

The specific heat capacity is the heat required to raise the temperature of a body by unit temperature (per unit mass). From the first law, 2.2.49, when there is no deformation ( $\dot{\mathbf{F}} = \mathbf{0}$ ), all the heat absorbed is transferred to internal energy. The **specific heat capacity at constant deformation** is then by definition (see Eqn. 1.1.15)

$$c_F = \frac{\partial u(\mathbf{F}, \theta)}{\partial\theta} \quad (2.2.58)$$

The heat capacity can also be expressed in terms of the free energy {▲ Problem 5}:

$$c_F = \theta \frac{\partial s(\mathbf{F}, \theta)}{\partial\theta} = -\theta \frac{\partial^2 \psi(\mathbf{F}, \theta)}{\partial\theta^2} \quad (2.2.59)$$

From 2.2.51, one then has the **equation of heat conduction** {▲ Problem 6}

$$-\theta \frac{\partial^2 \psi}{\partial\theta \partial\theta} \dot{\theta} - \theta \frac{\partial^2 \psi}{\partial\theta \partial\mathbf{F}} : \dot{\mathbf{F}} = -\frac{1}{\rho_0} \text{Div}\mathbf{Q} \quad (2.2.60)$$

Some of the heat energy results in a temperature change, the first term, which is the heat capacity term. The second term represents a thermoelastic coupling effect whereby a

deformation induces a temperature change; this term is often neglected as it is usually small in applications. This second term can be interpreted as a latent heat term, whereby heat can be absorbed without a change in temperature.

In terms of the enthalpy, the first law 2.2.49 can be expressed as

$$\dot{h} = \frac{1}{\rho_0} \mathbf{F} : \dot{\mathbf{P}} - \frac{1}{\rho_0} \text{Div} \mathbf{Q} \quad (2.2.61)$$

At constant stress, the heat energy now results in an increase in enthalpy. The **specific heat capacity at constant stress** is then by definition

$$c_p = \frac{\partial h(\mathbf{P}, \theta)}{\partial \theta} \quad (2.2.62)$$

The heat capacity can also be expressed in terms of the Gibbs energy (using the relations in Table 2.2.1):

$$c_p = \theta \frac{\partial s(\mathbf{P}, \theta)}{\partial \theta} = -\theta \frac{\partial^2 g(\mathbf{P}, \theta)}{\partial \theta^2} \quad (2.2.63)$$

For isotropic engineering materials, e.g. metals, concrete, which undergo small strains,  $c_F = c_\varepsilon \mathbf{I}$ , with  $c_\varepsilon \approx 10^3 \text{ Nm/kgK}$  and  $c_p = c_\sigma \mathbf{I}$ , with  $c_\sigma$  being slightly greater than  $c_\varepsilon$  (by a few percent).

### 2.2.3 Small Strain Thermoelasticity

#### The Free Energy and Thermal Strains

In the linear theory, the free energy is a function of the small-strain and the temperature,  $\psi(\boldsymbol{\varepsilon}, \theta)$ , and, as with the strains, temperature changes are assumed to be small. Assume that in the reference state the temperature is  $\theta_0$  and the material is strain-free. Then, expanding the free energy in a Taylor series and retaining only terms up to second order,

$$\begin{aligned} \psi(\boldsymbol{\varepsilon}, \theta) = & \psi|_0 + \left. \frac{\partial \psi}{\partial \boldsymbol{\varepsilon}} \right|_0 : \boldsymbol{\varepsilon} + \left. \frac{\partial \psi}{\partial \theta} \right|_0 (\theta - \theta_0) + \frac{1}{2} \boldsymbol{\varepsilon} : \left. \frac{\partial^2 \psi}{\partial \boldsymbol{\varepsilon}^2} \right|_0 : \boldsymbol{\varepsilon} \\ & + (\theta - \theta_0) \left. \frac{\partial^2 \psi}{\partial \boldsymbol{\varepsilon} \partial \theta} \right|_0 : \boldsymbol{\varepsilon} + \frac{1}{2} \left. \frac{\partial^2 \psi}{\partial \theta^2} \right|_0 (\theta - \theta_0)^2 \end{aligned} \quad (2.2.64)$$

where the notation  $|_0$  means that the quantity is evaluated at the reference state. Note that the specific heat at constant deformation (strain) occurs in the last term here (see Eqn. 2.2.59).

