



Thermodynamics of Materials with Memory

We now apply thermodynamic principles to field theories with memory. For general nonlinear, nonisothermal theories, we assume that a free energy is given, this being the fundamental constitutive assumption. Applying a generalization of the approach of Coleman [67], Coleman and Mizel [71], and Gurtin and Pipkin [191], we derive the constitutive equations for the theory in Sect. 5.1. Also, fundamental properties of free energies are derived. Furthermore, some observations are made on the case of periodic histories and in relation to constraints on the nonuniqueness of free energies. In Sect. 5.2, an expression for the maximum recoverable work is given for general materials, together with an integral equation for the process yielding this maximum. Finally, in Sect. 5.3, we discuss how free energies can be constructed from combinations of simpler free energies.

In Part III, the entire emphasis is on determining suitable explicit forms of free energies for materials with memory. All these involve quadratic functionals of histories.

5.1 Derivation of the Constitutive Equations

Let us begin by stating the first and second laws of thermodynamics. The theory is developed in terms of the material description.

The internal energy per unit mass and the entropy per unit mass at (\mathbf{X}, t) , both scalar quantities, are denoted, respectively, by $e(\mathbf{X}, t)$ and $\eta(\mathbf{X}, t)$. The local absolute temperature is $\theta(\mathbf{X}, t) \in \mathbb{R}^+$. The Piola–Kirchhoff heat flux vector, defined by (3.1.1), is denoted by $\mathbf{q}(\mathbf{X}, t) \in \mathbb{R}^3$; the subscript L is dropped. We introduce a variable $\kappa(\mathbf{X}, t)$, which is the coldness, given by $1/\theta > 0$. All these quantities can also be expressed in terms of the current position \mathbf{x} and time t . The quantity $\mathbf{g}_L \in \mathbb{R}^3$ is defined by (3.2.2). The subscript L will now be dropped. We also introduce $\mathbf{d} \in \mathbb{R}^3$ as the gradient of κ , so that

$$\mathbf{g} = \nabla_{\mathbf{X}}\theta, \quad \mathbf{d} = \nabla_{\mathbf{X}}\kappa = -\frac{1}{\theta^2}\mathbf{g}, \quad (5.1.1)$$

where the gradient $\nabla_{\mathbf{X}}$, here and below, is with respect to \mathbf{X} . The energy balance equation or the first law of thermodynamics has the form (see (3.3.8))

$$p - \rho \dot{e} - \text{Div}_{\mathbf{X}} \mathbf{q} + \rho r = 0, \quad p = \widehat{\mathbf{S}} \cdot \dot{\mathbf{E}}. \quad (5.1.2)$$

The quantity $\rho(\mathbf{X})$ (denoted by ρ_0 in Chap. 3) is the mass density in the material configuration, and r is the external radiation absorbed per unit time, per unit mass at (\mathbf{X}, t) . We write the second law of thermodynamics as

$$D = \dot{\eta} + \frac{1}{\rho} \text{Div}_{\mathbf{X}} \mathbf{j}_{\eta} - \kappa r \geq 0, \quad (5.1.3)$$

where \mathbf{j}_{η} is the entropy flux, which in the present work will be taken to have the equilibrium form (see (3.4.15))

$$\mathbf{j}_{\eta} = \kappa \mathbf{q}. \quad (5.1.4)$$

The quantity $D(\mathbf{X}, t)$ is the *total rate of entropy production* per unit mass.

The superimposed dot notation in (5.1.2), (5.1.3), and below indicates the material time derivative, i.e., holding \mathbf{X} constant.

The quantities $\widehat{\mathbf{S}}$, \mathbf{E} , \mathbf{q} , and \mathbf{g} are unaffected by a time-dependent coordinate transformation in \mathbf{x} . Thus, their components are objective scalars.

The Helmholtz free energy per unit mass, introduced in Sect. 3.4.2, is defined by

$$\psi_H = e - \theta \eta.$$

In terms of this quantity, we can write (5.1.2) as

$$\frac{p}{\rho} - \dot{\psi}_H - \eta \dot{\theta} - \frac{1}{\rho \theta} \mathbf{q} \cdot \mathbf{g} = \theta D. \quad (5.1.5)$$

The fact that D is nonnegative means that (5.1.5) implies the Clausius–Duhem inequality (3.4.16). Relation (5.1.5) is unsatisfactory for materials with memory because, as discussed in Chap. 4 for free energies, neither ψ_H nor η is in general uniquely defined. On the other hand, e is always uniquely defined. It is therefore advantageous to modify the above standard formulation. We introduce the following free energy:

$$\psi = \kappa e - \eta = \kappa \psi_H. \quad (5.1.6)$$

Instead of (5.1.5), we now have

$$\kappa \frac{p}{\rho} - \dot{\psi} + e \dot{\kappa} + \frac{1}{\rho} \mathbf{d} \cdot \mathbf{q} = D \geq 0. \quad (5.1.7)$$

Observe that in this formulation, the natural temperature variable is κ rather than θ .

In [159], an integral of \mathbf{g} was adopted as an independent variable, in a modification of the approach of [191, 260]. It was pointed out in [159] that an alternative and arguably better procedure would be to adopt the quantity $\mathbf{m} \in \mathbb{R}^3$, defined by

$$\mathbf{m}(t) = \int_0^t \mathbf{q}(u) du, \quad \dot{\mathbf{m}}(t) = \mathbf{q}(t), \quad (5.1.8)$$

as an independent variable. This choice has the advantage that \mathbf{m} has an immediate physical interpretation in that $\mathbf{m} \cdot \mathbf{a}$ is the cumulative heat flow over the time interval $[0, t]$, through a unit area perpendicular to the unit vector \mathbf{a} in the reference configuration. For the general development of the theory, we shall adopt \mathbf{m} as an independent variable rather than the time integral of \mathbf{g} , though it is an easy matter to exchange their roles where required.

