

Thermodynamic analysis based on the second-order variations of thermodynamic potentials

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Abstract

An analysis of the Gibbs conditions of stable thermodynamic equilibrium, based on the constrained minimization of the four fundamental thermodynamic potentials, is presented with a particular attention given to the previously unexplored connections between the second-order variations of thermodynamic potentials. These connections are used to establish the convexity properties of all potentials in relation to each other, which systematically deliver thermodynamic relationships between the specific heats, and the isentropic and isothermal bulk moduli and compressibilities. The comparison with the classical derivation is then given.

Keywords: Gibbs conditions, internal energy, second-order variations, specific heats, thermodynamic potentials

1 Introduction

The Gibbs conditions of thermodynamic equilibrium are of great importance in the analysis of the equilibrium and stability of homogeneous and heterogeneous thermodynamic systems [1]. The system is in a thermodynamic equilibrium if its state variables do not spontaneously change with time. As a consequence of the second law of thermodynamics, the equilibrium state of an isolated system at constant volume and internal energy is the state with the maximum value of the total entropy. Alternatively, among all neighboring states with the

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same volume and total entropy, the equilibrium state is one with the lowest total internal energy. Further equilibrium conditions can be stated in terms of other thermodynamic potentials (Helmholtz free energy, enthalpy, and Gibbs energy), which apply under different types of thermomechanical constraints. For example, among all neighboring states at the same temperature and pressure, the equilibrium state is one with the lowest Gibbs energy. A detailed analysis of these equilibrium conditions, with their applications, can be found in the standard texts on thermodynamics, such as [2-7].

The objective of this paper is to derive simple, previously unnoticed and unexplored, relationships between the second-order variations of thermodynamic potentials, which are then used to establish the relationships between the convexity and concavity properties of all thermodynamic potentials in terms of the convexity property of the internal energy function. Based on this, the fundamental thermodynamic connections between the specific heats, and between the isentropic and isothermal bulk moduli and compressibilities, are derived. The analysis is more general, yet simpler than the other analysis commonly used in the literature, which is based on the formal change of the independent state variables [4-6].

2 Internal energy

Consider a uniform body of current volume V and mass density $\rho = m/V$, which is in thermodynamic equilibrium at temperature T and pressure p .¹ 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 (per unit mass), respectively. The pressure p is a conjugate variable to volume V , and the temperature T is a conjugate variable to entropy S . The Gibbs condition of thermodynamic equilibrium states that any small (spatially nonuniform) virtual variations $(\delta s, \delta \vartheta)$ from a uniform stable equilibrium state, prescribed under the constraints of constant total entropy S and constant total volume V , give rise to an increase of the internal energy U . Thus,

$$\Delta U = \int_V \rho \Delta u(s, \vartheta) dV > 0, \quad (1)$$

¹Solid materials with a nonlinear pressure–volume relation under purely compressive loading are of primary concern here [8], although the analysis also applies to thermodynamics of fluid systems at rest [9].

subjected to the constraints²

$$\Delta S = \int_V \rho \delta s \, dV = 0, \quad \Delta V = \int_V \rho \delta \vartheta \, dV = 0. \quad (2)$$

The conservation of mass implies that $\delta(\rho \, dV) = 0$. The change of the specific internal energy Δu , due to nonuniform variations δs and $\delta \vartheta$, is

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

In particular, the first-order variation of u is

$$\delta u = T \delta s - p \delta \vartheta, \quad (4)$$

where $T = \partial u / \partial s$ is the temperature, and $p = -\partial u / \partial \vartheta$ is the pressure. The second-order variation of u is likewise

$$\delta^2 u = \frac{\partial^2 u}{\partial s^2} (\delta s)^2 + 2 \frac{\partial^2 u}{\partial s \partial \vartheta} \delta s \delta \vartheta + \frac{\partial^2 u}{\partial \vartheta^2} (\delta \vartheta)^2. \quad (5)$$

In view of the constraint conditions (2), from (1) it follows that

$$\Delta U = \sum_{k=2}^{\infty} \frac{1}{k!} \int_V \rho \delta^k u \, dV = \frac{1}{2} \int_V \rho \delta^2 u \, dV + \dots > 0. \quad (6)$$

This must hold for any admissible virtual variations δs and $\delta \vartheta$, subjected to (2), which is assured by the requirement that $u = u(s, \vartheta)$ is a convex function of its arguments. A sufficient condition for this is that the Hessian matrix of u is positive-definite, $\delta^2 u > 0$.³ When expressed in terms of the extensive properties, this is

$$\frac{\partial^2 U}{\partial S^2} (\delta S)^2 + 2 \frac{\partial^2 U}{\partial S \partial V} \delta S \delta V + \frac{\partial^2 U}{\partial V^2} (\delta V)^2 > 0. \quad (7)$$

The well-known consequences are that the specific heats and the isentropic and isothermal compressibilities are positive quantities [2-6].