The stress is now

$$\boldsymbol{\sigma} = \rho \frac{\partial \psi}{\partial \boldsymbol{\varepsilon}} = \rho \left. \frac{\partial \psi}{\partial \boldsymbol{\varepsilon}} \right|_0 + \rho \left. \frac{\partial^2 \psi}{\partial \boldsymbol{\varepsilon}^2} \right|_0 : \boldsymbol{\varepsilon} + \rho (\theta - \theta_0) \left. \frac{\partial^2 \psi}{\partial \boldsymbol{\varepsilon} \partial \theta} \right|_0 \quad (2.2.65)$$

Assuming the material is stress-free in the reference state,  $\boldsymbol{\varepsilon} = \mathbf{0}$ ,  $\theta = \theta_0$ , then  $(\partial \psi / \partial \boldsymbol{\varepsilon})|_0 = \mathbf{0}$ , and 2.2.65 can be expressed as

$$\sigma_{ij} = D_{ijkl} \varepsilon_{kl} - \beta_{ij} (\theta - \theta_0) \quad \boldsymbol{\sigma} = \mathbf{D} : \boldsymbol{\varepsilon} - \boldsymbol{\beta} (\theta - \theta_0) \quad (2.2.66)$$

where the stiffness tensor is

$$D_{ijkl} = \rho \frac{\partial^2 \psi}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} \quad \mathbf{D} = \rho \frac{\partial^2 \psi}{\partial \boldsymbol{\varepsilon}^2} \quad (2.2.67)$$

and

$$\beta_{ij} = -\rho \frac{\partial^2 \psi}{\partial \varepsilon_{ij} \partial \theta} \quad \boldsymbol{\beta} = -\rho \frac{\partial^2 \psi}{\partial \boldsymbol{\varepsilon} \partial \theta} \quad (2.2.68)$$

It was seen earlier that  $\mathbf{D}$  is positive definite and so is always invertible. Define then the tensor  $\boldsymbol{\alpha}$  through  $\mathbf{D} : \boldsymbol{\alpha} = \boldsymbol{\beta}$  (so  $\boldsymbol{\alpha} = \mathbf{C} : \boldsymbol{\beta}$ , where  $\mathbf{C}$  is the flexibility tensor) so that

$$\sigma_{ij} = D_{ijkl} [\varepsilon_{kl} - \alpha_{kl} (\theta - \theta_0)] \quad \boldsymbol{\sigma} = \mathbf{D} : [\boldsymbol{\varepsilon} - \boldsymbol{\alpha} (\theta - \theta_0)] \quad (2.2.69)$$

The quantity  $\boldsymbol{\alpha}(\theta - \theta_0)$  is called the **thermal strain** and  $\boldsymbol{\alpha}$  is the tensor of **thermal expansion coefficients**. For isotropic engineering materials,  $\boldsymbol{\alpha} = \alpha \mathbf{I}$ , with  $\alpha \approx 10^{-5} \text{ K}^{-1}$ .

Note that, from 2.2.67-8, with the derivatives evaluated at the reference configuration,  $\mathbf{D}$  and  $\boldsymbol{\alpha}$  are constant tensors. One can generalize to a theory with temperature-dependent properties, by expressing 2.2.64 in the form

$$\begin{aligned} \psi(\boldsymbol{\varepsilon}, \theta) = & A + B(\theta)(\theta - \theta_0) + \frac{1}{2} \boldsymbol{\varepsilon} : \frac{1}{\rho} \mathbf{D}(\theta) : \boldsymbol{\varepsilon} \\ & - (\theta - \theta_0) \frac{1}{\rho} \boldsymbol{\beta}(\theta) : \boldsymbol{\varepsilon} + \frac{1}{2} E(\theta) (\theta - \theta_0)^2 \end{aligned} \quad (2.2.70)$$

