



On the Gibbs conditions of stable equilibrium, convexity and the second-order variations of thermodynamic potentials in nonlinear thermoelasticity

V.A. Lubarda *

*Department of Mechanical and Aerospace Engineering, University of California, San Diego, La Jolla, CA 92093-0411, USA
Montenegrin Academy of Sciences and Arts, 81000 Podgorica, R. Stijovića 5, Montenegro*

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Abstract

The Gibbs conditions of stable thermodynamic equilibrium are formulated for nonlinear thermoelastic materials, based on the constrained minimization of four fundamental thermodynamic potentials. Sufficient conditions for incremental stability are stated in each case. The previously unexplored connections between the second-order variations of thermodynamic potentials are used to establish the convexity or concavity properties of all thermodynamic potentials in relation to each other, and to derive the relationships between the specific heats at constant stress and deformation, and between the isentropic and isothermal elastic moduli and compliances. The comparison with the derivation based on the classical thermodynamic approach is also given.

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1. Introduction

The classical conditions for stability of equilibrium of various thermodynamic states, with a particular emphasis to chemical equilibrium, were formulated by Gibbs (1875–1878). The system is in thermodynamic equilibrium if its state variables do not spontaneously change with time. The equilibrium state of an isolated system at constant volume and internal energy is the state with the maximum value of the total entropy. Consider a uniform body of volume V and mass density $\rho = m/V$, which is in a stable thermodynamic equilibrium at temperature T and pressure p . Let $\vartheta = 1/\rho$ be the specific volume, and let $u = U/m$ and $s = S/m$ be the uniform specific internal energy and entropy, respectively. Any (spatially nonuniform) virtual variation $(\delta u, \delta \vartheta)$ from a stable equilibrium state, prescribed under the constraints of constant total internal energy U and constant total volume V , gives rise to a decrease of the total entropy S . Thus,

* Tel.: +1 858 534 3169; fax: +1 858 534 5698.
E-mail address: vlubarda@ucsd.edu

Nomenclature

List of symbols

p, V	pressure, volume
ρ	mass density
ϑ	specific volume
T	temperature
s, S	entropy (specific and total)
u, U	internal energy
f, \mathcal{F}	Helmholtz free energy F
h, H	enthalpy
g, G	Gibbs energy
Π	potential energy
Π^*	complementary energy
X_J, x_i	referential and spatial coordinates
F_{iJ}	deformation gradient
P_{Ji}	nominal stress
b_i	body force
t_i	traction
A_{JiLk}	instantaneous elastic moduli
M_{iJKL}	instantaneous elastic compliances
l_{Ji}^F, l_{iJ}^P	latent heats at constant F and P
c_F, c_P	specific heats at constant F and P
α_{iJ}	coefficients of thermal expansion

$$\Delta S = \int_V \rho \Delta s(u, \vartheta) dV < 0, \quad S = \int_V \rho s(u, \vartheta) dV,$$

subjected to the constraints

$$\Delta U = \int_V \rho \delta u dV = 0, \quad \Delta V = \int_V \rho \delta \vartheta dV = 0.$$

Equivalently, among all neighboring states with the same volume and total entropy, the equilibrium state is one with the lowest total internal energy, *i.e.*,

$$\Delta U = \int_V \rho \Delta u(s, \vartheta) dV > 0,$$

under the constraints

$$\Delta S = \int_V \rho \delta s dV = 0, \quad \Delta V = \int_V \rho \delta \vartheta dV = 0.$$

Based on the Gibbs analysis, it furthermore follows that: (a) among all neighboring states with the same volume and temperature, the equilibrium state is one with the lowest Helmholtz free energy; (b) among all neighboring states with the same pressure and entropy, the equilibrium state is one with the lowest enthalpy; and (c) among all neighboring states at the same temperature and pressure, the equilibrium state is one with the lowest Gibbs energy. Detailed analysis of these assertions, with their consequences, can be found in standard texts on thermodynamics, such as Callen (1960); Kestin (1979), and Müller (1985).

The Gibbs conditions of equilibrium are most often formulated and applied to thermodynamic systems under pure hydrostatic pressure. The mathematical formulation of the Gibbs conditions for solids under arbitrary states of stress and deformation, such as arise in nonlinear finite strain elasticity, has received less attention. Coleman and Noll (1959) stated the conditions for thermomechanical stability of equilibrium states

under constant temperature (isothermal stability) and constant total entropy of the body (adiabatic stability), using the Helmholtz free energy in the first case, and the internal energy in the second case. They extended the Gibbs analysis by specifying the boundary conditions to be either the prescribed surface displacements or the prescribed surface tractions, so that the virtual variations from the equilibrium state are at constant overall geometry in the first case, and constant loading in the second case. Various aspects of the thermodynamics of elastic stability were further studied by Truesdell and Noll (1965), Ericksen (1966, 1991); Gurtin (1973); Koiter (1969, 1982), Šilhavý (1997), among others. There has also been a significant amount of research devoted to the stability of internally constrained thermoelastic materials, which are subject to either the deformation-temperature or the deformation-entropy constraints. Representative recent work in this area includes Chadwick and Scott (1992), Casey and Krishnaswamy (1998); Scott (2001), and Rooney and Bechtel (2004). The stability and the convexity properties of thermodynamic potentials for compressible viscous fluids have been recently examined by Bechtel et al. (2003, 2005); see also Woods (1986).

In the present paper we formulate the conditions of thermodynamic equilibrium under the constraint of zero net work of external tractions on small geometrically admissible virtual displacements from the equilibrium state, in addition to the usual constraints on the total entropy or the temperature. The mixed traction/displacement boundary conditions are also considered. The conditions are first formulated in terms of the constrained minimization of the internal energy (or the constrained maximization of the entropy), and then in terms of the constrained minimization of other thermodynamic potentials (Helmholtz free energy, enthalpy, and Gibbs energy). Sufficient conditions for the incremental stability of thermodynamic equilibrium, with respect to disturbances in a near neighborhood of the considered equilibrium state, are stated in each case. The relationships between the second-order variations of the thermodynamic potentials are derived, which reveal the convexity or concavity properties of all thermodynamic potentials, based on the convexity property of the internal energy function. These relationships, previously unexplored in the literature, are then used to construct the new derivation of the fundamental thermodynamic connections between the specific heats at constant stress and deformation, and between the isentropic and isothermal elastic moduli and compliances. The comparison with the classical derivation, based on the formal change of independent variables and the corresponding chain-rule partial differentiation, is also given.

2. Internal energy

Consider an elastic body under a self-equilibrated traction field t_i applied over the portion A_t of the bounding surface A of the body of current volume V at uniform temperature T . The Gibbs condition of stable equilibrium for such body can be stated as:

The internal energy of a stable equilibrium state is at minimum with respect to any small geometrically admissible virtual displacement field giving no net virtual work from external tractions, and any virtual local entropy variation subjected to the constraint of constant total entropy.