²More commonly the considerations are made in the literature by imagining that the system is subdivided into two equal parts that are given opposite virtual disturbances $(\Delta S/2, \Delta V/2)$ and $-(\Delta S/2, \Delta V/2)$; [4-6]. See also [10] for the microcanonical thermodynamics and phase transitions in small systems.

³If $\delta^2 u = 0$, higher-order variations need to be considered, *i.e.*, for the stability of equilibrium the first nonvanishing variation $\delta^k u$ ($k > 1$) must be positive and the corresponding k has to be even.

3 Helmholtz free energy

The total Helmholtz free energy of a stable equilibrium state,

$$F = \int_V \rho u(s, \vartheta) dV - T \int_V \rho s dV, \quad (8)$$

is at minimum with respect to small virtual variations $(\delta s, \delta \vartheta)$ at constant temperature T and constant volume V . Thus,

$$\Delta F = \int_V \rho \Delta u(s, \vartheta) dV - T \int_V \rho \delta s dV > 0. \quad (9)$$

In view of the Gibbs relation $\delta u = -p\delta\vartheta + T\delta s$, and the total volume constraint, this gives

$$\Delta F = \frac{1}{2} \int_V \rho \delta^2 u dV + \dots > 0, \quad (10)$$

where $\delta^2 u$ is given by (5). A sufficient condition for ΔF to be positive is that $\delta^2 u > 0$.

Next, by considering

$$F = \int_V \rho f(T, \vartheta) dV, \quad (11)$$

it follows that, at constant T and V ,

$$\Delta F = \frac{1}{2} \int_V \rho \frac{\partial^2 f}{\partial \vartheta^2} (\delta \vartheta)^2 dV + \dots > 0. \quad (12)$$

A sufficient condition for this positive-definiteness is that $\partial^2 f / \partial \vartheta^2 > 0$, *i.e.*,

$$\frac{\partial^2 F}{\partial V^2} > 0. \quad (13)$$

3.1 Relationships among the second-order variations of F and U

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

$$F(T, V) = U(S, V) - TS. \quad (14)$$

Consider a small variation of state $(\delta S, \delta V)$, which obeys the energy equation, and denote by δT the corresponding temperature variation. Then,

$$F(T + \delta T, V + \delta V) = U(S + \delta S, V + \delta V) - (T + \delta T)(S + \delta S). \quad (15)$$

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

$$\begin{aligned}\delta F &= \delta U - T\delta S - S\delta T = -p\delta V - S\delta T, \\ \delta^2 F &= \delta^2 U - 2\delta T\delta S, \\ \delta^k F &= \delta^k U, \quad k \geq 3.\end{aligned}\tag{16}$$

Since

$$T = \frac{\partial U}{\partial S} \Rightarrow \delta T = \frac{\partial^2 U}{\partial S^2} \delta S + \frac{\partial^2 U}{\partial S \partial V} \delta V,\tag{17}$$

$$S = -\frac{\partial F}{\partial T} \Rightarrow \delta S = -\frac{\partial^2 F}{\partial T^2} \delta T - \frac{\partial^2 F}{\partial T \partial V} \delta V,\tag{18}$$

the substitution into (16) yields

$$\begin{aligned}\frac{\partial^2 F}{\partial T^2} (\delta T)^2 + 2\frac{\partial^2 F}{\partial T \partial V} \delta T \delta V + \frac{\partial^2 F}{\partial V^2} (\delta V)^2 = \\ -\frac{\partial^2 U}{\partial S^2} (\delta S)^2 + \frac{\partial^2 U}{\partial V^2} (\delta V)^2,\end{aligned}\tag{19}$$

$$\begin{aligned}\frac{\partial^2 U}{\partial S^2} (\delta S)^2 + 2\frac{\partial^2 U}{\partial S \partial V} \delta S \delta V + \frac{\partial^2 U}{\partial V^2} (\delta V)^2 = \\ -\frac{\partial^2 F}{\partial T^2} (\delta T)^2 + \frac{\partial^2 F}{\partial V^2} (\delta V)^2.\end{aligned}\tag{20}$$

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

$$\frac{\partial^2 F}{\partial T^2} (\delta T)^2 = -\frac{\partial^2 U}{\partial S^2} (\delta S)^2.$$

Thus, at the state where the internal energy U is a convex function of S , the Helmholtz free energy F is a concave function of T , *i.e.*,

$$\frac{\partial^2 U}{\partial S^2} > 0 \Rightarrow \frac{\partial^2 F}{\partial T^2} < 0.\tag{21}$$

Furthermore, by considering isothermal variations of volume, (20) confirms (13), at any state where $\delta^2 U$, given by the left-hand side of (20), is a positive-definite quadratic form. It is also noted that (19) implies that $\delta^2 F$ itself is a positive-definite quadratic form for any isentropic variation of volume and temperature, at any state where U is a convex function of V , with $\partial^2 U / \partial V^2 > 0$. In retrospect, it is commonly assumed that that entropy is a monotonically increasing function of temperature, so that $\partial S / \partial T = -\partial^2 F / \partial T^2 > 0$, which is in accord with (21).