We shall be assuming that the free energy is a functional of the history of this quantity, namely $\mathbf{m}^t(s) = \mathbf{m}(t - s)$, $s > 0$, or specifically a functional of

$$\mathbf{m}(t) - \mathbf{m}^t(s) = \int_{t-s}^t \mathbf{q}(u) du, \quad (5.1.9)$$

with no separate dependence on $\mathbf{m}(t)$; such dependence cannot occur, because $\mathbf{m}(t)$ depends on the choice of the time origin. This is essentially the basis of the approach in [191], though in that reference, \mathbf{g} is used in (5.1.8) rather than \mathbf{q} .

Modifying and extending the compact notation of Coleman [67], we introduce $\Lambda : \mathbb{R} \mapsto \Gamma^+$, $\Sigma : \mathbb{R} \mapsto \Gamma^+$, where

$$\begin{aligned} \Lambda(t) &= (\mathbf{E}(t), \kappa(t), \mathbf{m}(t)), \\ \Sigma(t) &= \frac{1}{\rho} (\kappa \widehat{\mathbf{S}}(t), \rho e(t), \mathbf{d}(t)), \\ \Gamma^+ &= \text{Sym} \times \mathbb{R}^+ \times \mathbb{R}^3. \end{aligned} \quad (5.1.10)$$

We assume that Λ is continuously differentiable. In terms of this notation, (5.1.7)₁ can be written as

$$\dot{\psi} + D = \Sigma \cdot \dot{\Lambda} \quad (5.1.11)$$

with $\dot{\Lambda} \in \Gamma$, where*

$$\Gamma = \text{Sym} \times \mathbb{R} \times \mathbb{R}^3. \quad (5.1.12)$$

The dot product here denotes a scalar product in the space Γ (Appendix A). This relation is an expression of the first law and indicates that of the work done on the material element per unit time, some is stored ($\dot{\psi}$) and the rest is dissipated (D). The second law is imposed through the Clausius–Duhem inequality (5.1.7)₂ or

$$D = \Sigma \cdot \dot{\Lambda} - \dot{\psi} \geq 0, \quad (5.1.13)$$

where D is defined by (5.1.3) with (5.1.4).

Remark 5.1.1. Following (4.1.3), we choose $\dot{\Lambda}(t)$ to be the thermodynamic process in later chapters. If the time integral of \mathbf{g} , rather than \mathbf{q} , is used in (5.1.8) and $\theta(t)$ replaces $\kappa(t)$, then this corresponds to (3.2.2).

* The general developments described in later chapters go through for Γ understood to be any finite-dimensional vector space, rather than just that defined by (5.1.12) and therefore may apply to a variety of other physical applications, for example, those involving electromagnetic fields.

Let $\Lambda^t : \mathbb{R}^{++} \mapsto \Gamma^+$ be defined by

$$\Lambda^t(s) = \Lambda(t - s), \quad s \in \mathbb{R}^{++}. \quad (5.1.14)$$

We assume that these belong to a real Hilbert space \mathcal{H} of functions with values in Γ^+ , possessing a suitable inner product and fading memory norm, the latter denoted by $\|\cdot\|$ [67, 73]. A constitutive assumption is now made by requiring that the free energy ψ depends in a specified way on the history and current value of Λ . We put

$$\psi(t) = \tilde{\psi}(\Lambda^t, \Lambda(t)), \quad (5.1.15)$$

denoting that $\tilde{\psi}$ is a functional of the history Λ^t and depends also on the current value $\Lambda(t)$. Note that since all components of Λ^t, Λ are objective scalars, we have automatically that ψ is an objective scalar.

To eliminate the arbitrariness of an additive constant, which is a feature of all physical energies, we impose the condition

$$\tilde{\psi}(\mathbf{0}^\dagger, \mathbf{0}) = 0, \quad (5.1.16)$$

where $\mathbf{0}$ is the zero and $\mathbf{0}^\dagger$ is the zero history, both in Γ^+ .

We now summarize the core argument of rational thermodynamics [67]. The free energy given by (5.1.15) is constrained to obey the second law (5.1.13) for arbitrary choices of $\Lambda^t \in \mathcal{H}$. This yields constitutive equations and an expression for the rate of dissipation. The balance laws (1.3.2) and (1.3.50) with (1.3.52) (or, in the Eulerian description, (1.3.25)) and (5.1.2) must hold, and these involve elements of Λ^t . This can always be arranged by suitable choices of body forces \mathbf{b} in (1.3.50) and the external radiation r in (5.1.2).

An important aspect of this approach is that balance laws, which have universal application, are clearly separated from constitutive equations that apply to particular categories of materials.

Of course, once constitutive equations have been established from such general arguments, these relations, combined with the balance laws and suitable boundary and initial conditions, can be used to determine Λ^t for specified choices of \mathbf{b} and r .

