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International Journal of Solids and Structures 41 (2004) 7377–7398

INTERNATIONAL JOURNAL OF SOLIDS and STRUCTURES

www.elsevier.com/locate/ijsolstr

On thermodynamic potentials in linear thermoelasticity

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Received 13 March 2004; received in revised form 28 May 2004
Available online 13 August 2004

Abstract

The four thermodynamic potentials, the internal energy $u = u(\epsilon_{ij}, s)$, the Helmholtz free energy $f = f(\epsilon_{ij}, T)$, the Gibbs energy $g = g(\sigma_{ij}, T)$ and the enthalpy $h = h(\sigma_{ij}, s)$ are derived, independently of each other, by using the Duhamel–Neumann extension of Hooke's law and an assumed linear dependence of the specific heat on temperature. A systematic procedure is then presented to express all thermodynamic potentials in terms of four possible pairs of independent state variables. This procedure circumvents a tedious transition from one potential to another, based on the formal change of variables, and inversions of the stress–strain and entropy–temperature relations. The general results are applied to uniaxial loading paths under isothermal, adiabatic, constant stress, and constant strain conditions. An interplay of adiabatic and isothermal elastic constants in the expressions for exchanged heat along certain thermodynamic paths is indicated.

Keywords: Thermoelasticity; Thermodynamic potentials; Internal energy; Helmholtz free energy; Gibbs energy; Enthalpy; Entropy; Specific heats

1. Introduction

The structure of the constitutive equations relating the stress, strain, entropy, and temperature in linear thermoelasticity is well-known (e.g., Boley and Weiner, 1960; Sneddon, 1974). Most commonly, the derivation of these equations proceeds by assuming a quadratic representation of the Helmholtz free energy in terms of strain and temperature, with the coefficients specified in accord with the observed isothermal elastic behavior, the coefficient of thermal expansion, and the specific heat. This yields (e.g., Kovalenko, 1969)

$$f(\epsilon_{ij}, T) = \frac{1}{2}\lambda_T \epsilon_{kk}^2 + \mu \epsilon_{ij}\epsilon_{ij} - \kappa_T \alpha_0 (T - T_0)\epsilon_{kk} - \frac{c_V^0}{2T_0}(T - T_0)^2 - s_0(T - T_0) + f_0, \tag{1}$$

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0020-7683/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijsolstr.2004.05.070

where λ_T and μ are the isothermal Lamé elastic constants, $\kappa_T = \lambda_T + 2\mu/3$ is the isothermal bulk modulus, and α_0, c_V^0, and s_0 are, respectively, the coefficient of volumetric thermal expansion, the specific heat at constant strain, and the specific entropy, all in the reference state with temperature T_0. The corresponding free energy (per unit reference volume) is $f(0, T_0) = f_0$. The stress and entropy in the deformed state are the gradients of f with respect to strain and temperature. The specific heat at constant strain, associated with Eq. (1) is

$$c_V = T\left(\frac{\partial s}{\partial T}\right)_\epsilon = -T\left(\frac{\partial^2 f}{\partial T^2}\right)_\epsilon = c_V^0 \frac{T}{T_0}. \tag{2}$$

Once the Helmholtz free energy is specified as a function of strain and temperature, the internal energy $u = f + Ts$ can be expressed in terms of the same independent variables by simple substitution of Eq. (1) and the corresponding expression for the entropy. This yields (e.g., Ziegler, 1977)

$$u(\epsilon_{ij}, T) = \frac{1}{2}\lambda_T \epsilon_{kk}^2 + \mu\epsilon_{ij}\epsilon_{ij} + \kappa_T\alpha_0 T_0 \epsilon_{kk} + \frac{c_V^0}{2T_0}(T^2 - T_0^2) + u_0. \tag{3}$$

In the sequel, it will be assumed that the internal energy vanishes in the reference state, so that

$$u_0 = 0, \quad f_0 = -T_0 s_0. \tag{4}$$

However, the internal energy is a thermodynamic potential whose natural independent state variables are strain and entropy, rather than strain and temperature, since the energy equation specifies the increment of internal energy as

$$\mathrm{d}u = \sigma_{ij}\,\mathrm{d}\epsilon_{ij} + T\,\mathrm{d}s. \tag{5}$$

The desired representation $u = u(\epsilon_{ij}, s)$ can be obtained from $u = f + Ts$ by eliminating the temperature in terms of strain and entropy via Eq. (1). The end result is

$$u(\epsilon_{ij}, s) = \frac{1}{2}\lambda_S \epsilon_{kk}^2 + \mu\epsilon_{ij}\epsilon_{ij} - \frac{\kappa_T\alpha_0 T_0}{c_V^0}(s - s_0)\epsilon_{kk} + \frac{T_0}{2c_V^0}(s - s_0)^2 + T_0(s - s_0). \tag{6}$$

The adiabatic (isentropic) Lamé constant λ_S is related to its isothermal counterpart λ_T by

$$\lambda_S = \lambda_T + \frac{\alpha_0^2 T_0}{c_V^0}\kappa_T^2. \tag{7}$$

The purely algebraic transition from Eqs. (3)–(6) is simple, but little indicative of the underlying thermodynamics connecting Eqs. (5) and (6). An independent derivation of (6), starting from the energy equation (5), and utilizing the experimental data embedded in the Duhamel–Neumann extension of Hooke's law, and the assumed specific heat behavior, is therefore desirable. The systematic procedure to achieve this, and to derive the expressions for other thermodynamic potentials, the Helmholtz free energy $f = f(\epsilon_{ij}, T)$, the Gibbs energy $g = g(\sigma_{ij}, T)$, and the enthalpy $h = h(\sigma_{ij}, s)$, is presented. The four thermodynamic potentials are then expressed in terms of four possible pairs of independent state variables: (ϵ_{ij}, T), (ϵ_{ij}, s), (σ_{ij}, T), and (σ_{ij}, s). This furnishes a set of 16 alternative expressions, four for each thermodynamic potential. Analogous results in the scalar setting, using pressure and volume as pertinent variables, is commonly utilized in materials science thermodynamics (Swalin, 1972; DeHoff, 1993; Ragone, 1995). The obtained general results are applied to uniaxial and spherical stress and strain states, which are of importance in high-pressure material testing (e.g., Lubarda, 1986; Lubarda et al., 2004). Particular attention is given to uniaxial loading under isothermal, adiabatic, constant stress, and constant strain condition. A simple interplay of adiabatic and isothermal elastic constants in the expressions for exchanged heat along certain thermodynamic paths is obtained.

2. Thermodynamics potentials in terms of their natural independent state variables

The four thermodynamic potentials are derived in this section in terms of their natural independent state variables. The derivation is in each case based only on the Duhamel–Neumann extension of Hooke's law, and an assumed linear dependence of the specific heat on temperature.

2.1. Internal energy $u = u(\epsilon_{ij}, s)$

The increment of internal energy is expressed in terms of the increments of strain and entropy by the energy equation (5). Since u is a state function, du is a perfect differential, and the Maxwell relation holds

$$\left(\frac{\partial \sigma_{ij}}{\partial s}\right)_{\epsilon} = \left(\frac{\partial T}{\partial \epsilon_{ij}}\right)_{s}. \tag{8}$$

The thermodynamic potential $u = u(\epsilon_{ij}, s)$ is sought corresponding to the Duhamel–Neumann expression

$$\sigma_{ij} = \lambda_T \epsilon_{kk} \delta_{ij} + 2\mu\epsilon_{ij} - \kappa_T \alpha_0 (T - T_0)\delta_{ij}, \tag{9}$$

and an assumed linear dependence of the specific heat on temperature

$$c_V = c_V^0 \frac{T}{T_0}. \tag{10}$$

The Kronecker delta is denoted by δ_{ij}. By partial differentiation from Eq. (9) it follows that

$$\left(\frac{\partial \sigma_{ij}}{\partial s}\right)_{\epsilon} = \left(\frac{\partial \sigma_{ij}}{\partial T}\right)_{\epsilon}\left(\frac{\partial T}{\partial s}\right)_{\epsilon} = -\kappa_T \alpha_0 \left(\frac{\partial T}{\partial s}\right)_{\epsilon} \delta_{ij}, \tag{11}$$

so that the Maxwell relation (8) gives

$$\left(\frac{\partial T}{\partial \epsilon_{ij}}\right)_{s} = -\kappa_T \alpha_0 \left(\frac{\partial T}{\partial s}\right)_{\epsilon} \delta_{ij}. \tag{12}$$

The thermodynamic definition of the specific heat at constant strain is

$$c_V = T\left(\frac{\partial s}{\partial T}\right)_{\epsilon}, \tag{13}$$

which, in conjunction with Eq. (10), specifies the temperature gradient

$$\left(\frac{\partial T}{\partial s}\right)_{\epsilon} = \frac{T_0}{c_V^0}. \tag{14}$$

The substitution into Eq. (12) yields

$$\left(\frac{\partial T}{\partial \epsilon_{ij}}\right)_{s} = -\frac{\kappa_T \alpha_0 T_0}{c_V^0} \delta_{ij}. \tag{15}$$

The joint integration of Eqs. (14) and (15) provides

$$T = -\frac{\kappa_T \alpha_0 T_0}{c_V^0} \epsilon_{kk} + \frac{T_0}{c_V^0}(s - s_0) + T_0. \tag{16}$$

When this is inserted into Eq. (9), we obtain an expression for stress in terms of strain and entropy

$$\sigma_{ij} = \lambda_S \epsilon_{kk} \delta_{ij} + 2\mu\epsilon_{ij} - \frac{\kappa_T \alpha_0 T_0}{c_V^0}(s - s_0)\delta_{ij}. \tag{17}$$

The adiabatic Lamé constant λ_S is related to its isothermal counterpart λ_T by Eq. (7).