Phrased differently, the internal energy is at minimum in a stable equilibrium state with respect to any small virtual variation of the equilibrium state which is associated with zero net work from external loading and zero heat exchanged with the surroundings of the body.¹ To elaborate and examine the consequences of this condition, let s and u be the specific entropy and internal energy (per unit initial volume V^0). The total internal energy in the body is then

$$U = \int_{V^0} u(s, F_{iJ}) dV^0, \quad (1)$$

where $u = u(s, F_{iJ})$ is the so-called caloric equation of state of the material, and $F_{iJ} = \partial x_i / \partial X_J$ are the rectangular components of the deformation gradient, which maps a material element dX_J from its initial to its current position $dx_i = F_{iJ} dX_J$. The upper case index is used to indicate the referential and the lower case the spatial coordinates. For example, a two-point tensor of the deformation gradient is $\mathbf{F} = F_{iJ} \mathbf{e}_i \otimes \mathbf{e}_J^0$, where \mathbf{e}_i and \mathbf{e}_J^0 are the orthonormal base vectors in the deformed and undeformed configurations, respectively, and \otimes stands for the dyadic product. The function u is assumed to be objective, *i.e.*, properly invariant under a change of the reference frame – thus, dependent

¹ An alternative to the constrained internal energy minimization is the constrained entropy maximization, presented in the [Appendix](#) of this paper.

only on the stretch part U_{IJ} from the polar decomposition of the deformation gradient $F_{iJ} = R_{iK}U_{KJ}$. If the internal energy has a local minimum in the considered equilibrium configuration, then

$$\Delta U = \int_{V^0} \Delta u(s, F_{iJ}) dV^0 > 0, \quad (2)$$

for any small variations δs and δF_{iJ} , subjected to the constraints²

$$\int_{A_i^0} t_i^0 \delta x_i dA^0 = 0, \quad \int_{V^0} \delta s dV^0 = 0, \quad (3)$$

where t_i^0 is the nominal traction, per unit undeformed area ($t_i^0 dA^0 = t_i dA$).

The change of the specific internal energy due to variations δs and δF_{iJ} is

$$\Delta u = \sum_{k=1}^{\infty} \frac{1}{k!} \delta^k u, \quad \delta^k u = \left(\delta s \frac{\partial}{\partial s} + \delta F_{iJ} \frac{\partial}{\partial F_{iJ}} \right)^k u. \quad (4)$$

The first-order variation of u is

$$\delta u = T \delta s + P_{Ji} \delta F_{iJ}, \quad (5)$$

where $T = \partial u / \partial s$ is the temperature and $P_{Ji} = \partial u / \partial F_{iJ}$ are the components of the nominal stress (work conjugate to F_{iJ}). A local state (s, F_{iJ}) is an equilibrium state under the temperature/stress pair (T, P_{Ji}) .³ Eq. (5) is a generalized Gibbs relation (the energy equation of reversible nonlinear thermoelasticity; e.g.; Holzapfel, 2000). The second-order variation of u is

$$\delta^2 u = \frac{\partial^2 u}{\partial s^2} (\delta s)^2 + 2 \frac{\partial^2 u}{\partial s \partial F_{iJ}} \delta s \delta F_{iJ} + \frac{\partial^2 u}{\partial F_{iJ} \partial F_{kL}} \delta F_{iJ} \delta F_{kL}. \quad (6)$$

By the constraint conditions (3), we first have

$$\int_{V^0} T \delta s dV^0 = T \int_{V^0} \delta s dV^0 = 0. \quad (7)$$

Since $t_i^0 = n_J^0 P_{Ji}$ and $P_{Ji,J} = 0$ (by equilibrium equations in the absence of body forces), we can write

$$\int_{V^0} P_{Ji} \delta F_{iJ} dV^0 = \int_{A_i^0} t_i^0 \delta x_i dA^0 = \int_{A_i^0} t_i^0 \delta x_i dA^0 = 0, \quad (8)$$

where $\delta x_i = 0$ over $A_x^0 = A^0 - A_i^0$. From (2) it then follows that

$$\Delta U = \sum_{k=2}^{\infty} \frac{1}{k!} \int_{V^0} \delta^k u dV^0 = \frac{1}{2} \int_{V^0} \delta^2 u dV^0 + \text{higher order terms} > 0. \quad (9)$$

An obviously sufficient condition for (9) is that at each point of the body $u = u(s, F_{iJ})$ is a locally convex function of its arguments. A sufficient condition for this convexity is that the Hessian matrix of u is positive-definite, i.e.,

$$\frac{\partial^2 u}{\partial s^2} (\delta s)^2 + 2 \frac{\partial^2 u}{\partial s \partial F_{iJ}} \delta s \delta F_{iJ} + \frac{\partial^2 u}{\partial F_{iJ} \partial F_{kL}} \delta F_{iJ} \delta F_{kL} > 0. \quad (10)$$

In summary, if $\delta^2 u > 0$ at all points of the body, the considered equilibrium state is locally stable, relative to configurations in its near neighborhood, under the loading and entropy constraints (3).⁴

² For example, the zero external net work is assured by taking $\delta x_i = 0$ over the portion of S_i where the prescribed tractions do not vanish. Furthermore, if $A_i^0 = 0$, so that the displacement boundary conditions are prescribed over entire A^0 , the first of the conditions (3) is satisfied automatically (cf. Coleman and Noll, 1959).

³ The moment equilibrium requires that the Kirchhoff stress $\tau_{ij} = F_{iK} P_{Kj}$ is symmetric, which places the restriction on u given by $F_{iK} (\partial u / \partial F_{jK}) = (\partial u / \partial F_{iK}) F_{jK}$.

⁴ The constraint of zero net work of external traction on virtual displacement from the equilibrium state is too restrictive for buckling analysis (e.g., Bažant and Cedolin, 1991, for which the constraint of constant load is more physically appealing to calculate, in conjunction with an appropriate potential energy function, the critical buckling load. This type of constraint is discussed in the context of Gibbs energy in Section 5.

3. Helmholtz free energy

The Helmholtz free energy of a stable equilibrium state is at minimum with respect to any small geometrically admissible virtual displacement field giving no net virtual work from external tractions, and any virtual local entropy variation applied at constant temperature.

This means that the Helmholtz free energy is at minimum in a stable equilibrium state with respect to any isothermal small virtual variation of equilibrium state that is associated with zero net work from external loading. The total Helmholtz free energy of the body is

$$\mathcal{F} = \int_{V^0} u(s, F_{iJ}) dV^0 - T \int_{V^0} s dV^0. \quad (11)$$

The change of \mathcal{F} is

$$\Delta\mathcal{F} = \int_{V^0} \Delta u(s, F_{iJ}) dV^0 - T \int_{V^0} \delta s dV^0, \quad (12)$$

for any small variations δs and δF_{iJ} , subjected to the constraints $\int_{A^0} t_i^0 \delta x_i dA^0 = 0$ and $\delta T = 0$. In view of (4) and the energy Eq. (5), there follows

$$\Delta\mathcal{F} = \sum_{k=2}^{\infty} \frac{1}{k!} \int_{V^0} \delta^k u dV^0 = \frac{1}{2} \int_{V^0} \delta^2 u dV^0 + \text{higher order terms}. \quad (13)$$

Thus, if $\delta^2 u > 0$ at all points of the equilibrium state, it follows that $\Delta\mathcal{F} > 0$ in (13).