4 The enthalpy function

The total enthalpy,

$$H = \int_V \rho u(s, \vartheta) dV + p \int_V \rho \vartheta dV, \quad (22)$$

of a stable equilibrium state is at minimum with respect to small virtual variations $(\delta s, \delta \vartheta)$ at constant pressure and subjected to the constraint of constant total entropy ($\int_V \rho \delta s dV = 0$). The change of enthalpy is

$$\Delta H = \int_V \rho \delta u(s, \vartheta) dV + p \int_V \rho \delta \vartheta dV. \quad (23)$$

In view of the Gibbs relation, and the total entropy constraint, the minimum condition requires that

$$\Delta H = \frac{1}{2} \int_V \rho \delta^2 u dV + \dots > 0, \quad (24)$$

where $\delta^2 u$ is given by (5). A sufficient condition for ΔH to be positive is that $\delta^2 u > 0$.

Furthermore, by considering

$$H = \int_V \rho h(s, p) dV, \quad (25)$$

it follows that, at constant p and S ,

$$\Delta H = \frac{1}{2} \int_V \rho \frac{\partial^2 h}{\partial s^2} (\delta s)^2 dV + \dots > 0. \quad (26)$$

A sufficient condition for this positive-definiteness is that $\partial^2 h / \partial s^2 > 0$, *i.e.*,

$$\frac{\partial^2 H}{\partial S^2} > 0, \quad (27)$$

so that the enthalpy is a convex function of the entropy. This is in accord with the common assumption that the temperature $T = \partial H / \partial S$ is a monotonically increasing function of the entropy.

4.1 Relationships among the second-order variations of H and U

The enthalpy and internal energy are related by the Legendre transform

$$H(S, p) = U(S, V) + pV. \quad (28)$$

Consider a small variation of state $(\delta S, \delta V)$, which obeys the energy equation, and denote by δp the corresponding pressure variation. Then,

$$H(S + \delta S, p + \delta p) = U(S + \delta S, V + \delta V) + (p + \delta p)(V + \delta V). \quad (29)$$

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

$$\begin{aligned} \delta H &= \delta U + p\delta V + V\delta p = T\delta S + V\delta p, \\ \delta^2 H &= \delta^2 U + 2\delta p\delta V, \\ \delta^k H &= \delta^k U, \quad k \geq 3. \end{aligned} \quad (30)$$

Since

$$p = -\frac{\partial U}{\partial V} \Rightarrow \delta p = -\frac{\partial^2 U}{\partial V^2} \delta V - \frac{\partial^2 U}{\partial S \partial V} \delta S, \quad (31)$$

$$V = \frac{\partial H}{\partial p} \Rightarrow \delta V = \frac{\partial^2 H}{\partial p^2} \delta p + \frac{\partial^2 H}{\partial S \partial p} \delta S, \quad (32)$$

the substitution into (30) yields

$$\begin{aligned} \frac{\partial^2 H}{\partial S^2} (\delta S)^2 + 2\frac{\partial^2 H}{\partial S \partial p} \delta S \delta p + \frac{\partial^2 H}{\partial p^2} (\delta p)^2 = \\ \frac{\partial^2 U}{\partial S^2} (\delta S)^2 - \frac{\partial^2 U}{\partial V^2} (\delta V)^2, \end{aligned} \quad (33)$$

$$\begin{aligned} \frac{\partial^2 U}{\partial S^2} (\delta S)^2 + 2\frac{\partial^2 U}{\partial S \partial V} \delta S \delta V + \frac{\partial^2 U}{\partial V^2} (\delta V)^2 = \\ \frac{\partial^2 H}{\partial S^2} (\delta S)^2 - \frac{\partial^2 H}{\partial p^2} (\delta p)^2. \end{aligned} \quad (34)$$

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

$$\frac{\partial^2 H}{\partial p^2} (\delta p)^2 = -\frac{\partial^2 U}{\partial V^2} (\delta V)^2.$$

Thus, at the state where U is a convex function of volume, H is a concave function of pressure, *i.e.*,

$$\frac{\partial^2 U}{\partial V^2} > 0 \Rightarrow \frac{\partial^2 H}{\partial p^2} < 0. \quad (35)$$

4.2 Relationships among the second-order variations of H and F

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

$$H(S, p) = F(T, V) + TS + pV. \quad (36)$$

Consider a small variation of state $(\delta T, \delta V)$, with the corresponding variations of the conjugate variables $(\delta S, \delta p)$. Then,

$$\begin{aligned} H(S + \delta S, p + \delta p) &= F(T + \delta T, V + \delta V) + (T + \delta T)(S + \delta S) \\ &+ (p + \delta p)(V + \delta V). \end{aligned} \quad (37)$$

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

$$\begin{aligned} \delta H &= \delta F + T\delta S + S\delta T + p\delta V + V\delta p = T\delta S + V\delta p, \\ \delta^2 H &= \delta^2 F + 2\delta T\delta S + 2\delta p\delta V, \\ \delta^k H &= \delta^k F, \quad k \geq 3. \end{aligned} \quad (38)$$

