The Structure of Thermodynamics

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Abstract

Classical Thermodynamics has a beautiful formulation which is "rigid", simple, and elegant. It has been formulated in terms of thermodynamic potentials, in particular the internal energy, U, and the entropy, S. Both are extensive variables which scale with the mass of the system. At equilibrium, the constrained potential is a minimum in the energy representation and a maximum in the entropy representation. We discuss the properties of Thermodynamics in the energy representation in detail. In the last section we construct the transformation from the energy to the entropy representation.

To each extensive variable, E^α $(S, V, N_j, \cdots)$, there corresponds a conjugate intensive variable, $i_\alpha = \partial U / \partial E^\alpha$ $(T, -P, \mu_j, \cdots)$. The First Law of Thermodynamics expresses the change in energy as $dU = \sum_\alpha i_\alpha dE^\alpha$ $(dU = TdS + (-P)dV + \mu_j dN_j + \cdots)$. The Second Law of Thermodynamics is equivalent to the statement that the stability matrix, $U_{\alpha,\beta} = \partial^2 U / \partial E^\alpha \partial E^\beta$, is positive definite. The matrix elements of this matrix of mixed second partial derivatives can be measured because they are susceptibilities, giving the linear response of intensive thermodynamic variables to changes in the extensive thermodynamic variables: $\Delta i_\alpha = \sum_\beta U_{\alpha,\beta} \Delta E^\beta$. A large number of equalities and inequalities are obeyed by these linear response functions. Some equalities are consequences of the symmetry relations among the matrix elements $U_{\alpha,\beta} = U_{\beta,\alpha}$ (Maxwell Relations). The remainder are a consequence of the relation between the stability matrix and its inverse, $U^{\alpha,\beta}$. The inequalities are consequences of the Second Law requirement that $U_{\alpha,\beta}$ (and its inverse, $U^{\alpha,\beta}$) are positive definite.

A systematic way for constructing a change of basis transformation in the tangent plane to the equilibrium manifold is described. This leads directly to a systematic procedure for computing thermodynamic partial derivatives. They are simply expansion coefficients in a preferred basis set. The algorithm is simple and can be carried out in a finite (small) number of steps. A computer implementation of this algorithm is presented in the Appendix. A systematic procedure for constructing new potentials (Gibbs, Helmholtz, Enthalpy) from U is described. These new potentials are not positive-definite. Their metrics are block-diagonal and related to the matrix $U_{\alpha,\beta}$ in a precisely defined way.

1   Introduction

The formal structure of classical thermodynamics is simple, elegant, and beautiful. The properties of a physical system in thermodynamic equilibrium, and the fluctuations around thermodynamic equilibrium, are described by a single scalar function. This function can be regarded as a potential. The secrets of this potential can be unlocked by taking its first and second derivatives. In the most useful representations of thermodynamics, the potential is chosen as the total internal energy (U) or the total entropy (S) of the physical system.

Classical Thermodynamics was developed in the energy representation. The most important questions at that time concerned the conversion of heat into work. These questions are by now well-understood. The next set of questions to be addressed concern the effect of heat on information.
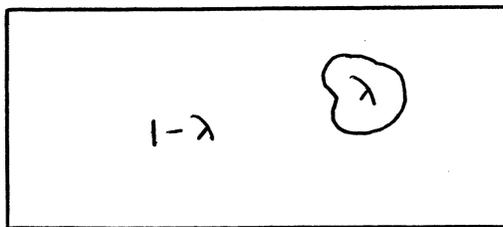
Figure 1: Extensive variables scale with the size (mass) of the subsystem. Intensive variables are scale independent.

We therefore expect the pendulum to swing from the energy to the entropy representation during the coming century. This transition is currently under way.

We will formulate classical thermodynamics in the energy representation. Modifications required for the formulation in the entropy representation are minor. They will be exhibited at the end of the chapter.

2   Internal Energy U

The internal energy, U, of a physical system is a function of the natural extensive variables required to describe the system. For a single component fluid, for example, these are S (entropy), V (volume), and N (particle number): $U = U(S, V, N)$. The function U is concave as seen from above. Concave means that the line segment joining any two points in the surface lies entirely above the surface.

The internal energy, as well as its natural variables, is extensive. This means that these variables scale with the 'size' of the system. To make this explicit, we consider a system as well as a small part of it, within the curved boundary of Fig. 3.1. Assume the mass of the entire system is M and that of the subsystem is λM. If the natural variables of the entire system are S, V, N and the internal energy is U, then the values of these extensive variables for the subsystem are $\lambda S, \lambda V, \lambda N$ and its internal energy is λU. The energy function obeys the important scaling property

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N) \tag{1}$$

In the general formulation of classical thermodynamics the internal energy U is a function of its natural extensive variables

$$U = U(E^1, E^2, \cdots) = U(E^\alpha) \tag{2}$$

This function obeys the scaling relation

$$U(\lambda E^1, \lambda E^2, \cdots) = U(\lambda E^\alpha) = \lambda U(E^\alpha) \tag{3}$$

The extensive variables are homogeneous of degree $+1$.