Assuming that $\tilde{\psi}$ is differentiable with respect to $\Lambda(t)$ and Fréchet differentiable with respect to Λ^t within \mathcal{H} (fading memory principle [67, 73], generalized in [71]), we can apply the chain rule to obtain

$$\frac{d}{dt} \tilde{\psi}(\Lambda^t, \Lambda(t)) = \partial_\Lambda \tilde{\psi}(\Lambda^t, \Lambda(t)) \cdot \dot{\Lambda}(t) + \delta \tilde{\psi} \left(\Lambda^t, \Lambda(t) \mid \frac{\partial}{\partial t} \Lambda^t \right), \quad (5.1.17)$$

where ∂_Λ indicates the derivative of $\tilde{\psi}$ with respect to the current value $\Lambda(t)$ and $\delta \tilde{\psi}$ is the Fréchet differential of $\tilde{\psi}$ at Λ^t in the direction $\partial \Lambda^t / \partial t$, where

$$\frac{\partial}{\partial t} \Lambda^t(s) = - \frac{\partial}{\partial s} \Lambda^t(s).$$

The functional $\delta \tilde{\psi}$ is linear in $\partial \Lambda^t / \partial t$. These derivatives with respect to field quantities are assumed to be continuous in their arguments. It follows from (5.1.17) combined with (5.1.13), by virtue of a standard argument [67], that

$$\boldsymbol{\Sigma}(t) = \widetilde{\boldsymbol{\Sigma}}(\boldsymbol{\Lambda}^t, \boldsymbol{\Lambda}(t)) = \partial_{\boldsymbol{\Lambda}} \widetilde{\psi}(\boldsymbol{\Lambda}^t, \boldsymbol{\Lambda}(t)), \quad (5.1.18)$$

which are the constitutive equations of the material and are objective relationships; in fact, all components of both sides are objective scalars. Also, with the aid of (5.1.11),

$$D(t) = -\delta \widetilde{\psi} \left(\boldsymbol{\Lambda}^t, \boldsymbol{\Lambda}(t) \mid \frac{\partial}{\partial t} \boldsymbol{\Lambda}^t \right). \quad (5.1.19)$$

Recalling that the free energy functional depends on $\mathbf{m}(t) - \mathbf{m}^t(s)$, with no separate dependence on $\mathbf{m}(t)$, we shall generally, except in Sect. 5.1.3, write (5.1.15) in the form

$$\psi(t) = \widetilde{\psi}_d(\boldsymbol{\Lambda}_r^t, \boldsymbol{\Lambda}_0(t)), \quad (5.1.20)$$

where

$$\boldsymbol{\Lambda}_r^t(s) = \boldsymbol{\Lambda}^t(s) - \boldsymbol{\Lambda}(t), \quad \boldsymbol{\Lambda}_0(t) = (\mathbf{E}(t), \kappa(t), \mathbf{0}_3), \quad \boldsymbol{\Lambda}_r^t, \boldsymbol{\Lambda}_0 \in \Gamma, \quad (5.1.21)$$

and the quantity $\mathbf{0}_3$ indicates the zero in \mathbb{R}^3 . Note that (5.1.17) can be written in terms of $\widetilde{\psi}_d$ as follows:

$$\frac{d}{dt} \widetilde{\psi}_d(\boldsymbol{\Lambda}_r^t, \boldsymbol{\Lambda}_0(t)) = \partial_{\boldsymbol{\Lambda}} \widetilde{\psi}_d(\boldsymbol{\Lambda}_r^t, \boldsymbol{\Lambda}_0(t)) \cdot \dot{\boldsymbol{\Lambda}} + \delta_r \widetilde{\psi}_d \left(\boldsymbol{\Lambda}_r^t, \boldsymbol{\Lambda}_0(t) \mid \frac{\partial}{\partial t} \boldsymbol{\Lambda}_r^t \right),$$

where $\delta_r \widetilde{\psi}_d$ is the Fréchet differential of $\widetilde{\psi}_d$ at $\boldsymbol{\Lambda}_r^t$ in the direction $\partial \boldsymbol{\Lambda}_r^t / \partial t$ with

$$\frac{\partial}{\partial t} \boldsymbol{\Lambda}_r^t(s) = \frac{\partial}{\partial t} \boldsymbol{\Lambda}^t(s) - \dot{\boldsymbol{\Lambda}}(t).$$

The quantity $\partial_{\boldsymbol{\Lambda}} \widetilde{\psi}_d(\boldsymbol{\Lambda}_r^t, \boldsymbol{\Lambda}_0(t)) \cdot \dot{\boldsymbol{\Lambda}}$ will have zero in the \mathbb{R}^3 contribution. Using the linearity of $\delta_r \widetilde{\psi}_d$ with respect to $\partial \boldsymbol{\Lambda}_r^t / \partial t$, we have that (5.1.18) can be written as follows:

$$\boldsymbol{\Sigma}(t) = \partial_{\boldsymbol{\Lambda}} \widetilde{\psi}_d(\boldsymbol{\Lambda}_r^t, \boldsymbol{\Lambda}_0(t)) - \delta_c \widetilde{\psi}_d(\boldsymbol{\Lambda}_r^t, \boldsymbol{\Lambda}_0(t)), \quad (5.1.22)$$

where the first term on the right is the derivative with respect to the second argument in $\widetilde{\psi}_d$, yielding zero for the \mathbb{R}^3 component, and $\delta_c \widetilde{\psi}_d \in \Gamma$ is defined by the relation

$$\delta_c \widetilde{\psi}_d(\boldsymbol{\Lambda}_r^t, \boldsymbol{\Lambda}_0(t)) \cdot \boldsymbol{\Lambda}_c = \delta_r \widetilde{\psi}_d(\boldsymbol{\Lambda}_r^t, \boldsymbol{\Lambda}_0(t) \mid \boldsymbol{\Lambda}_h(s)), \quad (5.1.23)$$