By using Eqs. (16) and (17), the joint integration of

$$\sigma_{ij} = \left(\frac{\partial u}{\partial \epsilon_{ij}}\right)_s, \quad T = \left(\frac{\partial u}{\partial s}\right)_\epsilon, \tag{18}$$

yields a desired expression for the internal energy in terms of its natural independent variables ϵ_{ij} and s. This is

$$u(\epsilon_{ij}, s) = \frac{1}{2}\lambda_S \epsilon_{kk}^2 + \mu\epsilon_{ij}\epsilon_{ij} - \frac{\kappa_T \alpha_0 T_0}{c_V^0}(s - s_0)\epsilon_{kk} + \frac{T_0}{2c_V^0}(s - s_0)^2 + T_0(s - s_0). \tag{19}$$

2.2. Helmholtz free energy $f = f(\epsilon_{ij}, T)$

An independent derivation of the Helmholtz free energy function $f = f(\epsilon_{ij}, T)$ again begins with the pair of expressions (9) and (10). The increment of f is

$$\mathrm{d}f = \sigma_{ij}\,\mathrm{d}\epsilon_{ij} - s\,\mathrm{d}T, \tag{20}$$

with the Maxwell relation

$$\left(\frac{\partial \sigma_{ij}}{\partial T}\right)_\epsilon = -\left(\frac{\partial s}{\partial \epsilon_{ij}}\right)_T. \tag{21}$$

By evaluating the temperature gradient of stress from Eq. (9), and by substituting the result into Eq. (21), we find

$$\left(\frac{\partial s}{\partial \epsilon_{ij}}\right)_T = \kappa_T \alpha_0 \delta_{ij}. \tag{22}$$

The integration of above, in conjunction with

$$\left(\frac{\partial s}{\partial T}\right)_\epsilon = \frac{c_V^0}{T_0}, \tag{23}$$

provides the entropy expression

$$s = \kappa_T \alpha_0 \epsilon_{kk} + \frac{c_V^0}{T_0}(T - T_0) + s_0. \tag{24}$$

By using Eqs. (9) and (24), the joint integration of

$$\sigma_{ij} = \left(\frac{\partial f}{\partial \epsilon_{ij}}\right)_T, \quad s = -\left(\frac{\partial f}{\partial T}\right)_\epsilon, \tag{25}$$

yields a desired expression for the Helmholtz free energy in terms of its natural independent variables ϵ_{ij} and T. This is

$$f(\epsilon_{ij}, T) = \frac{1}{2}\lambda_T \epsilon_{kk}^2 + \mu\epsilon_{ij}\epsilon_{ij} - \kappa_T \alpha_0 (T - T_0)\epsilon_{kk} - \frac{c_V^0}{2T_0}(T - T_0)^2 - s_0 T. \tag{26}$$

2.3. Gibbs energy $g = g(\sigma_{ij}, T)$

The increment of the Gibbs energy is

$$\mathrm{d}g = -\epsilon_{ij}\,\mathrm{d}\sigma_{ij} - s\,\mathrm{d}T, \tag{27}$$

with the Maxwell relation

$$\left(\frac{\partial \epsilon_{ij}}{\partial T}\right)_\sigma = \left(\frac{\partial s}{\partial \sigma_{ij}}\right)_T. \tag{28}$$

To derive the function $g(\sigma_{ij}, T)$, independently of the connection $g = f - \sigma_{ij}\epsilon_{ij}$ and without tedious change of variables, we begin with the thermoelastic stress–strain relation and an expression for the specific heat, i.e.,

$$\epsilon_{ij} = \frac{1}{2\mu}\left(\sigma_{ij} - \frac{\nu_T}{1+\nu_T}\sigma_{kk}\delta_{ij}\right) + \frac{\alpha_0}{3}(T - T_0)\delta_{ij}, \tag{29}$$

$$c_P(T) = c_P^0 \frac{T}{T_0}. \tag{30}$$

The first one is a simple extension of Hooke's law to include thermal strain, and the second one is the assumed linear dependence of the specific heat at constant stress on temperature. The thermodynamic definition of the specific heat c_P is

$$c_P = T\left(\frac{\partial s}{\partial T}\right)_\sigma. \tag{31}$$

By differentiating Eq. (29) to evaluate the temperature gradient of strain, and by substituting the result into the Maxwell relation (28), we find

$$\left(\frac{\partial s}{\partial \sigma_{ij}}\right)_T = \frac{\alpha_0}{3}\delta_{ij}. \tag{32}$$

The integration of this, in conjunction with

$$\left(\frac{\partial s}{\partial T}\right)_\sigma = \frac{c_P^0}{T_0}, \tag{33}$$

provides the entropy expression

$$s = \frac{\alpha_0}{3}\sigma_{kk} + \frac{c_P^0}{T_0}(T - T_0) + s_0. \tag{34}$$

Using Eqs. (29) and (34), the joint integration of

$$\epsilon_{ij} = -\left(\frac{\partial g}{\partial \sigma_{ij}}\right)_T, \quad s = -\left(\frac{\partial g}{\partial T}\right)_\sigma, \tag{35}$$

yields a desired expression for the Gibbs energy in terms of its natural independent variables σ_{ij} and T (e.g., Fung, 1965; Kovalenko, 1969). This is

$$g(\sigma_{ij}, T) = -\frac{1}{4\mu}\left(\sigma_{ij}\sigma_{ij} - \frac{\nu_T}{1+\nu_T}\sigma_{kk}^2\right) - \frac{\alpha_0}{3}(T - T_0)\sigma_{kk} - \frac{c_P^0}{2T_0}(T - T_0)^2 - s_0 T. \tag{36}$$

The relationship between the specific heats c_P^0 and c_V^0 can be obtained in various ways. For example, by reconciling the entropy expressions (24) and (34), and by using the relationship

$$\epsilon_{kk} = \frac{1}{3\kappa_T}\sigma_{kk} + \alpha_0(T - T_0), \tag{37}$$

following from (27), it is found that

$$c_P^0 - c_V^0 = \kappa_T \alpha_0^2 T_0. \tag{38}$$

2.4. Enthalpy function $h = h(\sigma_{ij}, s)$

The increment of enthalpy is

$$\mathrm{d}h = -\epsilon_{ij}\,\mathrm{d}\sigma_{ij} + T\,\mathrm{d}s, \tag{39}$$

with the Maxwell relation

$$\left(\frac{\partial \epsilon_{ij}}{\partial s}\right)_\sigma = -\left(\frac{\partial T}{\partial \sigma_{ij}}\right)_s. \tag{40}$$

To derive the function $h(\sigma_{ij}, s)$, we shall again begin with the expressions (29) and (30). By partial differentiation from Eq. (29) it follows that

$$\left(\frac{\partial \epsilon_{ij}}{\partial s}\right)_\sigma = \left(\frac{\partial \epsilon_{ij}}{\partial T}\right)_\sigma \left(\frac{\partial T}{\partial s}\right)_\sigma = \frac{\alpha_0}{3}\left(\frac{\partial T}{\partial s}\right)_\sigma \delta_{ij}. \tag{41}$$

The substitution into the Maxwell relation (40) gives

$$\left(\frac{\partial T}{\partial \sigma_{ij}}\right)_s = -\frac{\alpha_0}{3}\left(\frac{\partial T}{\partial s}\right)_\sigma \delta_{ij} = -\frac{\alpha_0 T_0}{3c_P^0}\delta_{ij}. \tag{42}$$

The definition (31), in conjunction with (30), was used in the last step. The joint integration of Eq. (42) and

$$\left(\frac{\partial T}{\partial s}\right)_\sigma = \frac{T_0}{c_P^0}, \tag{43}$$

provides the temperature expression

$$T = -\frac{\alpha_0 T_0}{3c_P^0}\sigma_{kk} + \frac{T_0}{c_P^0}(s - s_0) + T_0. \tag{44}$$