The First Law of Thermodynamics states that energy is conserved. It expresses the differential change in the internal energy as a sum over products of intensive variables multiplied by differentials of their conjugate intensive variables:

$$dU = \sum_\alpha i_\alpha dE^\alpha \tag{4}$$

2

The intensive variables are the derivatives of the potential with respect to the extensive variables:

$$i_\alpha = \frac{\partial U}{\partial E^\alpha} \tag{5}$$

The intensive variables are "scale independent," that it, homogeneous functions of degree 0.

Table 3.1 presents a list of commom extensive variables and their conjugate intensive variables. The physical interpretation of the intensive variables is as follows. The variable i_α is the amount of energy required to add one unit of the extensive variable E^α to the system, holding all other extensive variables constant. For example, the chemical potential is the amount of energy required to add one particle to a system, holding the entropy, volume, ... , constant. The angular velocity $\mathbf{\Omega}$ is the amount of energy required to add one unit of angular momentum $\mathbf{J}$ to the system, holding all other extensive variables constant.

We will discuss equilibrium and stability by constructing the Taylor series expansion of the potential U. First derivates are independent of scale:

$$\frac{\partial(\lambda U)}{\partial(\lambda E^\alpha)} = \frac{\partial U}{\partial E^\alpha} \tag{6}$$

Second derivatives scale like λ^{-1}:

$$\frac{\partial^2(\lambda U)}{\partial(\lambda E^\alpha)\partial(\lambda E^\beta)} = \lambda^{-1}\frac{\partial U^2}{\partial E^\alpha \partial E^\beta} \tag{7}$$

The nth derivatives scale like λ^{1-n}.

3 Taylor Series Expansion

The potential U can be expanded in the neighborhood of any point $(E_0^1, E_0^2, \cdots)$ in the usual way:

$$U(E^\alpha) = \Delta^{(0)}U + \Delta^{(1)}U + \Delta^{(2)}U + \text{h.o.t.} \tag{8}$$

$$\Delta^{(0)}U = U(E_0^\alpha)$$
$$\Delta^{(1)}U = \sum_\alpha \Delta E^\alpha \frac{\partial U}{\partial E^\alpha} \tag{9}$$
$$\Delta^{(2)}U = \frac{1}{2}\sum_{\alpha,\beta} \Delta E^\alpha \Delta E^\beta \frac{\partial^2 U}{\partial E^\alpha \partial E^\beta} \tag{10}$$

where $\Delta E^\alpha = E^\alpha - E_0^\alpha$. All derivatives are evaluated at $(E_0^1, E_0^2, \cdots)$.

4 Conservation of Extensive Quantities

We now consider two systems, 1 and 2, which are in thermodynamic equilibrium with each other. The sums of their extensive variables are conserved:

$$S_1 + S_2 = S_{Tot}$$
$$V_1 + V_2 = V_{Tot}$$

$$N_1 + N_2 = N_{Tot}$$

$$\vdots$$

$$E_1^\alpha + E_2^\alpha = E_{Tot}^\alpha \tag{11}$$

The total internal energy is the sum of the internal energies of the two systems:

$$U^{Tot}(E_{Tot}^\alpha) = U^{(1)}(E_1^\alpha) + U^{(2)}(E_2^\alpha) \tag{12}$$

Any fluctuation which increases E^α in system 1 does so at the expense of E^α in system 2, so that fluctuations are conserved:

$$\delta E_1^\alpha + \delta E_2^\alpha = 0 \tag{13}$$

We now expand the total energy around the thermodynamic equilibrium

$$U^{Tot} = U^{(1)}(E_1^\alpha + \delta E_1^\alpha) + U^{(2)}(E_2^\alpha + \delta E_2^\alpha) = \Delta^{(0)}(U^{(1)} + U^{(2)}) + \Delta^{(1)}(U^{(1)} + U^{(2)}) + \Delta^{(2)}(U^{(1)} + U^{(2)}) + \text{h.o.t.} \tag{14}$$

Using the conservation of fluctuations, $\delta E_1^\alpha = -\delta E_2^\alpha = \delta E^\alpha$, the first and second order terms can be expressed

$$\Delta^{(1)}(U^{(1)} + U^{(2)}) = \sum_\alpha \left(\frac{\partial U^{(1)}}{\partial E_1^\alpha} - \frac{\partial U^{(2)}}{\partial E_2^\alpha} \right) \delta E^\alpha \tag{15}$$

$$\Delta^{(2)}(U^{(1)} + U^{(2)}) = \frac{1}{2} \sum_{\alpha,\beta} \left(\frac{\partial^2 U^{(1)}}{\partial E_1^\alpha \partial E_1^\beta} + \frac{\partial^2 U^{(2)}}{\partial E_2^\alpha \partial E_2^\beta} \right) \delta E^\alpha \delta E^\beta \tag{16}$$

$$\tag{17}$$

5 Equilibrium

Equilibrium requires that all first derivatives vanish. At equilibrium, $\Delta^{(1)}(U^{(1)} + U^{(2)}) = 0$, so that the intensive variables of the two systems are equal:

$$i_\alpha^{(1)} = \frac{\partial U^{(1)}}{\partial E_1^\alpha} = \frac{\partial U^{(2)}}{\partial E_2^\alpha} = i_\alpha^{(2)} \tag{18}$$

In particular, when two substances are in thermodynamic equilibrium they have the same temperature, pressure, chemical potentials, angular velocity, ...