Since

$$p = -\frac{\partial F}{\partial V} \quad \Rightarrow \quad \delta p = -\frac{\partial^2 F}{\partial V^2} \delta V - \frac{\partial^2 F}{\partial T \partial V} \delta T, \quad (39)$$

$$T = \frac{\partial H}{\partial S} \quad \Rightarrow \quad \delta T = \frac{\partial^2 H}{\partial S^2} \delta S + \frac{\partial^2 H}{\partial S \partial p} \delta p, \quad (40)$$

the substitution into (38) yields $\delta^2 H = -\delta^2 F$, *i.e.*,

$$\begin{aligned} \frac{\partial^2 H}{\partial S^2} (\delta S)^2 + 2 \frac{\partial^2 H}{\partial S \partial p} \delta S \delta p + \frac{\partial^2 H}{\partial p^2} (\delta p)^2 = \\ - \left[\frac{\partial^2 F}{\partial T^2} (\delta T)^2 + 2 \frac{\partial^2 F}{\partial T \partial V} \delta T \delta V + \frac{\partial^2 F}{\partial V^2} (\delta V)^2 \right]. \end{aligned} \quad (41)$$

Both of these are indefinite quadratic forms; at the state where F is a concave function of temperature and convex function of volume, H is a convex function of entropy and a concave function of pressure.

5 Gibbs energy

The Gibbs energy,

$$G = \int_V \rho u(s, \vartheta) dV - T \int_V \rho s dV + p \int_V \rho \vartheta dV, \quad (42)$$

of a stable equilibrium state is at minimum with respect to any virtual variations $(\delta s, \delta \vartheta)$, applied at constant pressure and temperature ($\delta p = 0$ and $\delta T = 0$). The change of G , at constant pressure and temperature, is

$$\Delta G = \int_V \rho \Delta u(s, \vartheta) dV - T \int_V \rho \delta s dV + p \int_V \rho \delta \vartheta dV. \quad (43)$$

In view of the Gibbs relation, ΔG becomes

$$\Delta G = \frac{1}{2} \int_V \rho \delta^2 u dV + \dots, \quad (44)$$

where $\delta^2 u$ is defined by (5). An obviously sufficient condition for ΔG to be positive is that $\delta^2 u > 0$.

Alternatively, the total Gibbs energy of the deformed body is

$$G = \int_V \rho [f(T, \vartheta) dV + p\vartheta] dV, \quad (45)$$

with its change, at constant pressure and temperature,

$$\Delta G = \int_V \rho [\Delta f(T, \vartheta) + p\delta\vartheta] dV. \quad (46)$$

Since, under isothermal condition,

$$\Delta f = \frac{\partial f}{\partial \vartheta} \delta\vartheta + \frac{1}{2} \frac{\partial^2 f}{\partial \vartheta^2} (\delta\vartheta)^2 + \dots, \quad (47)$$

and $p = -\partial f / \partial \vartheta$, the change of Gibbs energy in (46) becomes

$$\Delta G = \frac{1}{2} \int_V \rho \frac{\partial^2 f}{\partial \vartheta^2} (\delta\vartheta)^2 dV + \dots. \quad (48)$$

A sufficient condition for this to be positive is that the second derivative $\partial^2 f / \partial \vartheta^2$ of the elastic strain energy is positive at the considered equilibrium state.

5.1 Relationships among second-order variations of G and U

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

$$G(T, p) = U(S, V) - TS + pV. \quad (49)$$

Consider a variation of state $(\delta S, \delta V)$, in compliance with the energy equation, and denote by δT and δp the corresponding temperature and pressure variations. Then,

$$G(T + \delta T, p + \delta p) = U(S + \delta S, V + \delta V) - (T + \delta T)(S + \delta S) + (p + \delta p)(V + \delta V). \quad (50)$$

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

$$\begin{aligned} \delta G &= \delta U - T\delta S - S\delta T + p\delta V + V\delta p = -S\delta T + V\delta p, \\ \delta^2 G &= \delta^2 U - 2\delta T\delta S + 2\delta p\delta V, \\ \delta^k G &= \delta^k U, \quad k \geq 3. \end{aligned} \quad (51)$$

Since

$$V = \frac{\partial G}{\partial p} \quad \Rightarrow \quad \delta V = \frac{\partial^2 G}{\partial p \partial T} \delta T + \frac{\partial^2 G}{\partial p^2} \delta p, \quad (52)$$

$$S = -\frac{\partial G}{\partial T} \quad \Rightarrow \quad \delta S = -\frac{\partial^2 G}{\partial T^2} \delta T - \frac{\partial^2 G}{\partial T \partial p} \delta p, \quad (53)$$

the substitution into (51) yields

$$\delta^2 G = -\delta^2 U, \quad (54)$$

or, in the expanded form,

$$\begin{aligned} \frac{\partial^2 G}{\partial T^2} (\delta T)^2 + 2\frac{\partial^2 G}{\partial T \partial p} \delta T \delta p + \frac{\partial^2 G}{\partial p^2} (\delta p)^2 = \\ - \left[\frac{\partial^2 U}{\partial S^2} (\delta S)^2 + 2\frac{\partial^2 U}{\partial S \partial V} \delta S \delta V + \frac{\partial^2 U}{\partial V^2} (\delta V)^2 \right]. \end{aligned} \quad (55)$$