When this is substituted into Eq. (29), there follows

$$\epsilon_{ij} = \frac{1}{2\mu}\left(\sigma_{ij} - \frac{\nu_S}{1+\nu_S}\sigma_{kk}\delta_{ij}\right) + \frac{\alpha_0 T_0}{3c_P^0}(s - s_0)\delta_{ij}. \tag{45}$$

The adiabatic Poisson's ratio ν_S is related to its isothermal counterpart ν_T by

$$\nu_S = \frac{\nu_T + 2\mu(1+\nu_T)a}{1 - 2\mu(1+\nu_T)a}, \quad \nu_T = \frac{\nu_S - 2\mu(1+\nu_S)a}{1 + 2\mu(1+\nu_S)a}, \quad a = \frac{\alpha_0^2 T_0}{9c_P^0}. \tag{46}$$

Note that the adiabatic and isothermal Young's moduli are related by

$$\frac{1}{E_T} - \frac{1}{E_S} = \frac{\alpha_0^2 T_0}{9c_P^0}, \tag{47}$$

in variance with an expression given by Fung (1965, p. 389), where the specific heat at constant strain appears in the denominator on the right-hand side. A simple relationship is also recorded (e.g., Chadwick, 1960)

$$\frac{c_P^0}{c_V^0} = \frac{\kappa_S}{\kappa_T}. \tag{48}$$

This easily follows by noting, from Eqs. (16) and (44), that for adiabatic loading

$$T_0 - T = \frac{\kappa_T \alpha_0 T_0}{c_V^0} \epsilon_{kk} = \frac{\alpha_0 T_0}{3c_P^0} \sigma_{kk}. \tag{49}$$

Since for adiabatic loading $\sigma_{kk} = 3\kappa_S \epsilon_{kk}$, the substitution into (49) yields (48).

Returning to the enthalpy function, by using Eqs. (44) and (45), the joint integration of

$$\epsilon_{ij} = -\left(\frac{\partial h}{\partial \sigma_{ij}}\right)_s, \quad T = \left(\frac{\partial h}{\partial s}\right)_\sigma, \tag{50}$$

yields the expression for the enthalpy in terms of its natural independent variables σ_{ij} and s. This is

$$h(\sigma_{ij}, s) = -\frac{1}{4\mu}\left(\sigma_{ij}\sigma_{ij} - \frac{\nu_S}{1+\nu_S}\sigma_{kk}^2\right) - \frac{\alpha_0 T_0}{3c_P^0}(s - s_0)\sigma_{kk} + \frac{T_0}{2c_P^0}(s - s_0)^2 + T_0(s - s_0). \tag{51}$$

2.5. List of thermodynamic potentials in terms of their natural independent state variables

$$\boxed{u(\epsilon_{ij}, s) = \frac{1}{2}\lambda_S \epsilon_{kk}^2 + \mu \epsilon_{ij}\epsilon_{ij} - \frac{\kappa_T \alpha_0 T_0}{c_V^0}(s - s_0)\epsilon_{kk} + \frac{T_0}{2c_V^0}(s - s_0)^2 + T_0(s - s_0)} \tag{52}$$

$$\boxed{f(\epsilon_{ij}, T) = \frac{1}{2}\lambda_T \epsilon_{kk}^2 + \mu \epsilon_{ij}\epsilon_{ij} - \kappa_T \alpha_0 (T - T_0)\epsilon_{kk} - \frac{c_V^0}{2T_0}(T - T_0)^2 - s_0 T} \tag{53}$$

$$\boxed{g(\sigma_{ij}, T) = -\frac{1}{4\mu}\left(\sigma_{ij}\sigma_{ij} - \frac{\nu_T}{1+\nu_T}\sigma_{kk}^2\right) - \frac{\alpha_0}{3}(T - T_0)\sigma_{kk} - \frac{c_P^0}{2T_0}(T - T_0)^2 - s_0 T} \tag{54}$$

$$\boxed{h(\sigma_{ij}, s) = -\frac{1}{4\mu}\left(\sigma_{ij}\sigma_{ij} - \frac{\nu_S}{1+\nu_S}\sigma_{kk}^2\right) - \frac{\alpha_0 T_0}{3c_P^0}(s - s_0)\sigma_{kk} + \frac{T_0}{2c_P^0}(s - s_0)^2 + T_0(s - s_0)} \tag{55}$$

3. Internal energy in terms of four pairs of independent state variables

The internal energy was expressed in Section 2.1 in terms of its natural independent state variables as $u = u(\epsilon_{ij}, s)$. We now derive its representation in terms of other three pairs of independent state variables.

3.1. Function $u = u(\epsilon_{ij}, T)$

We start with the relationship

$$u(\epsilon_{ij}, T) = f(\epsilon_{ij}, T) + Ts. \tag{56}$$

The partial derivative with respect to strain at constant temperature is

$$\left(\frac{\partial u}{\partial \epsilon_{ij}}\right)_T = \left(\frac{\partial f}{\partial \epsilon_{ij}}\right)_T + T\left(\frac{\partial s}{\partial \epsilon_{ij}}\right)_T. \tag{57}$$

Since

$$\sigma_{ij} = \left(\frac{\partial f}{\partial \epsilon_{ij}}\right)_T, \quad \left(\frac{\partial s}{\partial \epsilon_{ij}}\right)_T = -\left(\frac{\partial \sigma_{ij}}{\partial T}\right)_\epsilon, \tag{58}$$

we obtain

$$\left(\frac{\partial u}{\partial \epsilon_{ij}}\right)_T = \sigma_{ij} - T\left(\frac{\partial \sigma_{ij}}{\partial T}\right)_\epsilon. \tag{59}$$

By using the Duhamel–Neumann expression (9), this gives

$$\left(\frac{\partial u}{\partial \epsilon_{ij}}\right)_T = \lambda_T \epsilon_{kk}\delta_{ij} + 2\mu\epsilon_{ij} + \kappa_T \alpha_0 T_0 \delta_{ij}. \tag{60}$$

On the other hand, by taking a partial derivative of Eq. (56) with respect to temperature at constant strain, there follows

$$\left(\frac{\partial u}{\partial T}\right)_\epsilon = T\left(\frac{\partial s}{\partial T}\right)_\epsilon = c_V^0 \frac{T}{T_0}, \tag{61}$$

having regard to $s = -(\partial f/\partial T)_\epsilon$. Therefore, upon joint integration of Eqs. (60) and (61), there follows

$$u(\epsilon_{ij}, T) = \frac{1}{2}\lambda_T \epsilon_{kk}^2 + \mu\epsilon_{ij}\epsilon_{ij} + \kappa_T \alpha_0 T_0 \epsilon_{kk} + \frac{c_V^0}{2T_0}(T^2 - T_0^2). \tag{62}$$

This could have been also obtained directly from the relationship $u = f(\epsilon_{ij}, T) + Ts$, by using (24) and (26) (e.g., Ziegler, 1977, p. 118; Haddow and Ogden, 1990, p. 165, 167). The corresponding expression for internal energy in the case when it is assumed that $c_V = c_V^0$ can be found in Chadwick (1960, p. 275), or Noda et al. (2003, p. 445).

3.2. Function $u = u(\sigma_{ij}, s)$

We conveniently start with the relationship

$$u(\sigma_{ij}, s) = h(\sigma_{ij}, s) + \sigma_{ij}\epsilon_{ij}. \tag{63}$$

The partial differentiation with respect to stress at constant entropy is

$$\left(\frac{\partial u}{\partial \sigma_{ij}}\right)_s = \sigma_{kl}\left(\frac{\partial \epsilon_{kl}}{\partial \sigma_{ij}}\right)_s, \tag{64}$$

since $\epsilon_{ij} = -(\partial h/\partial \sigma_{ij})_s$. Incorporating Eq. (45), the above becomes

$$\left(\frac{\partial u}{\partial \sigma_{ij}}\right)_s = \frac{1}{2\mu}\left(\sigma_{ij} - \frac{\nu_S}{1+\nu_S}\sigma_{kk}\delta_{ij}\right). \tag{65}$$

On the other hand, by taking a partial derivative of Eq. (63) with respect to entropy at constant stress, there follows

$$\left(\frac{\partial u}{\partial s}\right)_\sigma = \left(\frac{\partial h}{\partial s}\right)_\sigma + \sigma_{ij}\left(\frac{\partial \epsilon_{ij}}{\partial s}\right)_\sigma = T + \frac{\alpha_0 T_0}{3c_P^0}\sigma_{kk}, \tag{66}$$

having regard to $T = (\partial h/\partial s)_\sigma$. Since T is given by Eq. (44), this reduces to

$$\left(\frac{\partial u}{\partial s}\right)_\sigma = T_0 + \frac{T_0}{c_P^0}(s - s_0). \tag{67}$$