where, for arbitrary $\boldsymbol{\Lambda}_c \in \Gamma^+$, $\boldsymbol{\Lambda}_h$ is a history such that

$$\boldsymbol{\Lambda}_h(s) = \boldsymbol{\Lambda}_c, \quad \forall s > 0.$$

For the quadratic free energy functional introduced in Chap. 7, it is not necessary to use (5.1.22). The simpler relation (5.1.18) can in fact be applied. Writing this out explicitly, we obtain

$$\frac{\kappa}{\rho} \widehat{\mathbf{S}} = \partial_{\mathbf{E}} \widetilde{\psi}, \quad e = \partial_{\kappa} \widetilde{\psi}, \quad \frac{1}{\rho} \mathbf{d} = \partial_{\mathbf{m}} \widetilde{\psi}.$$

Relation (5.1.19) becomes

$$D(t) = -\delta_r \widetilde{\psi} \left(\Lambda_r^t, \Lambda_0(t) \mid \frac{\partial}{\partial t} \Lambda^t \right).$$

We define the equilibrium free energy ϕ to be given by (5.1.15) for the static history $\Lambda^t(s) = \Lambda^\dagger(s) = \Lambda(t)$, $s \in \mathbb{R}^+$. It follows from (5.1.20) that this quantity depends only on Λ_0 , so that

$$\phi(t) = \widetilde{\phi}(\Lambda_0(t)). \quad (5.1.24)$$

It can be deduced from (5.1.13) that [67, 191]

$$\phi(t) \leq \psi(t), \quad \forall t \in \mathbb{R}, \quad (5.1.25)$$

giving that the equilibrium free energy is less than or equal to the free energy for an arbitrary history. From (5.1.16), we have $\widetilde{\phi}(\mathbf{0}) = 0$.

The notation $\phi(t)$ will be used in most cases instead of $\widetilde{\phi}(\Lambda_0(t))$. The quantity ϕ is conventionally chosen to be nonnegative so that ψ has the same property.

We can write (5.1.20) as

$$\psi(t) = \widetilde{\phi}(\Lambda_0(t)) + \widetilde{\psi}_h(\Lambda_r^t, \Lambda_0(t)) = \phi(t) + \psi_h(t), \quad (5.1.26)$$

where $\psi_h(t) > 0$ is the history-dependent part of the free energy. Note that by definition,

$$\widetilde{\psi}_h(\mathbf{0}, \Lambda_0(t)) = 0. \quad (5.1.27)$$

It follows from (5.1.22) that the generalized stress can also be expressed as the sum of an equilibrium part and a history-dependent part:

$$\Sigma(t) = \Sigma_e(t) + \Sigma_{rh}(t), \quad (5.1.28)$$

where

$$\begin{aligned} \Sigma_e(t) &= \widetilde{\Sigma}(\Lambda_0(t)) = \frac{d}{d\Lambda(t)} \widetilde{\phi}(\Lambda_0(t)), \\ \Sigma_{rh}(t) &= \widetilde{\Sigma}_{rh}(\Lambda_r^t, \Lambda_0(t)) = \partial_\Lambda \widetilde{\psi}_h(\Lambda_r^t, \Lambda_0(t)) - \delta_c \widetilde{\psi}_h(\Lambda_r^t, \Lambda_0(t)). \end{aligned} \quad (5.1.29)$$

The quantity $\widetilde{\Sigma}_{rh}$ vanishes as Λ_r^t tends to the zero history, provided that

$$\lim_{\Lambda^t \rightarrow \Lambda^\dagger} \partial_\Lambda \widetilde{\psi}_h(\Lambda^t, \Lambda(t)) = \partial_\Lambda \lim_{\Lambda^t \rightarrow \Lambda^\dagger} \widetilde{\psi}_h(\Lambda^t, \Lambda(t)),$$

where Λ^\dagger is defined before (5.1.24). We see this by observing that the right-hand side is $\Sigma_e(t)$, given by (5.1.29)₁, while the left-hand side is the static history limit of $\widetilde{\Sigma}(t)$ by virtue of (5.1.18).

5.1.1 Required Properties of a Free Energy

Let us draw together for future reference the properties of a free energy, stated earlier, which will be used to determine whether a given functional is a free energy. These are not independent conditions, since they include both a statement of the second law and consequences of that law.

P1 We have

$$\frac{\partial \tilde{\psi}(\mathbf{\Lambda}^t, \mathbf{\Lambda}(t))}{\partial \mathbf{\Lambda}(t)} = \frac{\partial \psi(t)}{\partial \mathbf{\Lambda}(t)} = \boldsymbol{\Sigma}(t) = \tilde{\boldsymbol{\Sigma}}(\mathbf{\Lambda}^t, \mathbf{\Lambda}(t)), \quad (5.1.30)$$

which is (5.1.18).[†]

P2 Let $\mathbf{\Lambda}^\dagger$ be a static history equal to $\mathbf{\Lambda}(t)$ at the current and all past times. Then,

$$\tilde{\psi}(\mathbf{\Lambda}^\dagger, \mathbf{\Lambda}(t)) = \tilde{\phi}(\mathbf{\Lambda}_0(t)), \quad (5.1.31)$$

where $\tilde{\phi}(\mathbf{\Lambda}_0(t))$ is the equilibrium free energy. This is, in fact, a definition of $\tilde{\phi}$, as given by (5.1.24), included here for completeness.