The specific Helmholtz free energy is a thermodynamic potential with T and F_{iJ} as its natural independent variables, so that

$$\mathcal{F} = \int_{V^0} f(T, F_{iJ}) dV^0, \quad \Delta\mathcal{F} = \int_{V^0} \Delta f(T, F_{iJ}) dV^0. \quad (14)$$

Under isothermal variation of deformation, the change of the free energy density is

$$\Delta f = \frac{\partial f}{\partial F_{iJ}} \delta F_{iJ} + \frac{1}{2} \frac{\partial^2 f}{\partial F_{iJ} \partial F_{kL}} \delta F_{iJ} \delta F_{kL} + \dots \quad (15)$$

Since $P_{Ji} = \partial f / \partial F_{iJ}$, and in view of the constraint $\int_{A^0} t_i^0 \delta x_i dA^0 = 0$, there follows

$$\Delta\mathcal{F} = \frac{1}{2} \int_{V^0} \frac{\partial^2 f}{\partial F_{iJ} \partial F_{kL}} \delta F_{iJ} \delta F_{kL} dV^0 + \dots \quad (16)$$

This must be positive for any isothermal small virtual variations δF_{iJ} , consistent with the specified boundary constraints. A sufficient condition for $\Delta\mathcal{F} > 0$ in (16) is that $f = f(T, F_{iJ})$ is locally convex function of F_{iJ} at all points of the body in the considered equilibrium state. In particular, this is assured if the Hessian matrix of the elastic strain energy density (free energy density under isothermal conditions) is positive-definite at all points of the body in the considered equilibrium state,⁵

$$\frac{\partial^2 f}{\partial F_{iJ} \partial F_{kL}} \delta F_{iJ} \delta F_{kL} > 0. \quad (17)$$

3.1. Relationships between the second-order variations of f and u

The internal and free energy densities are related by the Legendre transform

⁵ In finite strain elasticity, incremental uniqueness and stability are closely related. Hill (1957) was the first to show that strict convexity of the strain-energy function with respect to deformation gradient everywhere in the deformation gradient space implies uniqueness. Such convexity would be too restrictive, because global uniqueness of equilibrium in nonlinear elasticity is physically not expected. Thus, small variations from the equilibrium state are considered, which amounts to conditions for incremental (infinitesimal) uniqueness and stability, in a near neighborhood of the considered equilibrium state (Knops and Wilkes, 1973; Gurtin, 1982; Ogden, 1997).

$$f(T, F_{ij}) = u(s, F_{ij}) - Ts. \quad (18)$$

Consider a virtual variation of state $(\delta s, \delta F_{ij})$, which obeys the energy equation, and denote by δT the corresponding temperature variation. Then,

$$f(T + \delta T, F_{ij} + \delta F_{ij}) = u(s + \delta s, F_{ij} + \delta F_{ij}) - (T + \delta T)(s + \delta s). \quad (19)$$

Upon the expansion in the Taylor series and the collection of the same-order terms, there follows

$$\begin{aligned} \delta f &= \delta u - T\delta s - s\delta T = P_{ji}\delta F_{ij} - s\delta T, \\ \delta^2 f &= \delta^2 u - 2\delta T\delta s, \\ \delta^k f &= \delta^k u, \quad k \geq 3. \end{aligned} \quad (20)$$

Since

$$T = \frac{\partial u}{\partial s} \Rightarrow \delta T = \frac{\partial^2 u}{\partial s^2} \delta s + \frac{\partial^2 u}{\partial s \partial F_{ij}} \delta F_{ij}, \quad (21)$$

$$s = -\frac{\partial f}{\partial T} \Rightarrow \delta s = -\frac{\partial^2 f}{\partial T^2} \delta T - \frac{\partial^2 f}{\partial T \partial F_{ij}} \delta F_{ij}, \quad (22)$$

the substitution into (20) yields the desired relationships between the second-order variations of f and u . These are

$$\frac{\partial^2 f}{\partial T^2} (\delta T)^2 + 2 \frac{\partial^2 f}{\partial T \partial F_{ij}} \delta T \delta F_{ij} + \frac{\partial^2 f}{\partial F_{ij} \partial F_{kl}} \delta F_{ij} \delta F_{kl} = -\frac{\partial^2 u}{\partial s^2} (\delta s)^2 + \frac{\partial^2 u}{\partial F_{ij} \partial F_{kl}} \delta F_{ij} \delta F_{kl}, \quad (23)$$

$$\frac{\partial^2 u}{\partial s^2} (\delta s)^2 + 2 \frac{\partial^2 u}{\partial s \partial F_{ij}} \delta s \delta F_{ij} + \frac{\partial^2 u}{\partial F_{ij} \partial F_{kl}} \delta F_{ij} \delta F_{kl} = -\frac{\partial^2 f}{\partial T^2} (\delta T)^2 + \frac{\partial^2 f}{\partial F_{ij} \partial F_{kl}} \delta F_{ij} \delta F_{kl}. \quad (24)$$

Both of these imply that, for $\delta F_{ij} = 0$,

$$\frac{\partial^2 f}{\partial T^2} (\delta T)^2 = -\frac{\partial^2 u}{\partial s^2} (\delta s)^2.$$

Thus, at the state where u is a convex function of entropy, f is a concave function of temperature, i.e.,⁶

$$\frac{\partial^2 u}{\partial s^2} > 0 \Rightarrow \frac{\partial^2 f}{\partial T^2} < 0. \quad (25)$$

Furthermore, by considering isothermal variations of deformation, (24) confirms (17), whenever $\delta^2 u$, given by the left-hand side of (24), is a positive-definite quadratic form. It is also noted that (23) implies that $\delta^2 f$ itself is a positive-definite quadratic form for any isentropic variation of deformation gradient and temperature, whenever the Hessian matrix of u with respect to the deformation gradient is positive definite.⁷

4. The enthalpy function

The enthalpy of a stable equilibrium configuration, under prescribed traction boundary conditions, is at minimum with respect to any small geometrically admissible virtual displacement field, applied at constant external loading, and any virtual local entropy variation, subjected to the constraint of constant total entropy.

The total enthalpy of the body is

$$H = U - \int_{V^0} P_{ji} F_{ij} dV^0 = \int_{V^0} u(s, F_{ij}) dV^0 - \int_{V^0} b_i^0 x_i dV^0 - \int_{A^0} t_i^0 x_i dA^0, \quad (26)$$

⁶ It is commonly assumed that that entropy is a monotonically increasing function of temperature (e.g.; Callen, 1960), so that $\partial s / \partial T = -\partial^2 f / \partial T^2 > 0$, in accord with (25).

⁷ The explicit representations of all four thermodynamic potentials of linear thermoelasticity, in terms of their natural independent variables, are listed in Lubarda (2004) and Asaro and Lubarda (2006).

because $F_{iJ} = x_{i,J}$ and $P_{Ji} + b_i^0 = 0$ by equilibrium equations in the presence of body forces b_i^0 (per unit initial volume). In view of the loading constraints $\delta t_i^0 = 0$ over A^0 and $\delta b_i^0 = 0$ in V^0 (dead loading), the change of enthalpy is

$$\Delta H = \int_{V^0} \Delta u(s, F_{iJ}) dV^0 - \int_{V^0} b_i^0 \delta x_i dV^0 - \int_{A^0} t_i^0 \delta x_i dA^0. \quad (27)$$

Since $t_i^0 = n_J^0 P_{Ji}$, and in view of equilibrium equations and the Gauss divergence theorem, the above reduces to

$$\Delta H = \int_{V^0} [\Delta u(s, F_{iJ}) - P_{Ji} \delta F_{iJ}] dV^0. \quad (28)$$

By using (4), the energy Eq. (5), and the constraint $\int_{V^0} T \delta s dV^0 = 0$, with $T = \text{const.}$, ΔH becomes

$$\Delta H = \sum_{k=2}^{\infty} \frac{1}{k!} \int_{V^0} \delta^k u dV^0 = \frac{1}{2} \int_{V^0} \delta^2 u dV^0 + \text{higher order terms}. \quad (29)$$

Again, $\delta^2 u > 0$ at all points of the body implies that $\Delta H > 0$ in (29).