Thus, at the state where $\delta^2 U$ is a positive-definite quadratic form in δS and δV , $\delta^2 G$ is a negative-definite quadratic form in δT and δp . While the internal energy U is a convex function of the entropy and volume, the Gibbs energy G is a concave function of the temperature and pressure. This proof of the concavity of G with respect to p and T is appealing because it is simpler than, for example, a recent proof presented in [11]; see also [12].

5.2 Relationships among second-order variations of G and F

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

$$G(T, p) = F(T, V) + pV. \quad (56)$$

Consider an arbitrary virtual variation of state $(\delta T, \delta V)$, and denote by δp the corresponding stress variation. Then,

$$G(T + \delta T, p + \delta p) = f(T + \delta T, V + \delta V) + (p + \delta p)(V + \delta V). \quad (57)$$

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

$$\begin{aligned} \delta G &= \delta F + p\delta V + V\delta p = -S\delta T + V\delta p, \\ \delta^2 G &= \delta^2 F + 2\delta p\delta V, \\ \delta^k G &= \delta^k F, \quad k \geq 3. \end{aligned} \quad (58)$$

The substitution of (39) and (52) into (58) yields

$$\begin{aligned} \frac{\partial^2 G}{\partial T^2} (\delta T)^2 + 2\frac{\partial^2 G}{\partial T \partial p} \delta T \delta p + \frac{\partial^2 G}{\partial p^2} (\delta p)^2 = \\ \frac{\partial^2 F}{\partial T^2} (\delta T)^2 - \frac{\partial^2 F}{\partial V^2} (\delta V)^2, \end{aligned} \quad (59)$$

$$\begin{aligned} \frac{\partial^2 F}{\partial T^2} (\delta T)^2 + 2\frac{\partial^2 F}{\partial T \partial V} \delta T \delta V + \frac{\partial^2 F}{\partial V^2} (\delta V)^2 = \\ \frac{\partial^2 G}{\partial T^2} (\delta T)^2 - \frac{\partial^2 G}{\partial p^2} (\delta p)^2. \end{aligned} \quad (60)$$

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

$$\frac{\partial^2 G}{\partial p^2} (\delta p)^2 = -\frac{\partial^2 F}{\partial V^2} (\delta V)^2.$$

Thus, since at the state where F is a convex function of volume, G is a concave function of pressure, and *vice versa*, *i.e.*,

$$\frac{\partial^2 F}{\partial V^2} > 0 \quad \Leftrightarrow \quad \frac{\partial^2 G}{\partial p^2} < 0. \quad (61)$$

5.3 Relationships among second-order variations of G and H

The Gibbs energy and enthalpy are related by the Legendre transform

$$G(T, p) = H(S, p) - TS. \quad (62)$$

Consider a variation of state $(\delta T, \delta p)$, and denote by δS be the corresponding entropy variation. Then,

$$G(T + \delta T, p + \delta p) = H(S + \delta S, p + \delta p) - (T + \delta T)(S + \delta S). \quad (63)$$

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

$$\begin{aligned}\delta G &= \delta H - T\delta S - S\delta T = V\delta p - S\delta T, \\ \delta^2 G &= \delta^2 H - 2\delta T\delta S, \\ \delta^k G &= \delta^k H, \quad k \geq 3.\end{aligned}\tag{64}$$

In view of (40), and

$$S = -\frac{\partial G}{\partial T} \quad \Rightarrow \quad \delta S = -\frac{\partial^2 G}{\partial T^2} \delta T - \frac{\partial^2 G}{\partial T \partial p} \delta p,$$

the substitution into (64) yields

$$\begin{aligned}\frac{\partial^2 G}{\partial T^2} (\delta T)^2 + 2\frac{\partial^2 G}{\partial T \partial p} \delta T \delta p + \frac{\partial^2 G}{\partial p^2} (\delta p)^2 = \\ -\frac{\partial^2 H}{\partial S^2} (\delta S)^2 + \frac{\partial^2 H}{\partial p} (\delta p)^2,\end{aligned}\tag{65}$$

$$\begin{aligned}\frac{\partial^2 H}{\partial S^2} (\delta S)^2 + 2\frac{\partial^2 H}{\partial S \partial p} \delta S \delta p + \frac{\partial^2 H}{\partial p^2} (\delta p)^2 = \\ -\frac{\partial^2 G}{\partial T^2} (\delta T)^2 + \frac{\partial^2 G}{\partial p^2} (\delta p)^2.\end{aligned}\tag{66}$$