P3 For any history and current value $(\mathbf{\Lambda}^t, \mathbf{\Lambda}(t))$,

$$\tilde{\psi}(\mathbf{\Lambda}^t, \mathbf{\Lambda}(t)) \geq \tilde{\phi}(\mathbf{\Lambda}_0(t)), \quad (5.1.32)$$

which is (5.1.25).

P4 Condition (5.1.11) holds, namely

$$\dot{\psi}(t) + D(t) = \boldsymbol{\Sigma}(t) \cdot \dot{\mathbf{\Lambda}}(t), \quad D(t) \geq 0, \quad (5.1.33)$$

where $D(t)$ is given by (5.1.19). The first relation is a statement of the first law, while the non-negativity of $D(t)$ is in effect the second law.

These are the Grafti conditions for a free energy [174, 175].

5.1.2 Periodic Histories for General Materials

Integrating (5.1.33) from a past time when the material was undisturbed and assuming the integrals exist, we obtain

$$\begin{aligned} \mathcal{D}(t) = W(t) - \psi(t) &\geq 0, & \mathcal{D}(t) &= \int_{-\infty}^t D(u) du, \\ W(t) &= \int_{-\infty}^t \boldsymbol{\Sigma}(u) \cdot \dot{\mathbf{\Lambda}}(u) du, \end{aligned} \quad (5.1.34)$$

where $W(t)$ is the work function (see (4.1.4)) and $\mathcal{D}(t)$ is the total dissipation up to time t .

In the present context, the state is defined as the history and current value[‡] $(\mathbf{\Lambda}^t, \mathbf{\Lambda}(t))$, and ψ is a state variable by virtue of (5.1.15). Indeed, this is a very general requirement, as we see from Definition 4.1.6.

Let the history be periodic with period T . We have, for all t ,

$$\mathbf{\Lambda}(t + T) = \mathbf{\Lambda}(t). \quad (5.1.35)$$

[†] This applies only to simple materials, which are the focus of interest in all of the present work apart from Sect. 3.7 and Chap. 21. A generalization of (5.1.30) for certain nonsimple materials is given by (21.1.19).

[‡] In certain later contexts (for specific independent variables), we will also use what amounts to the convention $(\mathbf{\Lambda}(t), \mathbf{\Lambda}^t)$ to maintain consistency with some of the literature.

Differentiating with respect to t , we obtain

$$\dot{\Lambda}(t + T) = \dot{\Lambda}(t).$$

Once transient effects have faded away, all state functions will return to the same value after a time T has passed, and we have

$$\psi(t + T) = \psi(t), \quad \dot{\psi}(t + T) = \dot{\psi}(t).$$

The quantity $\tilde{\Sigma}$, defined by (5.1.18), is also a function of state, so that

$$\Sigma(t + T) = \Sigma(t).$$

From (5.1.33), it follows that

$$D(t + T) = D(t).$$

Each period is generated by a cyclic process as given by Definition 4.1.4. Integrating (5.1.33) over $[t, t + T]$, we obtain

$$\int_t^{t+T} D(u)du = \int_t^{t+T} \Sigma(u) \cdot \dot{\Lambda}(u)du > 0 \quad (5.1.36)$$

for materials with dissipation, or

$$\mathcal{D}(t + T) - \mathcal{D}(t) = W(t + T) - W(t) > 0. \quad (5.1.37)$$

Now,

$$\frac{d}{dt}[W(t + T) - W(t)] = \Sigma(t + T) \cdot \dot{\Lambda}(t + T) - \Sigma(t) \cdot \dot{\Lambda}(t) = 0,$$

so that both sides of (5.1.36)₁ are independent of t . The infinite integral defining \mathcal{D} and $W(t)$ in (5.1.34) therefore must diverge for periodic histories, since they consist of an infinite sum of integrals over a period, as in (5.1.36), each being equal to all the others.

Observe that if $\tilde{\psi}$ depends only on $\Lambda(t)$ and is independent of the history, then, using (5.1.30),

$$\begin{aligned} \int_t^{t+T} \Sigma(u) \cdot \dot{\Lambda}(u)du &= \int_{\Lambda(t)}^{\Lambda(t+T)} \frac{\partial}{\partial \Lambda(u)} \tilde{\psi}(\Lambda(u)) \cdot d\Lambda(u) \\ &= \tilde{\psi}(\Lambda(t + T)) - \tilde{\psi}(\Lambda(t)) = 0, \end{aligned}$$

so that the total dissipation must be zero, a result that is consistent with (5.1.19).

5.1.3 Constraints on the Nonuniqueness of the Free Energy

Let us consider in general terms the nature of the arbitrariness in ψ and the constraints imposed on this arbitrariness by the properties summarized in Sect. 5.1.1, which we will refer to as the thermodynamic constraints. It will be required also that the equilibrium free energy $\tilde{\phi}(\Lambda_0(t))$ contains no arbitrariness.