The specific enthalpy is a thermodynamic potential with s and P_{Ji} as its natural independent variables, so that

$$H = \int_{V^0} h(s, P_{Ji}) dV^0, \quad \Delta H = \int_{V^0} \Delta h(s, P_{Ji}) dV^0. \quad (30)$$

The change of the specific enthalpy under constant stress is

$$\Delta h = \frac{\partial h}{\partial s} \delta s + \frac{1}{2} \frac{\partial^2 h}{\partial s^2} (\delta s)^2 + \dots \quad (31)$$

Since $T = \partial h / \partial s$, and using the constraint of constant total entropy, there follows

$$\Delta H = \frac{1}{2} \int_{V^0} \frac{\partial^2 h}{\partial s^2} (\delta s)^2 dV^0 + \dots \quad (32)$$

This must be positive for any variation δs at constant stress, which is assured if h is a convex function of entropy at each point of the body in the considered equilibrium state. A sufficient condition for this is that

$$\frac{\partial^2 h}{\partial s^2} > 0. \quad (33)$$

4.1. Relationships between the second-order variations of h and u

The internal energy and enthalpy are related by the Legendre transform

$$h(s, P_{Ji}) = u(s, F_{iJ}) - P_{Ji} F_{iJ}. \quad (34)$$

Consider an arbitrary virtual variation of state $(\delta s, \delta F_{iJ})$, which obeys the energy equation, and denote by δP_{Ji} the corresponding stress variation. Then,

$$h(s + \delta s, F_{iJ} + \delta F_{iJ}) = u(s + \delta s, F_{iJ} + \delta F_{iJ}) - (P_{Ji} + \delta P_{Ji})(F_{iJ} + \delta F_{iJ}). \quad (35)$$

Upon the Taylor expansion and the collection of the same-order terms, there follows

$$\begin{aligned} \delta h &= \delta u - P_{Ji} \delta F_{iJ} - F_{iJ} \delta P_{Ji} = T \delta s - F_{iJ} \delta P_{Ji}, \\ \delta^2 h &= \delta^2 u - 2 \delta P_{Ji} \delta F_{iJ}, \\ \delta^k h &= \delta^k u, \quad k \geq 3. \end{aligned} \quad (36)$$

Since

$$P_{Ji} = \frac{\partial u}{\partial F_{iJ}} \Rightarrow \delta P_{Ji} = \frac{\partial^2 u}{\partial F_{iJ} \partial s} \delta s + \frac{\partial^2 u}{\partial F_{iJ} \partial F_{kL}} \delta F_{kL}, \quad (37)$$

$$F_{iJ} = -\frac{\partial h}{\partial P_{Ji}} \Rightarrow \delta F_{iJ} = -\frac{\partial^2 h}{\partial P_{Ji} \partial s} \delta s - \frac{\partial^2 h}{\partial P_{Ji} \partial P_{Lk}} \delta P_{Lk}, \quad (38)$$

the substitution into (36) yields

$$\frac{\partial^2 h}{\partial s^2} (\delta s)^2 + 2 \frac{\partial^2 h}{\partial s \partial P_{Ji}} \delta s \delta P_{Ji} + \frac{\partial^2 h}{\partial P_{Ji} \partial P_{Lk}} \delta P_{Ji} \delta P_{Lk} = \frac{\partial^2 u}{\partial s^2} (\delta s)^2 - \frac{\partial^2 u}{\partial F_{iJ} \partial F_{kL}} \delta F_{iJ} \delta F_{kL}, \quad (39)$$

$$\frac{\partial^2 u}{\partial s^2} (\delta s)^2 + 2 \frac{\partial^2 u}{\partial s \partial F_{iJ}} \delta s \delta F_{iJ} + \frac{\partial^2 u}{\partial F_{iJ} \partial F_{kL}} \delta F_{iJ} \delta F_{kL} = \frac{\partial^2 h}{\partial s^2} (\delta s)^2 - \frac{\partial^2 h}{\partial P_{Ji} \partial P_{Lk}} \delta P_{Ji} \delta P_{Lk}. \quad (40)$$

Both of these imply that, for $\delta s = 0$,

$$\frac{\partial^2 h}{\partial P_{Ji} \partial P_{Lk}} \delta P_{Ji} \delta P_{Lk} = -\frac{\partial^2 u}{\partial F_{iJ} \partial F_{kL}} \delta F_{iJ} \delta F_{kL}.$$

Thus, at the states where the internal energy u is a convex function of the deformation gradient, the enthalpy h is a concave function of the nominal stress, *i.e.*,

$$\frac{\partial^2 u}{\partial F_{iJ} \partial F_{kL}} \delta F_{iJ} \delta F_{kL} > 0 \Rightarrow \frac{\partial^2 h}{\partial P_{Ji} \partial P_{Lk}} \delta P_{Ji} \delta P_{Lk} < 0. \quad (41)$$

4.2. Relationships between the second-order variations of h and f

The free energy and enthalpy are related by the Legendre transform

$$h(s, P_{Ji}) = f(T, F_{iJ}) + Ts - P_{Ji} F_{iJ}. \quad (42)$$

Consider an arbitrary virtual variation of state $(\delta s, \delta F_{iJ})$, which obeys the energy equation. Denote by δT and δP_{Ji} the corresponding temperature and stress variations. Then,

$$h(s + \delta s, P_{Ji} + \delta P_{Ji}) = f(T + \delta T, F_{iJ} + \delta F_{iJ}) + (T + \delta T)(s + \delta s) - (P_{Ji} + \delta P_{Ji})(F_{iJ} + \delta F_{iJ}), \quad (43)$$

and

$$\begin{aligned} \delta h &= \delta f + T \delta s + s \delta T - P_{Ji} \delta F_{iJ} - F_{iJ} \delta P_{Ji} = T \delta s - F_{iJ} \delta P_{Ji}, \\ \delta^2 h &= \delta^2 f + 2 \delta T \delta s - 2 \delta P_{Ji} \delta F_{iJ}, \\ \delta^k h &= \delta^k f, \quad k \geq 3. \end{aligned} \quad (44)$$

Having in mind that

$$P_{Ji} = \frac{\partial f}{\partial F_{iJ}} \Rightarrow \delta P_{Ji} = \frac{\partial^2 f}{\partial F_{iJ} \partial T} \delta T + \frac{\partial^2 f}{\partial F_{iJ} \partial F_{kL}} \delta F_{kL}, \quad (45)$$

$$T = \frac{\partial h}{\partial s} \Rightarrow \delta T = \frac{\partial^2 h}{\partial s^2} \delta s + \frac{\partial^2 h}{\partial s \partial P_{Ji}} \delta P_{Ji}, \quad (46)$$

and by using (22) and (38), the substitution into (44) yields a simple relationship between the second-order variations of the enthalpy and the Helmholtz free energy,

$$\delta^2 h = -\delta^2 f. \quad (47)$$

In the expanded form, this is

$$\frac{\partial^2 h}{\partial s^2} (\delta s)^2 + 2 \frac{\partial^2 h}{\partial s \partial P_{Ji}} \delta s \delta P_{Ji} + \frac{\partial^2 h}{\partial P_{Ji} \partial P_{Lk}} \delta P_{Ji} \delta P_{Lk} = - \left[\frac{\partial^2 f}{\partial T^2} (\delta T)^2 + 2 \frac{\partial^2 f}{\partial T \partial F_{iJ}} \delta T \delta F_{iJ} + \frac{\partial^2 f}{\partial F_{iJ} \partial F_{kL}} \delta F_{iJ} \delta F_{kL} \right] \quad (48)$$

Both of these are indefinite quadratic forms; at the states where h is a convex function of entropy and concave function of stress, f is a concave function of temperature and convex function of deformation gradient.

5. Gibbs energy

The Gibbs energy of a stable equilibrium configuration is at minimum with respect to any small geometrically admissible virtual displacement and entropy fields, applied at constant external loading and constant temperature.