The joint integration of Eqs. (65) and (67) gives

$$u(\sigma_{ij}, s) = \frac{1}{4\mu}\left(\sigma_{ij}\sigma_{ij} - \frac{\nu_S}{1+\nu_S}\sigma_{kk}^2\right) + \frac{T_0}{2c_P^0}(s - s_0)^2 + T_0(s - s_0). \tag{68}$$

3.3. Function $u = u(\sigma_{ij}, T)$

The derivation in this case proceeds by starting with the relationship

$$u(\sigma_{ij}, T) = g(\sigma_{ij}, T) + \sigma_{ij}\epsilon_{ij} + Ts. \tag{69}$$

The partial differentiation with respect to stress at constant temperature is

$$\left(\frac{\partial u}{\partial \sigma_{ij}}\right)_T = \sigma_{kl}\left(\frac{\partial \epsilon_{kl}}{\partial \sigma_{ij}}\right)_T + T\left(\frac{\partial \epsilon_{ij}}{\partial T}\right)_\sigma. \tag{70}$$

The connections were used

$$\epsilon_{ij} = -\left(\frac{\partial g}{\partial \sigma_{ij}}\right)_T, \quad \left(\frac{\partial s}{\partial \sigma_{ij}}\right)_T = \left(\frac{\partial \epsilon_{ij}}{\partial T}\right)_\sigma. \tag{71}$$

Incorporating Eq. (29) into (70) yields

$$\left(\frac{\partial u}{\partial \sigma_{ij}}\right)_T = \frac{1}{2\mu}\left(\sigma_{ij} - \frac{\nu_T}{1+\nu_T}\sigma_{kk}\delta_{ij}\right) + \frac{\alpha_0}{3}T\delta_{ij}. \tag{72}$$

On the other hand, the partial derivative of Eq. (69) with respect to temperature at constant stress is

$$\left(\frac{\partial u}{\partial T}\right)_\sigma = \sigma_{ij}\left(\frac{\partial \epsilon_{ij}}{\partial T}\right)_\sigma + T\left(\frac{\partial s}{\partial T}\right)_\sigma = \frac{\alpha_0}{3}\sigma_{kk} + c_P^0\frac{T}{T_0}, \tag{73}$$

having regard to $s = -(\partial g/\partial T)_\sigma$. The joint integration of Eqs. (72) and (73) yields a desired expression

$$u(\sigma_{ij}, T) = \frac{1}{4\mu}\left(\sigma_{ij}\sigma_{ij} - \frac{\nu_T}{1+\nu_T}\sigma_{kk}^2\right) + \frac{\alpha_0}{3}T\sigma_{kk} + \frac{c_P^0}{2T_0}(T^2 - T_0^2). \tag{74}$$

3.4. List of internal energy functions in terms of four pairs of independent state variables

$$\boxed{u(\epsilon_{ij}, s) = \frac{1}{2}\lambda_S\epsilon_{kk}^2 + \mu\epsilon_{ij}\epsilon_{ij} - \frac{\kappa_T\alpha_0T_0}{c_V^0}(s - s_0)\epsilon_{kk} + \frac{T_0}{2c_V^0}(s - s_0)^2 + T_0(s - s_0)} \tag{75}$$

$$\boxed{u(\epsilon_{ij}, T) = \frac{1}{2}\lambda_T\epsilon_{kk}^2 + \mu\epsilon_{ij}\epsilon_{ij} + \kappa_T\alpha_0T_0\epsilon_{kk} + \frac{c_V^0}{2T_0}(T^2 - T_0^2)} \tag{76}$$

$$\boxed{u(\sigma_{ij}, s) = \frac{1}{4\mu}\left(\sigma_{ij}\sigma_{ij} - \frac{\nu_S}{1+\nu_S}\sigma_{kk}^2\right) + \frac{T_0}{2c_P^0}(s - s_0)^2 + T_0(s - s_0)} \tag{77}$$

$$\boxed{u(\sigma_{ij},T)=\frac{1}{4\mu}\left(\sigma_{ij}\sigma_{ij}-\frac{v_T}{1+v_T}\sigma_{kk}^2\right)+\frac{\alpha_0}{3}T\sigma_{kk}+\frac{c_P^0}{2T_0}(T^2-T_0^2)} \tag{78}$$

4. Helmholtz free energy in terms of four pairs of independent state variables

The Helmholtz free energy was expressed in Section 2.2 in terms of its natural independent state variables as $f=f(\epsilon_{ij},T)$. We now derive its representation in terms of other three pairs of independent state variables. The derivation is in many aspects analogous to that presented for the internal energy in Section 3. We accordingly record only its essential steps.

4.1. Function $f=f(\epsilon_{ij},s)$

We start with the relationship

$$f(\epsilon_{ij},s)=u(\epsilon_{ij},s)-Ts, \tag{79}$$

to obtain

$$\left(\frac{\partial f}{\partial\epsilon_{ij}}\right)_s=\sigma_{ij}-s\left(\frac{\partial\sigma_{ij}}{\partial s}\right)_\epsilon, \tag{80}$$

and

$$\left(\frac{\partial f}{\partial\epsilon_{ij}}\right)_s=\lambda_S\epsilon_{kk}\delta_{ij}+2\mu\epsilon_{ij}+\frac{\kappa_T\alpha_0T_0}{c_V^0}s_0\delta_{ij}. \tag{81}$$

On the other hand,

$$\left(\frac{\partial f}{\partial s}\right)_\epsilon=-s\left(\frac{\partial T}{\partial s}\right)_\epsilon=-\frac{T_0}{c_V^0}s. \tag{82}$$

The joint integration of Eqs. (81) and (82) gives

$$f(\epsilon_{ij},s)=\frac{1}{2}\lambda_S\epsilon_{kk}^2+\mu\epsilon_{ij}\epsilon_{ij}+\frac{\kappa_T\alpha_0T_0}{c_V^0}s_0\epsilon_{kk}-\frac{T_0}{2c_V^0}(s^2-s_0^2)-T_0s_0. \tag{83}$$

4.2. Function $f=f(\sigma_{ij},T)$

We start with the relationship

$$f(\sigma_{ij},T)=g(\sigma_{ij},T)+\sigma_{ij}\epsilon_{ij}, \tag{84}$$

to obtain

$$\left(\frac{\partial f}{\partial\sigma_{ij}}\right)_T=\sigma_{kl}\left(\frac{\partial\epsilon_{kl}}{\partial\sigma_{ij}}\right)_T, \tag{85}$$

and

$$\left(\frac{\partial f}{\partial \sigma_{ij}}\right)_T = \frac{1}{2\mu}\left(\sigma_{ij} - \frac{\nu_T}{1+\nu_T}\sigma_{kk}\delta_{ij}\right). \tag{86}$$

On the other hand,

$$\left(\frac{\partial f}{\partial T}\right)_\sigma = -s + \frac{\alpha_0}{3}\sigma_{kk} = -\frac{c_P^0}{T_0}(T - T_0) - s_0. \tag{87}$$

The joint integration of Eqs. (86) and (87) gives

$$f(\sigma_{ij}, T) = \frac{1}{4\mu}\left(\sigma_{ij}\sigma_{ij} - \frac{\nu_T}{1+\nu_T}\sigma_{kk}^2\right) - \frac{c_P^0}{2T_0}(T - T_0)^2 - s_0 T. \tag{88}$$

4.3. Function $f = f(\sigma_{ij}, s)$

We start with the relationship

$$f(\sigma_{ij}, s) = h(\sigma_{ij}, s) + \sigma_{ij}\epsilon_{ij} - Ts, \tag{89}$$

to obtain

$$\left(\frac{\partial f}{\partial \sigma_{ij}}\right)_s = \sigma_{kl}\left(\frac{\partial \epsilon_{kl}}{\partial \sigma_{ij}}\right)_s + s\left(\frac{\partial \epsilon_{ij}}{\partial s}\right)_\sigma, \tag{90}$$

and

$$\left(\frac{\partial f}{\partial \sigma_{ij}}\right)_s = \frac{1}{2\mu}\left(\sigma_{ij} - \frac{\nu_S}{1+\nu_S}\sigma_{kk}\delta_{ij}\right) + \frac{\alpha_0 T_0}{3c_P^0}s\delta_{ij}. \tag{91}$$

On the other hand,

$$\left(\frac{\partial f}{\partial s}\right)_\sigma = \sigma_{ij}\left(\frac{\partial \epsilon_{ij}}{\partial s}\right)_\sigma - s\left(\frac{\partial T}{\partial s}\right)_\sigma = \frac{T_0}{c_P^0}\left(\frac{\alpha_0}{3}\sigma_{kk} - s\right). \tag{92}$$