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

$$\frac{\partial^2 G}{\partial T^2} (\delta T)^2 = -\frac{\partial^2 H}{\partial S^2} (\delta S)^2.$$

Thus, at the state where G is a concave function of temperature, H is a convex function of entropy, and *vice versa*, *i.e.*,

$$\frac{\partial^2 G}{\partial T^2} < 0 \quad \Leftrightarrow \quad \frac{\partial^2 H}{\partial S^2} > 0.\tag{67}$$

5.4 Convexity of u by minimization of g

Consider a small portion (of unit mass) of the body at uniform temperature T and pressure p . The remaining part of the body may be regarded as an external medium to this small part [13]. Then, any small deviation from the equilibrium state of the considered part, caused by local virtual variations of entropy and volume $(\delta s, \delta \vartheta)$, at constant T and p , must increase the Gibbs energy $g = u(s, \vartheta) - Ts + p\vartheta$, *i.e.*,

$$\Delta g = \Delta u(s, \vartheta) - T\delta s + p\delta \vartheta > 0.\tag{68}$$

The change of the internal energy is

$$\Delta u = \frac{\partial u}{\partial s} \delta s + \frac{\partial u}{\partial \vartheta} \delta \vartheta + \frac{1}{2} \delta^2 u + \dots \quad (69)$$

Since $T = \partial u / \partial s$ and $p = -\partial u / \partial \vartheta$, the substitution of (69) into (68) gives

$$\Delta g = \frac{1}{2} \delta^2 u + \dots > 0. \quad (70)$$

This must hold for any small virtual variations δs and $\delta \vartheta$, which is assured by the requirement that the Hessian matrix of $u = u(s, \vartheta)$ is positive-definite (sufficient condition for the convexity of u in a near neighborhood of the equilibrium state).

6 Relationships among thermodynamic properties

We apply in this subsection the relationships between the second-order variations of thermodynamic potentials to deduce the classical thermodynamic connections between the specific heats at constant pressure and volume, and between the isentropic and isothermal bulk moduli and compressibilities. The Hessian matrices of the four thermodynamic potentials, with respect to their natural independent variables, are [6]

$$\begin{aligned} \begin{bmatrix} U_{SS} & U_{SV} \\ U_{VS} & U_{VV} \end{bmatrix} &= \begin{bmatrix} \frac{T}{c_V} & -\frac{l_V}{c_V} \\ -\frac{l_V}{c_V} & \frac{1}{V\beta_S} \end{bmatrix}, & \begin{bmatrix} F_{TT} & F_{TV} \\ F_{VT} & F_{VV} \end{bmatrix} &= \begin{bmatrix} -\frac{c_V}{T} & -\frac{l_V}{T} \\ \frac{l_V}{T} & \frac{1}{V\beta_T} \end{bmatrix}, \\ \begin{bmatrix} H_{SS} & H_{Sp} \\ H_{pS} & H_{pp} \end{bmatrix} &= \begin{bmatrix} \frac{T}{c_p} & -\frac{l_p}{c_p} \\ -\frac{l_p}{c_p} & -V\beta_S \end{bmatrix}, & \begin{bmatrix} G_{TT} & G_{Tp} \\ G_{pT} & G_{pp} \end{bmatrix} &= \begin{bmatrix} -\frac{c_p}{T} & -\frac{l_p}{T} \\ \frac{l_p}{T} & -V\beta_T \end{bmatrix}. \end{aligned}$$

The convexity of the internal energy $U = U(S, V)$ implies that

$$U_{SS} > 0 \quad \Rightarrow \quad c_V > 0; \quad U_{VV} > 0 \quad \Rightarrow \quad \beta_S > 0, \quad (71)$$

and

$$U_{SS}U_{VV} - U_{SV}^2 > 0 \quad \Rightarrow \quad l_V^2 < \frac{Tc_V}{V\beta_S}. \quad (72)$$

Similarly, the concavity of the Gibbs energy $G = G(T, p)$ yields

$$G_{TT} < 0 \quad \Rightarrow \quad c_p > 0; \quad G_{pp} < 0 \quad \Rightarrow \quad \beta_T > 0, \quad (73)$$

and

$$G_{TT}G_{pp} - G_{Tp}^2 > 0 \quad \Rightarrow \quad l_p^2 < VTc_p\beta_T. \quad (74)$$

Since

$$l_V = \frac{\alpha T}{\beta_T}, \quad l_p = -VT\alpha = -\beta_T V l_V, \quad (75)$$

from either (72) or (74) we also identify the upper bound on the square of the coefficient of volumetric thermal expansion, which is

$$\alpha^2 < \frac{c_p\beta_T}{VT}. \quad (76)$$

By dividing (59) with $(\delta T)^2$ at $V = \text{const.}$, we next obtain

$$G_{TT} + 2G_{Tp} \left(\frac{\partial p}{\partial T} \right)_V + G_{pp} \left(\frac{\partial p}{\partial T} \right)_V^2 = F_{TT}. \quad (77)$$