The total Gibbs energy of the deformed body is

$$G = \int_{V^0} u(s, F_{ij}) dV^0 - \int_{V^0} Ts dV^0 - \int_{V^0} b_i^0 x_i dV^0 - \int_{A^0} t_i^0 x_i dA^0. \quad (49)$$

Upon applying the variations δx_i and δs , at constant external load and constant temperature ($\delta t_i^0 = 0$ over A^0 , $\delta b_i^0 = 0$ in V^0 , and $\delta T = 0$), there follows

$$\Delta G = \int_{V^0} [\Delta u(s, F_{ij}) - T\delta s - P_{ji}\delta F_{ij}] dV^0. \quad (50)$$

In view of (4), and the energy Eq. (5), ΔG becomes

$$\Delta G = \frac{1}{2} \int_{V^0} \delta^2 u dV^0 + \text{higher order terms}. \quad (51)$$

An obviously sufficient condition for this to be positive is that $\delta^2 u > 0$ at every point of the body at the considered equilibrium state.

Alternatively, the total Gibbs energy of the deformed body is

$$G = \int_{V^0} f(T, F_{ij}) dV^0 - \int_{V^0} b_i^0 x_i dV^0 - \int_{A^0} t_i^0 x_i dA^0, \quad (52)$$

with its change, at constant loading and temperature,

$$\Delta G = \int_{V^0} \Delta f(T, F_{ij}) dV^0 - \int_{V^0} b_i^0 \delta x_i dV^0 - \int_{A^0} t_i^0 \delta x_i dA^0, \quad (53)$$

i.e.,

$$\Delta G = \int_{V^0} [\Delta f(T, F_{ij}) - P_{ji}\delta F_{ij}] dV^0. \quad (54)$$

Since $\delta f = P_{ji}\delta F_{ij}$ under isothermal condition, and by using (15), ΔG becomes

$$\Delta G = \frac{1}{2} \int_{V^0} \frac{\partial^2 f}{\partial F_{ij} \partial F_{kl}} \delta F_{ij} \delta F_{kl} dV^0 + \text{higher order terms}. \quad (55)$$

A sufficient condition for this to be positive is that the Hessian matrix of the elastic strain energy is positive definite at all points of the body at the considered equilibrium state.

5.1. Potential energy and complementary energy

For the boundary value problems with mixed traction/displacement boundary conditions, the potential energy of the body at a given temperature is defined by

$$\Pi = \int_{V^0} f(T, F_{ij}) dV^0 - \int_{V^0} b_i^0 x_i dV^0 - \int_{A_t^0} t_i^0 x_i dA^0, \quad (56)$$

where A_t^0 is the portion of A^0 where the tractions are prescribed. The potential energy Π is at local minimum in a considered stable equilibrium configuration, *i.e.*, $\Delta \Pi > 0$ for any small variation δF_{ij} at constant T . If $\Delta \Pi = 0$ for at least one variation, while $\Delta \Pi > 0$ for other variations, the equilibrium state may not be unique (it is not if the geometrically admissible variation of state is also statically admissible; in this case

the equilibrium state is a state of neutral incremental stability). If $\Delta\Pi < 0$ for at least one variation, while $\Delta\Pi > 0$ for all other geometrically admissible variations, the equilibrium state is unique but unstable (Hill, 1957; Ogden, 1997).

The change of potential energy, at constant temperature, associated with small geometrically admissible variations δx_i , is

$$\Delta\Pi = \int_{V^0} \Delta f(T, F_{iJ}) dV^0 - \int_{V^0} b_i^0 \delta x_i dV^0 - \int_{A^0} t_i^0 \delta x_i dA^0, \quad (57)$$

because $\delta x_i = 0$ on $A_x^0 = A^0 - A_t^0$. Thus, in view of the Gauss divergence theorem and the equilibrium equations, there follows

$$\Delta\Pi = \frac{1}{2} \int_{V^0} \frac{\partial^2 f}{\partial F_{iJ} \partial F_{kL}} \delta F_{iJ} \delta F_{kL} dV^0 + \dots \quad (58)$$

Again, an obviously sufficient condition for $\Delta\Pi > 0$ is that the Hessian matrix of f with respect to the deformation gradient is positive definite at every point of the stressed body.

The complementary energy is defined as

$$\Pi^* = - \int_{V^0} g(T, P_{Ji}) dV^0 - \int_{A_x^0} t_i^0 x_i dA^0, \quad (59)$$

where A_x^0 is the portion of A^0 where the displacements are prescribed. Evidently, $\Pi + \Pi^* = 0$.⁸ The change of the complementary energy, associated with small statically admissible variations $\delta t_i^0 = n_j^0 \delta P_{Ji}$ over A_x^0 , at constant temperature, is

$$\Delta\Pi^* = - \int_{V^0} \Delta g(T, P_{Ji}) dV^0 - \int_{A_x^0} \delta t_i^0 x_i dA^0, \quad (60)$$

because $\delta t_i^0 = 0$ on A_t^0 . Thus, since $\delta b_i^0 = 0$ in V^0 for the prescribed dead body forces, we have $\delta P_{Ji,J} = 0$, and since $F_{iJ} = -\partial g / \partial P_{Ji}$, there follows

$$\Delta\Pi^* = - \frac{1}{2} \int_{V^0} \frac{\partial^2 g}{\partial P_{Ji} \partial P_{Lk}} \delta P_{Ji} \delta P_{Lk} dV^0 + \dots \quad (61)$$

A sufficient condition for $\Delta\Pi^* > 0$ is that the Hessian matrix of g with respect to the nominal stress is negative definite at every point of the stressed body in the considered equilibrium configuration.

5.2. Relationships between the second-order variations of g and u

The Gibbs energy and internal energy densities are related by the Legendre transform

$$g(T, P_{Ji}) = u(s, F_{iJ}) - Ts - P_{Ji} F_{iJ}. \quad (62)$$

Consider an arbitrary virtual variation of state $(\delta s, \delta F_{iJ})$, in compliance with the energy equation, and denote by δT and δP_{Ji} the corresponding temperature and stress variations. Then,

$$g(T + \delta T, P_{Ji} + \delta P_{Ji}) = u(s + \delta s, F_{iJ} + \delta F_{iJ}) - (T + \delta T)(s + \delta s) - (P_{Ji} + \delta P_{Ji})(F_{iJ} + \delta F_{iJ}), \quad (63)$$

and

$$\begin{aligned} \delta g &= \delta u - T\delta s - s\delta T - P_{Ji}\delta F_{iJ} - F_{iJ}\delta P_{Ji} = -s\delta T - F_{iJ}\delta P_{Ji}, \\ \delta^2 g &= \delta^2 u - 2\delta T\delta s - 2\delta P_{Ji}\delta F_{iJ}, \\ \delta^k g &= \delta^k u, \quad k \geq 3. \end{aligned} \quad (64)$$

⁸ If $A_x^0 = 0$ (pure traction boundary conditions), then $\Pi = G$ and $\Pi^* = -G$.