The joint integration of Eqs. (91) and (92) gives

$$f(\sigma_{ij}, s) = \frac{1}{4\mu}\left(\sigma_{ij}\sigma_{ij} - \frac{\nu_S}{1+\nu_S}\sigma_{kk}^2\right) + \frac{\alpha_0 T_0}{3c_P^0}s\sigma_{kk} - \frac{T_0}{2c_P^0}(s^2 - s_0^2) - T_0 s_0. \tag{93}$$

4.4. List of Helmholtz free energy functions in terms of four pairs of independent state variables

$$\boxed{f(\epsilon_{ij}, T) = \frac{1}{2}\lambda_T\epsilon_{kk}^2 + \mu\epsilon_{ij}\epsilon_{ij} - \kappa_T\alpha_0(T - T_0)\epsilon_{kk} - \frac{c_V^0}{2T_0}(T - T_0)^2 - s_0 T} \tag{94}$$

$$\boxed{f(\epsilon_{ij}, s) = \frac{1}{2}\lambda_S\epsilon_{kk}^2 + \mu\epsilon_{ij}\epsilon_{ij} + \frac{\kappa_T\alpha_0 T_0}{c_V^0}s_0\epsilon_{kk} - \frac{T_0}{2c_V^0}(s^2 - s_0^2) - T_0 s_0} \tag{95}$$

$$\boxed{f(\sigma_{ij},T)=\frac{1}{4\mu}\left(\sigma_{ij}\sigma_{ij}-\frac{\nu_T}{1+\nu_T}\sigma_{kk}^2\right)-\frac{c_P^0}{2T_0}(T-T_0)^2-s_0T} \tag{96}$$

$$\boxed{f(\sigma_{ij},s)=\frac{1}{4\mu}\left(\sigma_{ij}\sigma_{ij}-\frac{\nu_S}{1+\nu_S}\sigma_{kk}^2\right)+\frac{\alpha_0T_0}{3c_P^0}s\sigma_{kk}-\frac{T_0}{2c_P^0}(s^2-s_0^2)-T_0s_0} \tag{97}$$

5. Gibbs energy in terms of four pairs of independent state variables

The Gibbs energy was expressed in Section 2.3 in terms of its natural independent state variables $g=g(\sigma_{ij},T)$. We now derive its representation in terms of other three pairs of independent state variables, recording only essential steps.

5.1. Function $g=g(\sigma_{ij},s)$

We start with the relationship

$$g(\sigma_{ij},s)=h(\sigma_{ij},s)-Ts, \tag{98}$$

to obtain

$$\left(\frac{\partial g}{\partial\sigma_{ij}}\right)_s=-\epsilon_{ij}+s\left(\frac{\partial\epsilon_{ij}}{\partial s}\right)_\sigma, \tag{99}$$

and

$$\left(\frac{\partial g}{\partial\sigma_{ij}}\right)_s=-\frac{1}{2\mu}\left(\sigma_{ij}-\frac{\nu_S}{1+\nu_S}\sigma_{kk}\delta_{ij}\right)+\frac{\alpha_0T_0}{3c_P^0}s_0\delta_{ij}. \tag{100}$$

On the other hand,

$$\left(\frac{\partial g}{\partial s}\right)_\sigma=-s\left(\frac{\partial T}{\partial s}\right)_\sigma=-\frac{T_0}{c_P^0}s. \tag{101}$$

The joint integration of Eqs. (100) and (101) gives

$$g(\sigma_{ij},s)=-\frac{1}{4\mu}\left(\sigma_{ij}\sigma_{ij}-\frac{\nu_S}{1+\nu_S}\sigma_{kk}^2\right)+\frac{\alpha_0T_0}{3c_P^0}s_0\sigma_{kk}-\frac{T_0}{2c_P^0}(s^2-s_0^2)-T_0s_0. \tag{102}$$

5.2. Function $g=g(\epsilon_{ij},T)$

We start with the relationship

$$g(\epsilon_{ij},T)=f(\epsilon_{ij},T)-\sigma_{ij}\epsilon_{ij}, \tag{103}$$

to obtain

$$\left(\frac{\partial g}{\partial\sigma_{ij}}\right)_T=-\epsilon_{kl}\left(\frac{\partial\sigma_{kl}}{\partial\epsilon_{ij}}\right)_T, \tag{104}$$

and

$$\left(\frac{\partial g}{\partial \epsilon_{ij}}\right)_T = -(\lambda_T \epsilon_{kk}\delta_{ij} + 2\mu\epsilon_{ij}). \tag{105}$$

On the other hand,

$$\left(\frac{\partial g}{\partial T}\right)_\epsilon = -s - \epsilon_{ij}\left(\frac{\partial \sigma_{ij}}{\partial T}\right)_\epsilon = -s + \kappa_T\alpha_0\epsilon_{kk} = -\frac{c_V^0}{T_0}(T - T_0) - s_0. \tag{106}$$

The joint integration of Eqs. (105) and (106) gives

$$g(\epsilon_{ij}, T) = -\left(\frac{1}{2}\lambda_T\epsilon_{kk}^2 + \mu\epsilon_{ij}\epsilon_{ij}\right) - \frac{c_V^0}{2T_0}(T - T_0)^2 - s_0 T. \tag{107}$$

5.3. Function $g = g(\epsilon_{ij}, s)$

We start with the relationship

$$g(\epsilon_{ij}, s) = u(\epsilon_{ij}, s) - \sigma_{ij}\epsilon_{ij} - Ts, \tag{108}$$

to obtain

$$\left(\frac{\partial g}{\partial \epsilon_{ij}}\right)_s = -\epsilon_{kl}\left(\frac{\partial \sigma_{kl}}{\partial \epsilon_{ij}}\right)_s - s\left(\frac{\partial \sigma_{ij}}{\partial s}\right)_\epsilon, \tag{109}$$

and

$$\left(\frac{\partial g}{\partial \epsilon_{ij}}\right)_s = -(\lambda_S \epsilon_{kk}\delta_{ij} + 2\mu\epsilon_{ij}) + \frac{\kappa_T\alpha_0 T_0}{c_V^0}s\delta_{ij}. \tag{110}$$

On the other hand,

$$\left(\frac{\partial g}{\partial s}\right)_\epsilon = -\epsilon_{ij}\left(\frac{\partial \sigma_{ij}}{\partial s}\right)_\epsilon - s\left(\frac{\partial T}{\partial s}\right)_\epsilon = \frac{T_0}{c_V^0}(\kappa_T\alpha_0\epsilon_{kk} - s). \tag{111}$$

The joint integration of Eqs. (110) and (111) gives

$$g(\epsilon_{ij}, s) = -\left(\frac{1}{2}\lambda_S\epsilon_{kk}^2 + \mu\epsilon_{ij}\epsilon_{ij}\right) + \frac{\kappa_T\alpha_0 T_0}{c_V^0}s\epsilon_{kk} - \frac{T_0}{2c_V^0}(s^2 - s_0^2) - T_0 s_0. \tag{112}$$

5.4. List of Gibbs energy functions in terms of four pairs of independent state variables

$$\boxed{g(\sigma_{ij}, T) = -\frac{1}{4\mu}\left(\sigma_{ij}\sigma_{ij} - \frac{\nu_T}{1+\nu_T}\sigma_{kk}^2\right) - \frac{\alpha_0}{3}(T - T_0)\sigma_{kk} - \frac{c_P^0}{2T_0}(T - T_0)^2 - s_0 T} \tag{113}$$

$$\boxed{g(\sigma_{ij}, s) = -\frac{1}{4\mu}\left(\sigma_{ij}\sigma_{ij} - \frac{\nu_S}{1+\nu_S}\sigma_{kk}^2\right) + \frac{\alpha_0 T_0}{3c_P^0}s_0\sigma_{kk} - \frac{T_0}{2c_P^0}(s^2 - s_0^2) - T_0 s_0} \tag{114}$$

$$\boxed{g(\epsilon_{ij}, T) = -\left(\frac{1}{2}\lambda_T\epsilon_{kk}^2 + \mu\epsilon_{ij}\epsilon_{ij}\right) - \frac{c_V^0}{2T_0}(T - T_0)^2 - s_0 T} \tag{115}$$

$$\boxed{g(\epsilon_{ij},s) = -\left(\frac{1}{2}\lambda_S\epsilon_{kk}^2 + \mu\epsilon_{ij}\epsilon_{ij}\right) + \frac{\kappa_T\alpha_0 T_0}{c_V^0}s\epsilon_{kk} - \frac{T_0}{2c_V^0}(s^2 - s_0^2) - T_0 s_0} \tag{116}$$

6. Enthalpy in terms of four pairs of independent state variables

The enthalpy was expressed in Section 2.4 in terms of its natural independent variables $h = h(\sigma_{ij}, s)$. We now derive its representation in terms of other three pairs of independent variables.