Proposition 5.1.2. *The most general form of the free energy (5.1.15) consistent with the thermodynamic constraints is*

$$\psi(t) = \tilde{\phi}(\Lambda_0(t)) + \tilde{\psi}_f(\Lambda^t, \Lambda(t)) + \tilde{\psi}_r(\Lambda^t),$$

where $\tilde{\phi}(\Lambda_0(t))$ is the equilibrium free energy, and $\tilde{\psi}_f$ is a fixed, nonnegative functional, with no restriction on its $\Lambda(t)$ dependence other than that $\tilde{\phi} + \tilde{\psi}_f$ yields a satisfactory form for (5.1.30). The quantity $\tilde{\psi}_r$, which is independent of $\Lambda(t)$, is arbitrary within thermodynamic constraints and in particular may be zero. These thermodynamic constraints give that $\tilde{\psi}_f$ and $\tilde{\psi}_f + \tilde{\psi}_r$ must be nonnegative-valued functionals and that $-\delta\tilde{\psi}_f$ and $-(\delta\tilde{\psi}_f + \delta\tilde{\psi}_r)$ also must be nonnegative, where, as before, δ indicates the Fréchet derivative specified in (5.1.17). Furthermore, $\tilde{\psi}_f$ and $\tilde{\psi}_r$ must vanish for the static history $\Lambda^t(s) = \Lambda(t)$, $s \in \mathbb{R}^+$.

Proof. Let

$$\psi_1(t) = \Psi_1(\Lambda^t(s), \Lambda(t))$$

be an alternative choice of free energy, obeying the thermodynamic constraints. Then P1 or (5.1.30) gives that

$$\partial_\Lambda(\tilde{\psi} - \tilde{\psi}_1) = \mathbf{0},$$

so that

$$\tilde{\psi}_1(\Lambda^t, \Lambda(t)) = \tilde{\psi}(\Lambda^t, \Lambda(t)) + \tilde{\psi}_r(\Lambda^t),$$

where $\tilde{\psi}_r$ is arbitrary within thermodynamic constraints on $\tilde{\psi}_1$ and of course may be zero. We can always separate out $\tilde{\phi}(\Lambda_0(t))$ (by adding and subtracting this quantity), and the resulting memory terms $\tilde{\psi}_f$ or $\tilde{\psi}_f + \tilde{\psi}_r$ must obey the thermodynamic constraints. Finally, since $\tilde{\phi}(\Lambda_0(t))$ is uniquely defined, $\tilde{\psi}_f$ must vanish for the static history if $\tilde{\psi}_r$ is zero, as noted in (5.1.27), and any choice of $\tilde{\psi}_r$ must have the same property, which completes the proof. \square

This result is a simpler version of a proposition given in [159]. The origin of the simplification is the use of ψ rather than ψ_n . It is also a general statement of a property noted below (see (7.1.16)) in connection with free energies that are quadratic in the memory terms.

The internal energy is unique. A list of other unique quantities involving the Helmholtz free energy ψ_n , entropy, and dissipation is given in [159].

5.2 The Maximum Recoverable Work for General Materials

In the next and subsequent chapters, we deal with the case of free energies given by quadratic functionals, leading to constitutive equations with linear memory terms. Before leaving the general formulation, it is of interest to note that results can be obtained, using functional differentiation, that correspond to key formulas derived later in the linear memory case. One example will be given, namely the formulas

determining the maximum recoverable work. Others can be derived, with somewhat greater difficulty, notably formulas for the work function as a double integral over histories, the generalization of (7.5.7).[§] Let us define

$$\mathbf{V}(t) = \dot{\Lambda}(t), \quad \mathbf{V} \in \Gamma,$$

noting that

$$\Lambda(t) = \Lambda(-\infty) + \int_{-\infty}^t \mathbf{V}(s) ds, \quad (5.2.1)$$

where $\Lambda(-\infty)$ is a constant, which is taken to be zero. The integral is assumed to exist. Let

$$\mathbf{V}^t = \{\mathbf{V}(s); s \leq t\}, \quad (5.2.2)$$

which is a similar convention to that in (5.1.14). The sum of two such sets is understood to mean

$$\mathbf{V}_1^t + \mathbf{V}_2^t = \{\mathbf{V}_1(s) + \mathbf{V}_2(s); s \leq t\}.$$

Relations (5.2.1) and (5.2.2) allow us to write $\tilde{\Sigma}(\Lambda^t, \Lambda(t))$ in (5.1.18) compactly as

$$\Sigma(t) = \tilde{\Sigma}(\mathbf{V}^t) = \Sigma_e(t) + \tilde{\Sigma}_{rh}(\mathbf{V}^t),$$

in the notation of (5.1.28) and (5.1.29). The work done on the material up to time t is given by (5.1.34)₃ or

$$W(t) = \tilde{W}(\mathbf{V}^t) = \int_{-\infty}^t \tilde{\Sigma}(\mathbf{V}^s) \cdot \mathbf{V}(s) ds,$$

where the integral is assumed to be finite. Using (5.1.29), the recoverable work from the state at time t may be written as

$$W_R(t) = \tilde{W}_R(\mathbf{V}^t) = - \int_t^{\infty} \tilde{\Sigma}(\mathbf{V}^s) \cdot \mathbf{V}(s) ds = \phi(t) - \int_t^{\infty} \tilde{\Sigma}_{rh}(\mathbf{V}^s) \cdot \mathbf{V}(s) ds, \quad (5.2.3)$$

where $\mathbf{V}(s)$, $s \geq t$, is the process determining the evolution of the state after time t , chosen so that the integrals in (5.2.3) exist. We take $\phi(\infty)$ to be zero. Let us assume that $\tilde{\Sigma}_{rh}$ is continuously Fréchet differentiable in the fading memory Hilbert space \mathcal{H} . Let $\mathcal{A} : \mathbb{R} \mapsto \Gamma$ belong to \mathcal{H} , and let \mathcal{A}^t be defined in the same way as \mathbf{V}^t by (5.2.2). Then,