Recalling that

$$F_{iJ} = -\frac{\partial g}{\partial P_{Ji}} \Rightarrow \delta F_{iJ} = -\frac{\partial^2 g}{\partial P_{Ji} \partial T} \delta T - \frac{\partial^2 g}{\partial P_{Ji} \partial P_{Lk}} \delta P_{Lk}, \quad (65)$$

$$s = -\frac{\partial g}{\partial T} \Rightarrow \delta s = -\frac{\partial^2 g}{\partial T^2} \delta T - \frac{\partial^2 g}{\partial T \partial P_{Ji}} \delta P_{Ji}, \quad (66)$$

the substitution into (64) yields

$$\delta^2 g = -\delta^2 u, \quad (67)$$

which, in the expanded form, reads

$$\frac{\partial^2 g}{\partial T^2} (\delta T)^2 + 2 \frac{\partial^2 g}{\partial T \partial P_{Ji}} \delta T \delta P_{Ji} + \frac{\partial^2 g}{\partial P_{Ji} \partial P_{Lk}} \delta P_{Ji} \delta P_{Lk} = - \left[\frac{\partial^2 u}{\partial s^2} (\delta s)^2 + 2 \frac{\partial^2 u}{\partial s \partial F_{iJ}} \delta s \delta F_{iJ} + \frac{\partial^2 u}{\partial F_{iJ} \partial F_{kL}} \delta F_{iJ} \delta F_{kL} \right] \quad (68)$$

Thus, if $\delta^2 u$ is a positive-definite quadratic form in δs and δF_{iJ} , $\delta^2 g$ is a negative-definite quadratic form in δT and δP_{Ji} . At the states where the internal energy u is a convex function of the entropy and deformation gradient, the Gibbs energy g is a concave function of the temperature and nominal stress.

5.3. Relationships between the second-order variations of g and f

The Gibbs energy and the Helmholtz free energy are related by the Legendre transform

$$g(T, P_{Ji}) = f(T, F_{iJ}) - P_{Ji} F_{iJ}. \quad (69)$$

Consider an arbitrary virtual variation of state $(\delta T, \delta F_{iJ})$, and denote by δP_{Ji} the corresponding stress variation. Then,

$$g(T + \delta T, P_{Ji} + \delta P_{Ji}) = f(T + \delta T, F_{iJ} + \delta F_{iJ}) - (P_{Ji} + \delta P_{Ji})(F_{iJ} + \delta F_{iJ}), \quad (70)$$

and

$$\begin{aligned} \delta g &= \delta f - P_{Ji} \delta F_{iJ} - F_{iJ} \delta P_{Ji} = -s \delta T - F_{iJ} \delta P_{Ji}, \\ \delta^2 g &= \delta^2 f - 2 \delta P_{Ji} \delta F_{iJ}, \\ \delta^k g &= \delta^k f, \quad k \geq 3. \end{aligned} \quad (71)$$

The substitution of (45) and (65) into (71) yields

$$\frac{\partial^2 g}{\partial T^2} (\delta T)^2 + 2 \frac{\partial^2 g}{\partial T \partial P_{Ji}} \delta T \delta P_{Ji} + \frac{\partial^2 g}{\partial P_{Ji} \partial P_{Lk}} \delta P_{Ji} \delta P_{Lk} = \frac{\partial^2 f}{\partial T^2} (\delta T)^2 - \frac{\partial^2 f}{\partial F_{iJ} \partial F_{kL}} \delta F_{iJ} \delta F_{kL} \quad (72)$$

$$\frac{\partial^2 f}{\partial T^2} (\delta T)^2 + 2 \frac{\partial^2 f}{\partial T \partial F_{iJ}} \delta T \delta F_{iJ} + \frac{\partial^2 f}{\partial F_{iJ} \partial F_{kL}} \delta F_{iJ} \delta F_{kL} = \frac{\partial^2 g}{\partial T^2} (\delta T)^2 - \frac{\partial^2 g}{\partial P_{Ji} \partial P_{Lk}} \delta P_{Ji} \delta P_{Lk} \quad (73)$$

Both of these imply that, for $\delta T = 0$,

$$\frac{\partial^2 g}{\partial P_{Ji} \partial P_{Lk}} \delta P_{Ji} \delta P_{Lk} = - \frac{\partial^2 f}{\partial F_{iJ} \partial F_{kL}} \delta F_{iJ} \delta F_{kL}.$$

Thus, if f is a convex function of the deformation gradient, g is a concave function of the nominal stress, and vice versa, i.e.,

$$\frac{\partial^2 f}{\partial F_{iJ} \partial F_{kL}} \delta F_{iJ} \delta F_{kL} > 0 \iff \frac{\partial^2 g}{\partial P_{Ji} \partial P_{Lk}} \delta P_{Ji} \delta P_{Lk} < 0. \quad (74)$$

5.4. Relationships between the second-order variations of g and h

The Gibbs energy and enthalpy are related by the Legendre transform

$$g(T, P_{Ji}) = h(s, P_{Ji}) - Ts. \quad (75)$$

Consider a virtual variation of state $(\delta T, \delta P_{Ji})$, and denote by δs be the corresponding entropy variation. Then,

$$g(T + \delta T, P_{Ji} + \delta P_{Ji}) = h(s + \delta s, P_{Ji} + \delta P_{Ji}) - (T + \delta T)(s + \delta s), \quad (76)$$

and

$$\begin{aligned} \delta g &= \delta h - T\delta s - s\delta T = -F_{ij}\delta P_{Ji} - s\delta T, \\ \delta^2 g &= \delta^2 h - 2\delta T\delta s, \\ \delta^k g &= \delta^k h, \quad k \geq 3. \end{aligned} \quad (77)$$

In view of (46) and (66), (77) gives

$$\frac{\partial^2 g}{\partial T^2}(\delta T)^2 + 2\frac{\partial^2 g}{\partial T\partial P_{Ji}}\delta T\delta P_{Ji} + \frac{\partial^2 g}{\partial P_{Ji}\partial P_{Lk}}\delta P_{Ji}\delta P_{Lk} = -\frac{\partial^2 h}{\partial s^2}(\delta s)^2 + \frac{\partial^2 h}{\partial P_{Ji}\partial P_{Lk}}\delta P_{Ji}\delta P_{Lk} \quad (78)$$

$$\frac{\partial^2 h}{\partial s^2}(\delta s)^2 + 2\frac{\partial^2 h}{\partial s\partial P_{Ji}}\delta s\delta P_{Ji} + \frac{\partial^2 h}{\partial P_{Ji}\partial P_{Lk}}\delta P_{Ji}\delta P_{Lk} = -\frac{\partial^2 g}{\partial T^2}(\delta T)^2 + \frac{\partial^2 g}{\partial P_{Ji}\partial P_{Lk}}\delta P_{Ji}\delta P_{Lk} \quad (79)$$

Both of these imply that, for $\delta P_{Ji} = 0$,

$$\frac{\partial^2 g}{\partial T^2}(\delta T)^2 = -\frac{\partial^2 h}{\partial s^2}(\delta s)^2.$$

Thus, the concavity of g with respect to the temperature implies the convexity of h with respect to the entropy, and *vice versa*, *i.e.*,

$$\frac{\partial^2 g}{\partial T^2} < 0 \iff \frac{\partial^2 h}{\partial s^2} > 0. \quad (80)$$

6. Applications

The established relationships between the second-order variations of thermodynamic potentials are applied in this section to derive the connections between the specific heats at constant deformation and stress, and between the isentropic and isothermal elastic moduli and compliances. The derivation is then compared with the classical thermodynamic derivation, based on the formal change of independent variables and the corresponding chain-rule partial differentiation.