Since

$$l_V = T \left(\frac{\partial S}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V, \quad (78)$$

and in view of the expressions for F_{TT} , G_{TT} , G_{Tp} , and G_{pp} , equation (77) yields the relationship between the specific heats,

$$c_p - c_V = -\frac{l_p l_V}{T} = \frac{\alpha^2 VT}{\beta_T}. \quad (79)$$

By dividing (20) with $(\delta V)^2$ at $T = \text{const.}$, we obtain

$$U_{SS} \left(\frac{\partial S}{\partial V} \right)_T^2 + 2U_{SV} \left(\frac{\partial S}{\partial V} \right)_T + U_{VV} = F_{VV}. \quad (80)$$

In view of (78), and the expressions for U_{SS} , U_{SV} , U_{VV} , and F_{VV} , equation (80) delivers the relationship between the isentropic and isothermal bulk moduli,

$$\frac{1}{\beta_S} - \frac{1}{\beta_T} = \frac{V l_V^2}{T c_V}. \quad (81)$$

Finally, by dividing (66) with $(\delta p)^2$ at $T = \text{const.}$, we have

$$H_{SS} \left(\frac{\partial S}{\partial p} \right)_T^2 + 2H_{Sp} \left(\frac{\partial S}{\partial p} \right)_T + H_{pp} = G_{pp}. \quad (82)$$

Recalling that

$$l_p = T \left(\frac{\partial S}{\partial p} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_p, \quad (83)$$

and in view of the expressions for H_{SS} , H_{Sp} , H_{pp} , and G_{pp} , equation (82) delivers the relationship between the isentropic and isothermal compressibilities,

$$\beta_T - \beta_S = \frac{l_p^2}{VTc_p}. \quad (84)$$

Clearly, from either (81) or (84), $\beta_T > \beta_S$.

If (79) is divided by c_p , and (84) by β_T , there follows

$$1 - \frac{c_V}{c_p} = -\frac{l_p l_V}{c_p T}, \quad 1 - \frac{\beta_S}{\beta_T} = \frac{l_p^2}{VTc_p \beta_T}.$$

The right-hand side of these expressions are equal to each other, because $l_p = -\beta_T V l_V$, by (75). Thus, the well-known connection [2-6]

$$\frac{\beta_S}{\beta_T} = \frac{c_V}{c_p}. \quad (85)$$

To compare the with the classical derivation, we recall that a commonly used route to derive the relationship (81) is based on the transition $p = p[V, T(S, V)]$ and the chain-rule partial differentiation

$$\left(\frac{\partial p}{\partial V} \right)_S = \left(\frac{\partial p}{\partial V} \right)_T + \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial T}{\partial V} \right)_S. \quad (86)$$

Since

$$\left(\frac{\partial T}{\partial V} \right)_S = -\frac{\left(\frac{\partial S}{\partial V} \right)_T}{\left(\frac{\partial S}{\partial T} \right)_V} = -\frac{l_V}{c_V}, \quad (87)$$

and in view of the thermodynamic definitions of the isothermal and isentropic bulk moduli

$$\frac{1}{\beta_T} = -V \left(\frac{\partial p}{\partial V} \right)_T, \quad \frac{1}{\beta_S} = -V \left(\frac{\partial p}{\partial V} \right)_S, \quad (88)$$

and the definition of the latent heat l_V in (78), equation (86) reproduces (81).

Similarly, the relationship (79) can be derived from $S = S[V(T, p), T]$, and

$$\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p. \quad (89)$$

The multiplication of (89) by T and the use of the defining expressions for the specific and latent heats (c_p , c_V , l_p , and l_V) yields (79). Finally, the relationship (84) follows from $V = V[p, T(S, p)]$, and

$$\left(\frac{\partial V}{\partial p}\right)_S = \left(\frac{\partial V}{\partial p}\right)_T + \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_S, \quad (90)$$

because

$$\left(\frac{\partial T}{\partial p}\right)_S = -\frac{\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_p} = -\frac{l_p}{c_p}. \quad (91)$$

7 Constrained entropy maximization

In a dual analysis to that presented for internal energy in Section 2, the entropy maximization can be pursued as follows. Any spatially nonuniform virtual variations of the internal energy density and the specific volume ($\delta u, \delta \vartheta$) from a state of stable equilibrium, under the constraints of constant total internal energy U and constant total volume V , give rise to a decrease of the total entropy S . Thus,

$$\Delta S = \int_V \rho \Delta s(u, \vartheta) dV < 0, \quad S = \int_V \rho s(u, \vartheta) dV, \quad (92)$$

subjected to the constraints

$$\Delta U = \int_V \rho \delta u dV = 0, \quad \Delta V = \int_V \rho \delta \vartheta dV = 0. \quad (93)$$

The change of the specific entropy Δs , due to nonuniform variations δu and $\delta \vartheta$, is

$$\Delta s = \sum_{k=1}^{\infty} \frac{1}{k!} \delta^k s, \quad \delta^k s = \left(\delta u \frac{\partial}{\partial u} + \delta \vartheta \frac{\partial}{\partial \vartheta} \right)^k s. \quad (94)$$