6.1. Function $h = h(\sigma_{ij}, T)$

We start with the relationship

$$h(\sigma_{ij}, T) = g(\sigma_{ij}, T) + Ts, \tag{117}$$

to obtain

$$\left(\frac{\partial h}{\partial \sigma_{ij}}\right)_T = -\epsilon_{ij} + T\left(\frac{\partial \epsilon_{ij}}{\partial T}\right)_\sigma, \tag{118}$$

and

$$\left(\frac{\partial h}{\partial \sigma_{ij}}\right)_T = -\frac{1}{2\mu}\left(\sigma_{ij} - \frac{\nu_T}{1+\nu_T}\sigma_{kk}\delta_{ij}\right) + \frac{\alpha_0}{3}T_0\delta_{ij}. \tag{119}$$

On the other hand,

$$\left(\frac{\partial h}{\partial T}\right)_\sigma = T\left(\frac{\partial s}{\partial T}\right)_\sigma = \frac{c_P^0}{T_0}T. \tag{120}$$

The joint integration of Eqs. (119) and (120) gives

$$h(\sigma_{ij}, T) = -\frac{1}{4\mu}\left(\sigma_{ij}\sigma_{ij} - \frac{\nu_T}{1+\nu_T}\sigma_{kk}^2\right) + \frac{\alpha_0}{3}T_0\sigma_{kk} + \frac{c_P^0}{2T_0}(T^2 - T_0^2). \tag{121}$$

6.2. Function $h = h(\epsilon_{ij}, s)$

We start with the relationship

$$h(\epsilon_{ij}, s) = u(\epsilon_{ij}, s) - \sigma_{ij}\epsilon_{ij}, \tag{122}$$

to obtain

$$\left(\frac{\partial h}{\partial \epsilon_{ij}}\right)_s = -\epsilon_{kl}\left(\frac{\partial \sigma_{kl}}{\partial \epsilon_{ij}}\right)_s, \tag{123}$$

and

$$\left(\frac{\partial h}{\partial \epsilon_{ij}}\right)_s = -(\lambda_S\epsilon_{kk}\delta_{ij} + 2\mu\epsilon_{ij}). \tag{124}$$

On the other hand,

$$\left(\frac{\partial h}{\partial s}\right)_{\epsilon} = T - \epsilon_{ij}\left(\frac{\partial \sigma_{ij}}{\partial s}\right)_{\epsilon} = T + \frac{\kappa_T \alpha_0 T_0}{c_V^0}\epsilon_{kk} = \frac{T_0}{c_V^0}(s - s_0) + T_0. \tag{125}$$

The joint integration of Eqs. (124) and (125) gives

$$h(\epsilon_{ij}, s) = -\left(\frac{1}{2}\lambda_S \epsilon_{kk}^2 + \mu\epsilon_{ij}\epsilon_{ij}\right) + \frac{T_0}{2c_V^0}(s - s_0)^2 + T_0(s - s_0). \tag{126}$$

6.3. Function $h = h(\epsilon_{ij}, T)$

We start with the relationship

$$h(\epsilon_{ij}, T) = f(\epsilon_{ij}, T) - \sigma_{ij}\epsilon_{ij} - Ts, \tag{127}$$

to obtain

$$\left(\frac{\partial h}{\partial \epsilon_{ij}}\right)_{T} = -\epsilon_{kl}\left(\frac{\partial \sigma_{kl}}{\partial \epsilon_{ij}}\right)_{T} - T\left(\frac{\partial \sigma_{ij}}{\partial T}\right)_{\epsilon}, \tag{128}$$

and

$$\left(\frac{\partial h}{\partial \epsilon_{ij}}\right)_{T} = -(\lambda_T \epsilon_{kk}\delta_{ij} + 2\mu\epsilon_{ij}) + \kappa_T \alpha_0 T \delta_{ij}. \tag{129}$$

On the other hand,

$$\left(\frac{\partial h}{\partial T}\right)_{\epsilon} = -\epsilon_{ij}\left(\frac{\partial \sigma_{ij}}{\partial T}\right)_{\epsilon} + T\left(\frac{\partial s}{\partial T}\right)_{\epsilon} = \kappa_T \alpha_0 \epsilon_{kk} + \frac{c_V^0}{T_0}T. \tag{130}$$

The joint integration of Eqs. (129) and (130) gives

$$h(\epsilon_{ij}, T) = -\left(\frac{1}{2}\lambda_T \epsilon_{kk}^2 + \mu\epsilon_{ij}\epsilon_{ij}\right) + \kappa_T \alpha_0 T \epsilon_{kk} + \frac{c_V^0}{2T_0}(T^2 - T_0^2). \tag{131}$$

6.4. List of enthalpy functions in terms of four pairs of independent variables

$$\boxed{h(\sigma_{ij}, s) = -\frac{1}{4\mu}\left(\sigma_{ij}\sigma_{ij} - \frac{\nu_S}{1+\nu_S}\sigma_{kk}^2\right) - \frac{\alpha_0 T_0}{3c_P^0}(s - s_0)\sigma_{kk} + \frac{T_0}{2c_P^0}(s - s_0)^2 + T_0(s - s_0)} \tag{132}$$

$$\boxed{h(\sigma_{ij}, T) = -\frac{1}{4\mu}\left(\sigma_{ij}\sigma_{ij} - \frac{\nu_T}{1+\nu_T}\sigma_{kk}^2\right) + \frac{\alpha_0}{3}T_0\sigma_{kk} + \frac{c_P^0}{2T_0}(T^2 - T_0^2)} \tag{133}$$

$$\boxed{h(\epsilon_{ij}, s) = -\left(\frac{1}{2}\lambda_S \epsilon_{kk}^2 + \mu\epsilon_{ij}\epsilon_{ij}\right) + \frac{T_0}{2c_V^0}(s - s_0)^2 + T_0(s - s_0)} \tag{134}$$

$$\boxed{h(\epsilon_{ij}, T) = -\left(\frac{1}{2}\lambda_T \epsilon_{kk}^2 + \mu\epsilon_{ij}\epsilon_{ij}\right) + \kappa_T \alpha_0 T \epsilon_{kk} + \frac{c_V^0}{2T_0}(T^2 - T_0^2)} \tag{135}$$

7. Uniaxial loading and thermoelastic effect

The derived representations of thermodynamic potentials for arbitrary three-dimensional states of stress and strain are greatly simplified in the case of uniaxial and spherical states of stress and strain. The corresponding results are listed in Appendices A–D. To illustrate the use of some of the derived formulas, consider uniaxial loading paths shown in Fig. 1. The path OAB is an adiabatic (fast loading) path, the path OC is an isothermal (slow loading) path, the path AC is a constant stress path, and the path BC is a constant longitudinal strain path. Along the adiabatic path OAB (see the expression for $u(\sigma, s)$ from Appendix A)

$$u = -h = \frac{1}{2E_S}\sigma^2, \tag{136}$$

while along the isothermal path OC (see the expressions for $f(\sigma, T)$ and $g(\sigma, T)$ from Appendix A)

$$f - f_0 = g_0 - g = \frac{1}{2E_T}\sigma^2, \quad f_0 = g_0 = -T_0 s_0. \tag{137}$$

The temperature drop along the adiabatic path is

$$T - T_0 = -\frac{\alpha_0 T_0}{3c_P^0}\sigma, \tag{138}$$

in accord with Kelvin's formula describing Joule's thermoelastic effect (Fung, 1965, p. 388). The entropy increase along the isothermal path is

$$s - s_0 = \frac{\alpha_0}{3}\sigma, \tag{139}$$

with the corresponding absorbed heat given by $T_0(s - s_0)$.

The heat absorbed along the constant stress path AC is equal to the enthalpy change

$$h_C - h_A = \frac{\alpha_0 T_0}{3}\sigma_A - \frac{\alpha_0^2 T_0}{18c_P^0}\sigma_A^2. \tag{140}$$

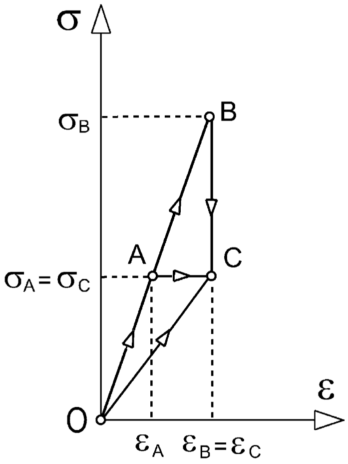

Fig. 1. Uniaxial loading along isothermal path OC, and along adiabatic path OAB. The paths AC and BC are the constants stress and constant longitudinal strain paths, respectively.