The instantaneous elastic moduli under isothermal and isentropic conditions are defined by

$$A_{JiLk}^T = \left(\frac{\partial P_{Ji}}{\partial F_{kL}} \right)_T = \left(\frac{\partial^2 f}{\partial F_{ij}\partial F_{kL}} \right)_T, \quad (81)$$

$$A_{JiLk}^S = \left(\frac{\partial P_{Ji}}{\partial F_{kL}} \right)_s = \left(\frac{\partial^2 u}{\partial F_{ij}\partial F_{kL}} \right)_s. \quad (82)$$

Their inverse tensors are the instantaneous elastic compliances,

$$M_{ijKL}^T = \left(\frac{\partial F_{ij}}{\partial P_{Lk}} \right)_T = -\left(\frac{\partial^2 g}{\partial P_{Ji}\partial P_{Lk}} \right)_T, \quad (83)$$

$$M_{ijKL}^S = \left(\frac{\partial F_{ij}}{\partial P_{Lk}} \right)_s = -\left(\frac{\partial^2 h}{\partial P_{Ji}\partial P_{Lk}} \right)_s. \quad (84)$$

The second-order tensors of latent heats are defined by

$$l_{Ji}^F = T \left(\frac{\partial s}{\partial F_{ij}} \right)_T = -T \left(\frac{\partial P_{Ji}}{\partial T} \right)_F = -T \frac{\partial^2 f}{\partial F_{ij}\partial T}, \quad (85)$$

$$l_{ij}^P = T \left(\frac{\partial s}{\partial P_{Ji}} \right)_T = T \left(\frac{\partial F_{ij}}{\partial T} \right)_P = -T \frac{\partial^2 g}{\partial P_{Ji}\partial T}, \quad (86)$$

with the connections

$$l_{ji}^F = A_{jilkl}^T l_{kl}^P, \quad l_{ij}^P = M_{ijkl}^T l_{lk}^F. \quad (87)$$

The two scalar specific heats, at constant deformation and stress, are

$$c_F = T \left(\frac{\partial s}{\partial T} \right)_F = -T \left(\frac{\partial^2 f}{\partial T^2} \right)_F, \quad (88)$$

$$c_P = T \left(\frac{\partial s}{\partial T} \right)_P = -T \left(\frac{\partial^2 g}{\partial T^2} \right)_P. \quad (89)$$

They are defined such that (e.g.; Fung, 1965; Lubarda, 2002)

$$T ds = l_{ji}^F dF_{ij} + c_F dT = l_{ij}^P dP_{ji} + c_P dT, \quad (90)$$

and

$$dP_{ji} = A_{jilkl}^T dF_{kl} - \frac{1}{T} l_{ji}^F dT = A_{jilkl}^S dF_{kl} - \frac{1}{c_F} l_{ji}^F ds, \quad (91)$$

$$dF_{ij} = M_{ijkl}^T dP_{lk} + \frac{1}{T} l_{ij}^P dT = M_{ijkl}^S dP_{lk} + \frac{1}{c_P} l_{ij}^P ds. \quad (92)$$

Finally, the second-order tensor of the coefficients of thermal expansion is

$$\alpha_{ij} = \left(\frac{\partial F_{ij}}{\partial T} \right)_P, \quad l_{ij}^P = T \alpha_{ij}. \quad (93)$$

With these preliminaries, the concavity of the Helmholtz free energy f and the Gibbs energy g with respect to the temperature implies that the specific heats at constant deformation and stress are both positive, *i.e.*,

$$\left(\frac{\partial^2 f}{\partial T^2} \right)_F < 0 \quad \Rightarrow \quad c_F > 0, \quad (94)$$

$$\left(\frac{\partial^2 g}{\partial T^2} \right)_P < 0 \quad \Rightarrow \quad c_P > 0. \quad (95)$$

Furthermore, by dividing (72) with $(\delta T)^2$, keeping $F_{ij} = \text{const.}$, gives

$$\left(\frac{\partial^2 g}{\partial T^2} \right)_P + 2 \frac{\partial^2 g}{\partial T \partial P_{ji}} \left(\frac{\partial P_{ji}}{\partial T} \right)_F + \frac{\partial^2 g}{\partial P_{ji} \partial P_{lk}} \left(\frac{\partial P_{ji}}{\partial T} \right)_F \left(\frac{\partial P_{lk}}{\partial T} \right)_F = \left(\frac{\partial^2 f}{\partial T^2} \right)_F. \quad (96)$$

Upon the substitution of (85)–(89), this yields the relationship between the specific heats,

$$c_P - c_F = \frac{1}{T} M_{ijkl}^T l_{ji}^F l_{lk}^F = \frac{1}{T} l_{ij}^P l_{ji}^F = \alpha_{ij} l_{ji}^F. \quad (97)$$

Next, by dividing (23) with $\delta P_{Nm} \delta P_{Qp}$, keeping $T = \text{const.}$, we obtain

$$\left(\frac{\partial^2 f}{\partial F_{ij} \partial F_{kl}} \right)_T \left(\frac{\partial F_{ij}}{\partial P_{Nm}} \right)_T \left(\frac{\partial F_{kl}}{\partial P_{Qp}} \right)_T = \left(\frac{\partial^2 u}{\partial F_{ij} \partial F_{kl}} \right)_s \left(\frac{\partial F_{ij}}{\partial P_{Nm}} \right)_T \left(\frac{\partial F_{kl}}{\partial P_{Qp}} \right)_T - \left(\frac{\partial^2 u}{\partial s^2} \right)_F \left(\frac{\partial s}{\partial P_{Nm}} \right)_T \left(\frac{\partial s}{\partial P_{Qp}} \right)_T. \quad (98)$$

Recalling that

$$T = \left(\frac{\partial u}{\partial s} \right)_F \quad \Rightarrow \quad \left(\frac{\partial^2 u}{\partial s^2} \right)_F = \left(\frac{\partial T}{\partial s} \right)_F = \frac{T}{c_F}, \quad (99)$$

and in view of (81)–(83) and (86), Eq. (98) delivers the relationship between the isentropic and isothermal elastic moduli,

$$A_{jilkl}^S = A_{jilkl}^T + \frac{1}{T c_F} l_{ji}^F l_{lk}^F. \quad (100)$$

Similarly, by dividing (78) with $\delta F_{mN}\delta F_{pQ}$, keeping $T = \text{const.}$, gives

$$\left(\frac{\partial^2 g}{\partial P_{Ji}\partial P_{Lk}}\right)_T \left(\frac{\partial P_{Ji}}{\partial F_{mN}}\right)_T \left(\frac{\partial P_{Lk}}{\partial F_{pQ}}\right)_T = \left(\frac{\partial^2 h}{\partial P_{Ji}\partial P_{Lk}}\right)_s \left(\frac{\partial P_{Ji}}{\partial F_{mN}}\right)_T \left(\frac{\partial P_{Lk}}{\partial F_{pQ}}\right)_T - \left(\frac{\partial^2 h}{\partial s^2}\right)_F \left(\frac{\partial s}{\partial F_{mN}}\right)_T \left(\frac{\partial s}{\partial F_{pQ}}\right)_T. \quad (101)$$

Since

$$T = \left(\frac{\partial h}{\partial s}\right)_P \Rightarrow \left(\frac{\partial^2 h}{\partial s^2}\right)_P = \left(\frac{\partial T}{\partial s}\right)_P = \frac{T}{c_P}, \quad (102)$$

and in view of (81)–(85), Eq. (101) yields

$$M_{iJkL}^S = M_{iJkL}^T - \frac{1}{T c_P} l_{ij}^P l_{kl}^P, \quad (103)$$

which is a desired relationship between the isentropic and isothermal elastic compliances. Having regard to (97), we finally note that the multiplication of (100) by $c_F l_{kl}^P$, and (103) by $c_P l_{Ji}^F$ gives

$$c_F A_{JiLk}^S l_{kl}^P = c_P l_{Ji}^F, \quad c_P M_{iJkL}^S l_{Lk}^F = c_F l_{ij}^P. \quad (104)$$

Thus, in view of the connections (87), l^F is an eigenmatrix of $\Lambda^S \cdot \cdot M^T$, and l^P is an eigenmatrix of $M^T \cdot \cdot \Lambda^S$, both corresponding to the eigenvalue c_P/c_F (Hill, 1981). The trace product $\cdot \cdot$ is defined such that the $(JikL)$ component of the fourth-order tensor $\Lambda^S \cdot \cdot M^T$ is $A_{JiNm}^S M_{mNkL}^T$.