The first-order variation of s is

$$\delta s = \frac{1}{T} \delta u + \frac{p}{T} \delta \vartheta, \quad (95)$$

where $T^{-1} = \partial s / \partial u$, and $p = T \partial s / \partial \vartheta$. The second-order variation of s is

$$\delta^2 s = \frac{\partial^2 s}{\partial u^2} (\delta u)^2 + 2 \frac{\partial^2 s}{\partial u \partial \vartheta} \delta u \delta \vartheta + \frac{\partial^2 s}{\partial \vartheta^2} (\delta \vartheta)^2. \quad (96)$$

In view of the constraint conditions (93), from (92) it follows that

$$\Delta S = \sum_{k=2}^{\infty} \frac{1}{k!} \int_V \rho \delta^k s \, dV = \frac{1}{2} \int_V \rho \delta^2 s \, dV + \text{higher order terms} < 0. \quad (97)$$

This must hold for any admissible virtual variations δu and $\delta \vartheta$, subjected to (93), which is assured by the requirement that $s = s(u, \vartheta)$ is a concave function of u and ϑ . A sufficient condition for this is that the Hessian matrix of s is negative-definite, $\delta^2 s < 0$. When expressed in terms of the extensive properties, this is

$$\frac{\partial^2 S}{\partial U^2} (\delta U)^2 + 2 \frac{\partial^2 S}{\partial U \partial V} \delta U \delta V + \frac{\partial^2 S}{\partial V^2} (\delta V)^2 < 0. \quad (98)$$

The well-known consequences are that the specific heats and the compressibilities are positive quantities [4-6]. Indeed, the Hessian matrix of $S = S(U, V)$ is

$$\begin{bmatrix} S_{UU} & S_{UV} \\ S_{VU} & S_{VV} \end{bmatrix} = \begin{bmatrix} -\frac{1}{c_V T^2} & \frac{l_V - p}{c_V T^2} \\ \frac{l_V - p}{c_V T^2} & -\frac{1}{VT\beta_T} - \frac{(l_V - p)^2}{c_V T^2} \end{bmatrix}.$$

Thus,

$$S_{UU} = -\frac{1}{c_V T^2} < 0 \quad \Rightarrow \quad c_V > 0,$$

$$S_{UU} S_{VV} - S_{UV}^2 = \frac{1}{c_V T^2} \frac{1}{VT\beta_T} > 0 \quad \Rightarrow \quad \beta_T > 0,$$

$$S_{VV} = -\frac{1}{VT\beta_T} - \frac{(l_V - p)^2}{c_V T^2} < 0 \quad \Rightarrow \quad c_p > \frac{pV}{T} (2\alpha T - \beta_T p).$$

8 Conclusion

An analysis of the Gibbs conditions of stable thermodynamic equilibrium based on the constrained minimization of the four fundamental thermodynamic potentials is presented, with a particular attention given to the previously unexplored connections between the second-order variations of thermodynamic potentials. These connections are used to establish the convexity or concavity properties of all thermodynamic potentials in relation to each other. The derivation is more general, yet simpler than that commonly used in the literature. The connections between the second-order variations of thermodynamic potentials are used to derive the relationships among the thermodynamic properties, *i.e.*, between the specific heats at constant pressure and volume, and between the isentropic and isothermal bulk moduli and compressibilities. The comparison with the classical derivation, based on the formal change of independent variables and the corresponding chain-rule partial differentiation, is given. Although the analysis is developed by using the pressure and volume as the conjugate variables, it can be extended to other problems with different conjugate variables, such as those that appear in the thermodynamic analysis of the effective continua models and damage evolution [14,15], or in the analysis of nonlinear thermoelastic materials under arbitrary states of stress and deformation [16,17]. In the latter case the deformation gradient and the non-symmetric nominal stress are the conjugate mechanical variables. Due to the inherent nonuniqueness of the equilibrium state in the finite strain elasticity, the Gibbs conditions of infinitesimal stability are there considered, relative to small disturbances in a near neighborhood of the equilibrium state.

Acknowledgment

Research support from the NSF Grant No. CMS-0555280 and the Montenegrin Academy of Sciences and Arts is kindly acknowledged.

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Submitted on February 2008.

Termodinamička analiza na bazi varijacija drugog reda termodinamičkih potencijala

U radu je data analiza Gibsovih uslova stabilne termodinamičke ravnoteže na bazi vezane minimizacije četiri fundamentalna termodinamička potencijala, uz poseban naglasak na ranije neispitane relacije između varijacija drugog reda termodinamičkih potencijala. Na bazi njih uspostavljena je veza između konveksnih i konkavnih svojstava svih potencijala, što na sistematski način omogućuje uspostavljanje korelacija između termodinamičkih osobina materijala, kao što su specifične toplote i izotermalni i izentropski moduli kompresibilnosti.