This is in agreement with the result following from

$$\int_{T_A}^{T_C} c_P(T)\,\mathrm{d}T = \frac{c_P^0}{2T_0}(T_0^2 - T_A^2). \tag{141}$$

The heat absorbed along the constant longitudinal strain path BC is

$$u_C - u_B = \left(\frac{1}{2E_T}\sigma_C^2 + \frac{\alpha_0 T_0}{3}\sigma_C\right) - \frac{1}{2E_S}\sigma_B^2, \tag{142}$$

which gives

$$u_C - u_B = \frac{\alpha_0 T_0}{3}\sigma_A - \frac{E_S}{E_T}\frac{\alpha_0^2 T_0}{18 c_P^0}\sigma_A^2. \tag{143}$$

This can be confirmed by integrating

$$\int_{s_B}^{s_C} T\,\mathrm{d}s = \int_{s_B}^{s_C}\left[T_0 + \frac{T_0}{c_P^0}\left(s - s_0 - \frac{\alpha_0}{3}\sigma\right)\right]\mathrm{d}s, \tag{144}$$

with the stress variation, along the path BC, given by

$$\sigma = \frac{E_S}{E_T}\sigma_A - \frac{\alpha_0 T_0}{3c_P^0}E_S(s - s_0). \tag{145}$$

For metals, the second term on the right-hand side of Eq. (143) is much smaller than the first term, being associated with small departures of c_P and c_V from their reference values c_P^0 and c_V^0, inherent in linear approximations $c_P = c_P^0 T/T_0$ and $c_V = c_V^0 T/T_0$, which are valid for sufficiently small temperature differences $(T - T_0)$.

An alternative derivation of (143) proceeds by noting that $\mathrm{d}\sigma = -E_T\alpha_0\,\mathrm{d}T/3$ along the path BC (because the longitudinal component of strain is fixed along that path). The corresponding increment of entropy is

$$\mathrm{d}s = \frac{\alpha_0}{3}\,\mathrm{d}\sigma + \frac{c_P^0}{T_0}\,\mathrm{d}T = \frac{c_P^0}{T_0}\frac{E_T}{E_S}\,\mathrm{d}T, \tag{146}$$

recalling the relationship (47) between isothermal and adiabatic Young's moduli. Therefore,

$$\int_{T_B}^{T_C} T\,\mathrm{d}s = \frac{c_P^0}{2T_0}\frac{E_T}{E_S}\left(T_0^2 - T_B^2\right). \tag{147}$$

The incorporation of Eq. (138) reproduces Eq. (143).

Yet another derivation is possible by starting from an expression for the heat increment in terms of the latent and specific heats, i.e.,

$$T\,\mathrm{d}s = l_{ij}^{\epsilon}\,\mathrm{d}\epsilon_{ij} + c_V\,\mathrm{d}T. \tag{148}$$

The components of the latent heat tensor at constant strain are defined by

$$l_{ij}^{\epsilon} = T\left(\frac{\partial s}{\partial \epsilon_{ij}}\right)_T = \kappa_T\alpha_0 T\delta_{ij}, \tag{149}$$

which gives

$$T\,\mathrm{d}s = \kappa_T\alpha_0 T\,\mathrm{d}\epsilon_{kk} + c_V\,\mathrm{d}T, \tag{150}$$

Since, along the path BC,

$$\mathrm{d}\epsilon_{kk} = \frac{2}{3}(1+\nu_T)\alpha_0\,\mathrm{d}T, \tag{151}$$

the substitution into Eq. (150), and integration from T_B to $T_C = T_0$, gives Eq. (143). This derivation is facilitated by noting that, in view of Eq. (46),

$$(1+\nu_T)\frac{\alpha_0^2 T_0}{9c_P^0} = \frac{\nu_S - \nu_T}{E_S}. \tag{152}$$

The individual contributions of the latent and specific heat to total heat absorbed along the path BC are

$$\int_B^C c_V\,\mathrm{d}T = \frac{1-2\nu_S}{1-2\nu_T}(u_C - u_B), \tag{153}$$

$$\int_B^C l_{ij}^{\epsilon}\,\mathrm{d}\epsilon_{ij} = 2\frac{\nu_S-\nu_T}{1-2\nu_T}(u_C - u_B). \tag{154}$$

The contribution given by (153) is smaller than $(u_C - u_B)$, because $\nu_S > \nu_T$. Since the lateral strain is not held constant along the path BC, there is a small but positive contribution to absorbed heat from the latent heat, and this is represented by Eq. (154). Both, Eqs. (143) and (153) display in their structure a simple combination of adiabatic and isothermal elastic constants, via the ratio terms E_S/E_T and

$$\frac{c_V^0}{c_P^0}\frac{E_S}{E_T} = \frac{1-2\nu_S}{1-2\nu_T}. \tag{155}$$

8. Conclusions

The thermodynamic analysis is presented which yields the expressions for all thermodynamic potentials (internal energy, Helmholtz free energy, Gibbs energy, and enthalpy) in terms of four possible pairs of independent state variables from the set of stress, strain, temperature, and entropy. The derived results for some of the considered potentials, and for the particular pairs of independent state variables, are well-known from linear thermoelasticity, but are presented here in conjunction with other results for the completeness of general formulation. The presented analysis is, in essence, an extension of the classical thermodynamics analysis, which is cast within the scalar setting (involving pressure and volume), to the three-dimensional tensorial setting (involving stress and strain tensors). When the stress is an independent variable, the thermodynamic potentials involve in their structure the specific heat c_P. With the strain as an independent variable, the specific heat c_V appears in the representation of the thermodynamic potentials. If the temperature is used as an independent variable, the thermodynamic potentials are expressed in terms of the isothermal elastic constants (λ_T, ν_T, κ_T). With the entropy as an independent variable, the adiabatic counterparts (λ_S, ν_S, κ_S) appear in the representation of the thermodynamic potentials. If a thermodynamic potential contains a mixed strain–entropy term, such as $\epsilon_{kk}s$, either the ratio κ_T/c_V^0 or κ_S/c_P^0 multiplies that term. The presented thermodynamic analysis also delivers the relationships between different types of involved elastic and thermodynamic constants. The general results are applied to uniaxial and spherical states of stress and strain, with a particular attention given to uniaxial loading under isothermal, adiabatic, constant stress, and constant strain conditions. A simple combination of adiabatic and isothermal elastic constants appears in the expression for the exchanged heat along the constant strain path.

Acknowledgement

Research support from the NSF Grant No. 0243695 is kindly acknowledged.

Appendix A. Thermodynamic potentials for uniaxial stress

For the uniaxial state of stress

$$\sigma_{ij} = \sigma\delta_{i1}\delta_{j1}, \quad \sigma_{ij}\sigma_{ij} = \sigma^2, \quad \sigma_{kk} = \sigma.$$

The corresponding thermodynamic potentials are

$$u(\sigma, s) = \frac{1}{2E_S}\sigma^2 - \frac{T_0}{2c_P^0}(s - s_0)^2 + T_0(s - s_0),$$

$$u(\sigma, T) = \frac{1}{2E_T}\sigma^2 + \frac{\alpha_0}{3}T\sigma + \frac{c_P^0}{2T_0}(T^2 - T_0^2),$$

$$f(\sigma, s) = \frac{1}{2E_S}\sigma^2 + \frac{\alpha_0 T_0}{3c_P^0}s\sigma - \frac{T_0}{2c_P^0}(s^2 - s_0^2) - T_0 s_0,$$

$$f(\sigma, T) = \frac{1}{2E_T}\sigma^2 - \frac{c_P^0}{2T_0}(T - T_0)^2 - s_0 T,$$

$$g(\sigma, s) = -\frac{1}{2E_S}\sigma^2 + \frac{\alpha_0 T_0}{3c_P^0}s_0\sigma - \frac{T_0}{2c_P^0}(s^2 - s_0^2) - T_0 s_0,$$

$$g(\sigma, T) = -\frac{1}{2E_T}\sigma^2 - \frac{\alpha_0}{3}(T - T_0)\sigma - \frac{c_P^0}{2T_0}(T - T_0)^2 - s_0 T,$$

$$h(\sigma, s) = -\frac{1}{2E_S}\sigma^2 - \frac{\alpha_0 T_0}{3c_P^0}(s - s_0)\sigma + \frac{T_0}{2c_P^0}(s - s_0)^2 + T_0(s - s_0),$$

$$h(\sigma, T) = -\frac{1}{2E_T}\sigma^2 + \frac{\alpha_0}{3}T_0\sigma + \frac{c_P^0}{2T_0}(T^2 - T_0^2).$$