6.1. The classical derivation

The relationship between the specific heats (97) can be deduced independently of (96), by direct transition from

$$s = s[F_{ij}(P_{Lk}, T), T] \Rightarrow \left(\frac{\partial s}{\partial T}\right)_P = \left(\frac{\partial s}{\partial T}\right)_F + \left(\frac{\partial s}{\partial F_{ij}}\right)_T \left(\frac{\partial F_{ij}}{\partial T}\right)_P, \quad (105)$$

and the definition of the specific and latent heats, and the coefficients of thermal expansion (e.g.; Lubarda, 2002).

The relationships (100) and (103) can also be derived directly. For example, from $P_{Ji} = P_{Ji}(F_{kL}, T)$, there follows

$$\left(\frac{\partial P_{Ji}}{\partial F_{kL}}\right)_s = \left(\frac{\partial P_{Ji}}{\partial F_{kL}}\right)_T + \left(\frac{\partial P_{Ji}}{\partial T}\right)_F \left(\frac{\partial T}{\partial F_{kL}}\right)_s. \quad (106)$$

Since

$$\left(\frac{\partial T}{\partial F_{kL}}\right)_s = -\frac{\left(\frac{\partial s}{\partial F_{kL}}\right)_T}{\left(\frac{\partial s}{\partial T}\right)_F} = -\frac{l_{Lk}^F}{c_F}, \quad (107)$$

and in view of (81) and (82), Eq. (106) reproduces (100).

Similarly, from $F_{ij} = F_{ij}(P_{Lk}, T)$, there follows

$$\left(\frac{\partial F_{ij}}{\partial P_{Lk}}\right)_s = \left(\frac{\partial F_{ij}}{\partial P_{Lk}}\right)_T + \left(\frac{\partial F_{ij}}{\partial T}\right)_P \left(\frac{\partial T}{\partial P_{Lk}}\right)_s. \quad (108)$$

Since

$$\left(\frac{\partial T}{\partial P_{Lk}}\right)_s = -\frac{\left(\frac{\partial s}{\partial P_{Lk}}\right)_T}{\left(\frac{\partial s}{\partial T}\right)_P} = -\frac{l_{kL}^P}{c_P}, \quad (109)$$

and in view of (83) and (84), Eq. (108) reproduces (103).

Yet another derivation of the relationships between isentropic and isothermal elastic moduli and compliances is possible by noting that an isentropic increment of temperature, from (90), is

$$ds = 0 \quad \Rightarrow \quad dT = -\frac{l_{Ji}^F}{c_F} dF_{iJ} = -\frac{l_{iJ}^P}{c_P} dP_{Ji}. \quad (110)$$

When this is substituted into (91) and (92), there follows

$$dP_{Ji} = \left(A_{JiLk}^T + \frac{1}{c_F T} l_{Ji}^F l_{Lk}^F \right) dF_{kL}, \quad dF_{iJ} = \left(M_{iJKL}^T - \frac{1}{c_P T} l_{iJ}^P l_{KL}^P \right) dP_{Lk}, \quad (111)$$

which establishes A_{JiLk}^S and M_{iJKL}^S as in (100) and (103). Further discussion of the relationships between the isentropic and isothermal elastic moduli and compliances can be found in McLellan (1980); Hill (1981); Holzapfel (2000), and Scott (2001).

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Appendix. Entropy maximization

A well-known alternative to the constrained internal energy minimization, explored in Section 2, is the constrained entropy maximization. In the context of nonlinear finite strain elasticity, we state:

The total entropy of a stable thermodynamically equilibrated state is at maximum with respect to any geometrically admissible virtual displacement field giving no net virtual work from external traction, and any virtual local internal energy variation subjected to the constraint of constant total internal energy in the body.

If S is at maximum in the considered equilibrium configuration, then⁹

$$\Delta S = \int_{V^0} \Delta s(u, F_{iJ}) dV^0 < 0, \quad S = \int_{V^0} s(u, F_{iJ}) dV^0, \quad (A.1)$$

for any small variations δu and δF_{iJ} , subjected to the constraints

$$\int_{A^0} t_i^0 \delta x_i dA^0 = 0, \quad \int_{V^0} \delta u dV^0 = 0. \quad (A.2)$$

The change of the specific entropy due to variations δu and δF_{iJ} is

$$\Delta s = \sum_{k=1}^{\infty} \frac{1}{k!} \delta^k s, \quad \delta^k s = \left(\delta u \frac{\partial}{\partial u} + \delta F_{iJ} \frac{\partial}{\partial F_{iJ}} \right)^k s. \quad (A.3)$$

The first-order variation of s is

$$\delta s = \frac{1}{T} \delta u - \frac{1}{T} P_{Ji} \delta F_{iJ}, \quad (A.4)$$

where $1/T = \partial s / \partial u$, and $P_{Ji} = -T \partial s / \partial F_{iJ}$. The second-order variation of s is

$$\delta^2 s = \frac{\partial^2 s}{\partial u^2} (\delta u)^2 + 2 \frac{\partial^2 s}{\partial u \partial F_{iJ}} \delta u \delta F_{iJ} + \frac{\partial^2 s}{\partial F_{iJ} \partial F_{kL}} \delta F_{iJ} \delta F_{kL}. \quad (A.5)$$

Since

$$\int_{V^0} \frac{1}{T} \delta u dV^0 = \frac{1}{T} \int_{V^0} \delta u dV^0 = 0, \quad (A.6)$$

and

⁹ We assumed that internal energy u is a strictly increasing function of entropy s ; thus, the caloric equation of state $u = u(s, F_{iJ})$ can be inverted uniquely for $s = s(u, F_{iJ})$, and s is a strictly increasing function of u for any fixed F_{iJ} .

$$\int_{V^0} \frac{1}{T} P_{Ji} \delta F_{iJ} dV^0 = \frac{1}{T} \int_{V^0} P_{Ji} \delta x_{i,J} dV^0 = \frac{1}{T} \int_{A^0} t_i^0 \delta x_i dA^0 = 0, \quad (\text{A.7})$$

by the constraint conditions (A.2), from (A.1) it follows that

$$\Delta S = \sum_{k=2}^{\infty} \frac{1}{k!} \int_{V^0} \delta^k s dV^0 = \frac{1}{2} \int_{V^0} \delta^2 s dV^0 + \text{higher order terms} < 0. \quad (\text{A.8})$$

This must hold for any admissible virtual variations δu and δF_{iJ} , as defined above, which is assured by the requirement that $s = s(u, F_{iJ})$ is a concave function of its arguments at all points of the body at the considered equilibrium configuration. A sufficient condition for this is that the Hessian matrix of s is negative-definite at those states of (u, F_{iJ}) , i.e.,

$$\frac{\partial^2 s}{\partial u^2} (\delta u)^2 + 2 \frac{\partial^2 s}{\partial u \partial F_{iJ}} \delta u \delta F_{iJ} + \frac{\partial^2 s}{\partial F_{iJ} \partial F_{kL}} \delta F_{iJ} \delta F_{kL} < 0. \quad (\text{A.9})$$

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