$$\tilde{\Sigma}_{rh}(\mathbf{V}^s + \mathcal{A}^s) = \tilde{\Sigma}_{rh}(\mathbf{V}^s) + \delta\tilde{\Sigma}_{rh}(\mathbf{V}^s|\mathcal{A}^s) + \mathbf{o}\|\mathcal{A}^s\| \quad \forall \mathcal{A}^s \in \Gamma, \quad (5.2.4)$$

where $\delta\tilde{\Sigma}$ is the Fréchet differential, continuous in \mathbf{V}^s and linear in \mathcal{A}^s . Also, $\|\cdot\|$ is the norm in \mathcal{H} . By the Riesz representation theorem, we can write

$$\delta\tilde{\Sigma}_{rh}(\mathbf{V}^s|\mathcal{A}^s) = \int_{-\infty}^{\infty} \mathbb{L}(s, u; \mathbf{V}^s)\mathcal{A}(u) du, \quad (5.2.5)$$

where $\mathbb{L} \in \text{Lin}(\Gamma)$ and

$$\mathbb{L}(s, u; \mathbf{V}^s) = \mathbf{0}, \quad s < u, \quad (5.2.6)$$

since values of $\mathcal{A}(u)$, $u > s$, cannot contribute.

[§] J. M. Golden, unpublished notes.

Proposition 5.2.1. *The maximum recoverable work, which, by Theorem 4.2.3, is equal to the minimum free energy, can be expressed in the form*

$$W_{rm}(t) = \phi(t) + \frac{1}{2} \int_t^\infty ds \int_t^\infty du \mathbb{L}_S(u, s; \mathbf{V}_m) \mathbf{V}_m(u, t) \cdot \mathbf{V}_m(s, t)$$

with

$$\mathbb{L}_S(u, s; \mathbf{V}_m) = \begin{cases} \mathbb{L}(s, u; \mathbf{V}_m^s), & s > u, \\ \mathbb{L}^\top(u, s; \mathbf{V}_m^u), & s < u, \end{cases} \quad (5.2.7)$$

where $\mathbf{V}_m(\cdot, t)$ is the solution of the equation

$$\tilde{\Sigma}_{rh}(\mathbf{V}^s) + \int_s^\infty \mathbb{L}^\top(u, s; \mathbf{V}^u) \mathbf{V}(u) du = \mathbf{0}, \quad s \geq t. \quad (5.2.8)$$

Proof. We seek to maximize the recoverable work given by (5.2.3). Applying a variation

$$\mathbf{V}^s \rightarrow \mathbf{V}^s + \mathcal{A}^s, \quad \mathcal{A}(u) = \mathbf{0} \text{ if } u < t,$$

we obtain the condition

$$\int_t^\infty \tilde{\Sigma}_{rh}(\mathbf{V}^s) \cdot \mathcal{A}(s) ds + \int_t^\infty ds \int_t^s du \mathbb{L}(s, u; \mathbf{V}^s) \mathcal{A}(u) \cdot \mathbf{V}(s) = 0, \quad (5.2.9)$$

with the aid of (5.2.4)–(5.2.6). Noting the identities

$$\int_t^\infty ds \int_t^s du F(s, u) = \int_t^\infty du \int_u^\infty ds F(s, u) = \int_t^\infty ds \int_s^\infty du F(u, s), \quad (5.2.10)$$

relation (5.2.9) becomes, using (A.2.3),

$$\begin{aligned} & \int_t^\infty \tilde{\Sigma}_{rh}(\mathbf{V}^s) \cdot \mathcal{A}(s) ds + \int_t^\infty ds \int_s^\infty du \mathbb{L}(u, s; \mathbf{V}^u) \mathcal{A}(s) \cdot \mathbf{V}(u) \\ &= \int_t^\infty \tilde{\Sigma}_{rh}(\mathbf{V}^s) \cdot \mathcal{A}(s) ds + \int_t^\infty ds \int_s^\infty du \mathbb{L}^\top(u, s; \mathbf{V}^u) \mathbf{V}(u) \cdot \mathcal{A}(s) = 0. \end{aligned}$$

The arbitrariness of \mathcal{A} gives (5.2.8), the solution of which yields the optimal future process $\mathbf{V}_m(\cdot, t)$. Using (5.2.8) in (5.2.3), we obtain, by adding the leftmost and rightmost forms of (5.2.10), an expression for the maximum recoverable work or the minimum free energy

$$\begin{aligned} W_{rm}(t) &= \psi_m(t) \\ &= \phi(t) + \int_t^\infty ds \int_s^\infty du \mathbb{L}^\top(u, s; \mathbf{V}_m^u) \mathbf{V}_m(u, t) \cdot \mathbf{V}_m(s, t) \\ &= \phi(t) + \frac{1}{2} \int_t^\infty ds \int_t^\infty du \mathbb{L}_S(u, s; \mathbf{V}_m) \mathbf{V}_m(u, t) \cdot \mathbf{V}_m(s, t), \end{aligned} \quad (5.2.11)$$

where \mathbb{L}_S is given by (5.2.7). □

Note that

$$\mathbb{L}_S^\top(u, s; \mathbf{V}_m) = \mathbb{L}_S(s, u; \mathbf{V}_m).$$

We observe that the form (5.2.11)₂ is a generalization of a result given in Sect. 7.5, while (5.2.8) is a generalized form of the Wiener–Hopf equation (11.2.26).