### The Gibbs Energy

The temperature dependence of a thermoelastic material can be conveniently expressed using the Gibbs free energy,  $g = g(\boldsymbol{\sigma}, \theta)$ :

$$\varepsilon_{ij} = -\rho \frac{\partial g}{\partial \sigma_{ij}} \quad \boldsymbol{\varepsilon} = -\rho \frac{\partial g}{\partial \boldsymbol{\sigma}} \quad (2.2.71)$$

Then, immediately,

$$\dot{\varepsilon}_{ij} = C_{ijkl} \dot{\sigma}_{kl} + \alpha_{ij} \dot{\theta} \quad \dot{\boldsymbol{\varepsilon}} = \mathbf{C} : \dot{\boldsymbol{\sigma}} + \boldsymbol{\alpha} \dot{\theta} \quad (2.2.72)$$

where now

$$\begin{aligned} C_{ijkl} &= -\rho \frac{\partial^2 g}{\partial \sigma_{ij} \partial \sigma_{kl}} & \mathbf{C} &= -\rho \frac{\partial^2 g}{\partial \boldsymbol{\sigma} \partial \boldsymbol{\sigma}} \\ \alpha_{ij} &= -\rho \frac{\partial^2 g}{\partial \sigma_{ij} \partial \theta} & \boldsymbol{\alpha} &= -\rho \frac{\partial^2 g}{\partial \boldsymbol{\sigma} \partial \theta} \end{aligned} \quad (2.2.73)$$

To complete the set of second derivatives of the Gibbs function, one also has the heat capacity at constant stress (see Eqn. 2.2.63):

$$c_{\sigma} = -\theta \frac{\partial^2 g}{\partial \theta \partial \theta} \quad (2.2.74)$$

## Heat Capacity

Just as the stress, Eqn. 2.2.65, was expressed in terms of the free energy 2.2.64, the entropy can be expressed as the linear function

$$s = -\frac{\partial \psi}{\partial \theta} = -\frac{\partial \psi}{\partial \theta} \Big|_0 - \frac{\partial^2 \psi}{\partial \boldsymbol{\varepsilon} \partial \theta} \Big|_0 : \boldsymbol{\varepsilon} - (\theta - \theta_0) \frac{\partial^2 \psi}{\partial \theta^2} \Big|_0 \quad (2.2.75)$$

The first term on the right represents the reference entropy, at the reference state, and can be omitted. The last term involves the specific heat at constant strain. The second term involves the tensor  $\boldsymbol{\beta}$  (see Eqn. 2.2.68). Thus

$$s = \frac{1}{\rho} \boldsymbol{\alpha} : \mathbf{D} : \boldsymbol{\varepsilon} + \frac{\theta - \theta_0}{\theta} c_{\varepsilon} \quad (2.2.76)$$

For an isotropic material, the stiffness tensor is given by Part III, Eqn. 4.1.12,

$$\mathbf{D} = \lambda \mathbf{I} \otimes \mathbf{I} + \mu (\mathbf{I} + \bar{\mathbf{I}}), \quad D_{ijmn} = \lambda \delta_{ij} \delta_{mn} + \mu (\delta_{im} \delta_{jn} + \delta_{in} \delta_{jm}) \quad (2.2.77)$$

in which case

$$\alpha_{ij} D_{ijkl} \varepsilon_{kl} = \alpha \delta_{ij} (\lambda \delta_{ij} \varepsilon_{kk} + 2\mu \varepsilon_{ij}) = \alpha (3\lambda + 2\mu) \varepsilon_{kk} = 3K\alpha \varepsilon_{kk} \quad (2.2.78)$$

where  $K$  is the bulk modulus. With  $(\theta - \theta_0)/\theta \approx (\theta - \theta_0)/\theta_0$ , the entropy is now

$$s(\boldsymbol{\varepsilon}, \theta) = \frac{3K\alpha}{\rho} \text{tr} \boldsymbol{\varepsilon} + \frac{\theta - \theta_0}{\theta_0} c_{\varepsilon} \quad (2.2.79)$$