The constitutive equations are

$$\epsilon_{ij} = \frac{\sigma}{2\mu}\left(\delta_{i1}\delta_{j1} - \frac{v_T}{1 + v_T}\delta_{ij}\right) + \frac{\alpha_0}{3}(T - T_0)\delta_{ij},$$

or

$$\epsilon_{ij} = \frac{\sigma}{2\mu}\left(\delta_{i1}\delta_{j1} - \frac{v_S}{1 + v_S}\delta_{ij}\right) + \frac{\alpha_0 T_0}{3c_P^0}(s - s_0)\delta_{ij},$$

and

$$s - s_0 = \frac{\alpha_0}{3}\sigma + \frac{c_P^0}{T_0}(T - T_0).$$

Appendix B. Thermodynamic potentials for uniaxial strain

For the uniaxial state of strain

$$\epsilon_{ij} = \epsilon\delta_{i1}\delta_{j_1}, \quad \epsilon_{ij}\epsilon_{ij} = \epsilon^2, \quad \epsilon_{kk} = \epsilon.$$

The corresponding thermodynamic potentials are

$$u(\epsilon, s) = \frac{1}{2}(\lambda_S + 2\mu)\epsilon^2 - \frac{\kappa_T\alpha_0 T_0}{c_V^0}(s - s_0)\epsilon + \frac{T_0}{2c_V^0}(s - s_0)^2 + T_0(s - s_0),$$

$$u(\epsilon, T) = \frac{1}{2}(\lambda_T + 2\mu)\epsilon^2 + \kappa_T\alpha_0 T_0\epsilon + \frac{c_V^0}{2T_0}(T^2 - T_0^2),$$

$$f(\epsilon, s) = \frac{1}{2}(\lambda_S + 2\mu)\epsilon^2 + \frac{\kappa_T\alpha_0 T_0}{c_V^0}s_0\epsilon - \frac{T_0}{2c_V^0}(s^2 - s_0^2) - T_0 s_0,$$

$$f(\epsilon, T) = \frac{1}{2}(\lambda_T + 2\mu)\epsilon^2 - \kappa_T\alpha_0(T - T_0)\epsilon - \frac{c_V^0}{2T_0}(T - T_0)^2 - s_0 T,$$

$$g(\epsilon, s) = -\frac{1}{2}(\lambda_S + 2\mu)\epsilon^2 + \frac{\kappa_T\alpha_0 T_0}{c_V^0}s\epsilon - \frac{T_0}{2c_V^0}(s^2 - s_0^2) - T_0 s_0,$$

$$g(\epsilon, T) = -\frac{1}{2}(\lambda_T + 2\mu)\epsilon^2 - \frac{c_V^0}{2T_0}(T - T_0)^2 - s_0 T,$$

$$h(\epsilon, s) = -\frac{1}{2}(\lambda_S + 2\mu)\epsilon^2 + \frac{T_0}{2c_V^0}(s - s_0)^2 + T_0(s - s_0),$$

$$h(\epsilon, T) = -\frac{1}{2}(\lambda_T + 2\mu)\epsilon^2 + \kappa_T\alpha_0 T\epsilon + \frac{c_V^0}{2T_0}(T^2 - T_0^2).$$

The constitutive equations are

$$\sigma_{ij} = \epsilon(\lambda_T\delta_{ij} + 2\mu\delta_{i1}\delta_{j1}) - \kappa_T\alpha_0(T - T_0)\delta_{ij},$$

or

$$\sigma_{ij} = \epsilon(\lambda_S\delta_{ij} + 2\mu\delta_{i1}\delta_{j1}) - \frac{\kappa_S\alpha_0 T_0}{c_P^0}(s - s_0)\delta_{ij},$$

and

$$s - s_0 = \kappa_T\alpha_0\epsilon + \frac{c_V^0}{T_0}(T - T_0).$$

Appendix C. Thermodynamic potentials for spherical stress

For the spherical state of stress

$$\sigma_{ij} = \sigma\delta_{ij}, \quad \sigma_{ij}\sigma_{ij} = 3\sigma^2, \quad \sigma_{kk} = 3\sigma.$$

The corresponding thermodynamic potentials are

$$u(\sigma, s) = \frac{1}{2\kappa_S}\sigma^2 - \frac{T_0}{2c_P^0}(s - s_0)^2 + T_0(s - s_0),$$

$$u(\sigma, T) = \frac{1}{2\kappa_T}\sigma^2 + \alpha_0 T\sigma + \frac{c_P^0}{2T_0}(T^2 - T_0^2),$$

$$f(\sigma, s) = \frac{1}{2\kappa_S}\sigma^2 + \frac{\alpha_0 T_0}{c_P^0}s\sigma - \frac{T_0}{2c_P^0}(s^2 - s_0^2) - T_0 s_0,$$

$$f(\sigma, T) = \frac{1}{2\kappa_T}\sigma^2 - \frac{c_P^0}{2T_0}(T - T_0)^2 - s_0 T,$$

$$g(\sigma, s) = -\frac{1}{2\kappa_S}\sigma^2 + \frac{\alpha_0 T_0}{c_P^0}s_0\sigma - \frac{T_0}{2c_P^0}(s^2 - s_0^2) - T_0 s_0,$$

$$g(\sigma, T) = -\frac{1}{2\kappa_T}\sigma^2 - \alpha_0(T - T_0)\sigma - \frac{c_P^0}{2T_0}(T - T_0)^2 - s_0 T,$$

$$h(\sigma, s) = -\frac{1}{2\kappa_S}\sigma^2 - \frac{\alpha_0 T_0}{c_P^0}(s - s_0)\sigma + \frac{T_0}{2c_P^0}(s - s_0)^2 + T_0(s - s_0),$$

$$h(\sigma, T) = -\frac{1}{2\kappa_T}\sigma^2 + \alpha_0 T_0\sigma + \frac{c_P^0}{2T_0}(T^2 - T_0^2).$$

The constitutive equations are

$$\epsilon = \frac{\sigma}{3\kappa_T} + \frac{\alpha_0}{3}(T - T_0),$$

or

$$\epsilon = \frac{\sigma}{3\kappa_S} + \frac{\alpha_0 T_0}{3c_P^0}(s - s_0),$$

and

$$s - s_0 = \alpha_0\sigma + \frac{c_P^0}{T_0}(T - T_0).$$

Appendix D. Thermodynamic potentials for spherical strain

For the spherical strain

$$\epsilon_{ij} = \epsilon\delta_{ij}, \quad \epsilon_{ij}\epsilon_{ij} = 3\epsilon^2, \quad \epsilon_{kk} = 3\epsilon.$$

The corresponding thermodynamic potentials are

$$u(\epsilon, s) = \frac{9}{2}\kappa_S\epsilon^2 - \frac{3\kappa_T\alpha_0 T_0}{c_V^0}(s - s_0)\epsilon + \frac{T_0}{2c_V^0}(s - s_0)^2 + T_0(s - s_0),$$

$$u(\epsilon, T) = \frac{9}{2}\kappa_T\epsilon^2 + 3\kappa_T\alpha_0 T_0\epsilon + \frac{c_V^0}{2T_0}(T^2 - T_0^2),$$

$$f(\epsilon, s) = \frac{9}{2}\kappa_S\epsilon^2 + \frac{3\kappa_T\alpha_0 T_0}{c_V^0}s_0\epsilon - \frac{T_0}{2c_V^0}(s^2 - s_0^2) - T_0 s_0,$$

$$f(\epsilon, T) = \frac{9}{2}\kappa_T\epsilon^2 - 3\kappa_T\alpha_0(T - T_0)\epsilon - \frac{c_V^0}{2T_0}(T - T_0)^2 - s_0 T,$$

$$g(\epsilon, s) = -\frac{9}{2}\kappa_S\epsilon^2 + \frac{3\kappa_T\alpha_0 T_0}{c_V^0}s\epsilon - \frac{T_0}{2c_V^0}(s^2 - s_0^2) - T_0 s_0,$$

$$g(\epsilon, T) = -\frac{9}{2}\kappa_T\epsilon^2 - \frac{c_V^0}{2T_0}(T - T_0)^2 - s_0 T,$$

$$h(\epsilon, s) = -\frac{9}{2}\kappa_S\epsilon^2 + \frac{T_0}{2c_V^0}(s - s_0)^2 + T_0(s - s_0),$$

$$h(\epsilon, T) = -\frac{9}{2}\kappa_T\epsilon^2 + 3\kappa_T\alpha_0 T\epsilon + \frac{c_V^0}{2T_0}(T^2 - T_0^2).$$

The constitutive equations are

$$\sigma = 3\kappa_T\epsilon - \kappa_T\alpha_0(T - T_0),$$

or

$$\sigma = 3\kappa_S\epsilon - \frac{\kappa_S\alpha_0 T_0}{c_P^0}(s - s_0),$$

and

$$s - s_0 = 3\kappa_T\alpha_0\epsilon + \frac{c_V^0}{T_0}(T - T_0).$$

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