5.3 Generation of New Free Energies

If some free energies are known for a certain category of materials, for example, those with constitutive equations that have linear memory, we ask in this section, and answer affirmatively, whether it is possible to construct (for example, nonlinear) functions of the known quantities that are free energies relating to more general materials (for example, those with constitutive equations that have nonlinear memory). Note that the findings discussed here are quite different from those in Chap. 17, which deals only with quadratic functionals producing linear memory constitutive equations.

Let $\psi_1(t), \psi_2(t), \dots, \psi_n(t)$ be a set of n free energies relating to a state $(\mathbf{\Lambda}^t, \mathbf{\Lambda}(t))$ in a given material, or perhaps in different materials, at time t . To allow for the latter possibility, we assign to each $\psi_i(t)$, $i = 1, 2, \dots, n$, different constitutive equations

$$\Sigma_i(t) = \tilde{\Sigma}_i(\mathbf{\Lambda}^t, \mathbf{\Lambda}(t))$$

and work functions

$$W_i(t) = \int_{-\infty}^t \Sigma_i(s) \cdot \dot{\mathbf{\Lambda}}(s) ds,$$

where

$$\frac{\partial \psi_i(t)}{\partial \mathbf{\Lambda}(t)} = \Sigma_i(t), \quad i = 1, 2, \dots, n, \quad (5.3.1)$$

and, by virtue of (5.1.33),

$$\dot{\psi}_i(t) \leq \Sigma_i(t) \cdot \dot{\mathbf{\Lambda}}(t), \quad i = 1, 2, \dots, n.$$

If all these free energies belong to the same material, the dependent field variables Σ_i are all equal and the index i refers to different free energies of the same material.

Proposition 5.3.1. *The quantity*

$$\psi(t) = f(\psi_1(t), \psi_2(t), \dots, \psi_n(t)) \quad (5.3.2)$$

is a free energy for the state $(\mathbf{\Lambda}^t, \mathbf{\Lambda}(t))$ with the dependent field given by

$$\Sigma(t) = \sum_{i=1}^n \frac{\partial f}{\partial \psi_i(t)} \Sigma_i(t), \quad (5.3.3)$$

provided that $f : (\mathbb{R}^+)^n \mapsto \mathbb{R}^+$ has the properties

$$\frac{\partial}{\partial y_i} f(y_1, y_2, \dots, y_n) \geq 0, \quad i = 1, 2, \dots, n, \quad (5.3.4)$$

and

$$f(0, 0, \dots, 0) = 0. \quad (5.3.5)$$

Proof. We have

$$\dot{\psi}(t) = \sum_{i=1}^n \frac{\partial f}{\partial \psi_i(t)} \dot{\psi}_i(t) \leq \sum_{i=1}^n \frac{\partial f}{\partial \psi_i(t)} \Sigma_i(t) \cdot \dot{\Lambda}(t) = \Sigma(t) \cdot \dot{\Lambda}(t),$$

where Σ is defined by (5.3.3). Thus, property 4 of a free energy, given by (5.1.33), holds. Also, by virtue of (5.3.1) and (5.3.3),

$$\frac{\partial \psi(t)}{\partial \Lambda(t)} = \Sigma(t), \quad (5.3.6)$$

which is property 1 as given by (5.1.30). If $\phi_i(t)$, $i = 1, 2, \dots, n$, are the equilibrium free energies corresponding to $\psi_i(t)$, according to the prescription (5.1.31), then

$$\phi(t) = f(\phi_1(t), \phi_2(t), \dots, \phi_n(t))$$

and property 3, i.e., (5.1.32), is obeyed by virtue of the assumptions (5.3.4).

If (5.1.16) is to hold for all free energies ψ and $\psi_i(t)$, $i = 1, 2, \dots, n$, then we must have (5.3.5). \square

This result can be used, for example, as follows: assume we have a nonlinear dependent field variable of the form (5.3.3), where f obeys (5.3.4) and the Σ_i are determined by (5.3.1). Then (5.3.2) immediately gives a free energy that generates $\Sigma(t)$ through (5.3.6).

Taking f to be an analytic function of its arguments at the origin, we can write

$$\psi(t) = \sum_{i=1}^n \lambda_i \psi_i(t) + \text{higher powers}. \quad (5.3.7)$$

A constant term is excluded by (5.3.5). If we omit higher powers, taking ψ to be a linear combination of the ψ_i , it follows from (5.3.4) that

$$\lambda_i \geq 0, \quad i = 1, 2, \dots, n. \quad (5.3.8)$$

If the free energies ψ_i , $i = 1, 2, \dots, n$, relate to the same material, then (5.3.3) becomes

$$\Sigma(t) = \kappa(t) \Sigma_{sm}(t), \quad \kappa(t) = \sum_{i=1}^n \frac{\partial f}{\partial \psi_i(t)},$$

$$\Sigma_{sm}(t) = \Sigma_1(t) = \Sigma_2(t) = \dots = \Sigma_n(t).$$

Let higher powers be neglected in (5.3.7). If ψ is assumed to relate to the same material as the ψ_i , $i = 1, 2, \dots, n$, then

$$\Sigma_{sm}(t) = \Sigma(t)$$

and

$$\sum_{i=1}^n \frac{\partial f}{\partial \psi_i(t)} = \sum_{i=1}^n \lambda_i = 1.$$

This, together with (5.3.8), amounts to convexity (see Proposition 4.1.7).

The next chapter is something of a diversion from the main flow of the discussion, to consider Thermoelectromagnetism.