With Fourier's law,  $\mathbf{q} = -k\text{grad}\theta$ , the equation of heat conduction, 2.2.60, can be expressed as (with  $\theta \approx \theta_0$ )

$$c_\varepsilon \dot{\theta} + \theta_0 \frac{3K\alpha}{\rho} \text{tr}\dot{\boldsymbol{\varepsilon}} = \frac{k}{\rho} \text{div}(\text{grad}\theta) \quad (2.2.80)$$

In order to express these relations in terms of stress, from 2.2.69, the isotropic stiffness tensor 2.2.77 and Part III, 4.1.20,

$$\boldsymbol{\sigma} = 2\mu\text{dev}\boldsymbol{\varepsilon} + K(\text{tr}\boldsymbol{\varepsilon})\mathbf{I} - 3\alpha K(\theta - \theta_0)\mathbf{I} \quad (2.2.81)$$

Then, with the trace of a deviator zero,

$$\text{tr}\boldsymbol{\sigma} = 3K(\text{tr}\boldsymbol{\varepsilon}) - 9\alpha K(\theta - \theta_0) \quad (2.2.82)$$

Thus 2.2.79 can be expressed as

$$s(\boldsymbol{\sigma}, \theta) = \frac{\alpha}{\rho} \text{tr}\boldsymbol{\sigma} + \frac{9\alpha^2 K}{\rho} (\theta - \theta_0) + \frac{\theta - \theta_0}{\theta_0} c_\varepsilon \quad (2.2.83)$$

The specific heat capacity at constant stress is then, from 2.2.63,

$$c_\sigma = \theta \frac{\partial s(\boldsymbol{\sigma}, \theta)}{\partial \theta} \approx \theta_0 \frac{\partial s(\boldsymbol{\sigma}, \theta)}{\partial \theta} \quad (2.2.84)$$

leading to the relation

$$c_\sigma - c_\varepsilon = \theta_0 \frac{9\alpha^2 K}{\rho} \quad (2.2.85)$$

In terms of stress, the equation of heat conduction 2.2.80 reads

$$c_\sigma \dot{\theta} + \theta_0 \frac{\alpha}{\rho} \text{tr}\dot{\boldsymbol{\sigma}} = \frac{k}{\rho} \text{div}(\text{grad}\theta) \quad (2.2.86)$$

## 2.2.4 Problems

1. Differentiate the invariants 2.2.16 to derive relations 2.2.18.
2. Derive the complementary function 2.2.26.
3. Derive the Gibbs relations 2.2.41 for an elastic material.

4. Use the conservation of mass relation  $\rho_0 = J\rho$  and the relation Part III, 2.5.19,  $\dot{J} = \mathbf{J}\mathbf{F}^{-T} : \dot{\mathbf{F}}$ , to derive the relation 2.2.47,  $\dot{\rho} / \rho = -\mathbf{F}^{-T} : \dot{\mathbf{F}}$ .
5. Show that the heat capacity is proportional to the second derivative of the free energy, Eqn. 2.2.59.
6. By taking the entropy  $s$  to be a function of the variables  $(\mathbf{F}, \theta)$ , use the relation 2.2.51,  $\rho_0 \theta \dot{s} = -\text{Div}\mathbf{Q}$ , and the relation between entropy and free energy, Eqn. 2.2.35a, to derive the equation of heat conduction 2.2.60,

$$-\theta \frac{\partial^2 \psi}{\partial \theta \partial \theta} \dot{\theta} - \theta \frac{\partial^2 \psi}{\partial \theta \partial \mathbf{F}} : \dot{\mathbf{F}} = -\frac{1}{\rho_0} \text{Div}\mathbf{Q}$$

7. Derive the equation of heat conduction 2.2.86.