6 Stability

Stability at an equilibrium requires that all fluctuations away from equilibrium increase the value of the potential. Stability requires that the sum of the two matrices of mixed second partial derivatives, $\partial^2 U^{(1)}/\partial E_1^\alpha \partial E_1^\beta + \partial^2 U^{(2)}/\partial E_2^\alpha \partial E_2^\beta$, is positive definite. Each matrix separately must be positive definite by the following simple argument. Assume that the two systems are the subsystem of mass λM shown in Fig. 3.1 and its complement of mass $(1 - \lambda)M$. Then, by scaling, the sum of the two matrices of mixed second partial derivatives is

$$\frac{\partial^2 U^{(1)}}{\partial E_1^\alpha \partial E_1^\beta} + \frac{\partial^2 U^{(2)}}{\partial E_2^\alpha \partial E_2^\beta} \longrightarrow \left(\frac{1}{\lambda} + \frac{1}{1-\lambda} \right) \frac{\partial^2 U}{\partial E^\alpha \partial E^\beta} \tag{19}$$

This argument can be applied to any system. The positive-definiteness condition is equivalent to the condition that the function $U(E^\alpha)$ is concave as seen from above.

Remark: It is often assumed that system 1 is of interest and system 2 is a "reservoir." One way of enforcing this assumption is to allow $M \to \infty$, $\lambda \to 0$, and $\lambda M \to$ finite. Then $(1 - \lambda)M \to \infty$. In this case, at thermodynamic equilibrium

- **First Derivatives**: The intensive variables of the system are equal to those of the reservoir.

- **Second Derivatives**: Fluctuations around the equilibrium are determined *entirely* by fluctuations in the system of interest.

Most discussions of thermodynamics have been carried out in the system-reservoir dichotomy. In the more interesting case of finite interacting systems, small modifications must be made at the level of the stability matrix (second derivatives).

7   Gibbs-Duhem Duality

Homogeneous functions of degree n are well-studied and have magical properties. Euler's Theorem states that, for a homogeneous function of degree n, defined by $f(\lambda x_1, \lambda x_2, \cdots) = \lambda^n f(x_1, x_2, \cdots)$,

$$\sum_{i=1} x_i \frac{\partial}{\partial x_i} f(x) = n f(x) \tag{20}$$

This theorem can be applied to the thermodynamic potential U, which is homogeneous of degree $+1$:

$$\sum_\alpha E^\alpha \frac{\partial}{\partial E^\alpha} U(E) = \sum_\alpha E^\alpha i_\alpha = U \tag{21}$$

This form for the potential function emphasizes the duality between the intensive and extensive variables. For many purposes they should be treated on an equal footing.

In particular, the differential of U can be constructed treating the extensive variables E^α and conjugate intensive variables i_α as independent:

$$dU = \sum_\alpha i_\alpha dE^\alpha + \sum_\alpha E^\alpha di_\alpha \tag{22}$$

The First Law of Thermodynamics (4) can be used to simplify this equation. The result is that

$$\sum_\alpha E^\alpha di_\alpha = 0 \tag{23}$$

This is known as the Gibbs-Duhem relation. For a simple single component fluid it is

$$SdT + Vd(-P) + Nd\mu = 0 \tag{24}$$

This means that there is some functional relation among the intensive variables $T, -P, \mu$: $f(T, P, \mu) = 0$, where $S = \partial f/\partial T$, $V = -\partial f/\partial P$, and $N = \partial f/\partial \mu$.

Remark: It is suggestive to write the First Law of Thermodynamics and the Gibbs-Duhem relation in the following forms

$$\sum_\alpha i_\alpha dE^\alpha = dU \qquad \sum_\alpha E^\alpha di_\alpha = 0 \tag{25}$$

In this form the duality between the two laws become apparent. Further, these two relations have the same structure as Maxwell's equations $\partial_\mu F^{\mu\nu} = \frac{4\pi}{c} j^\nu$, $\partial^\mu F_{\mu\nu} = 0$: One equation has a source term, the dual equation has none. This observation raises an obvious question.

8 Linear Response Coefficients

Intensive thermodynamic variables have a natural interpretation as derivatives of the thermodynamic potential U by the conjugate extensive thermodynamic variables: $i_\alpha = \partial U/\partial E^\alpha$. As a next step in understanding thermodynamics, we seek the physical interpretation of the stability coefficients: $U_{\alpha,\beta} = \partial^2 U/\partial E^\alpha \partial E^\beta$. These are the matrix elements of the thermodynamic stability matrix. Normally, to determine curvature coefficients (k in $\frac{p^2}{2m} + \frac{1}{2}kx^2$) we would perturb the system and monitor the dynamics of its return to equilibrium. However, in Thermodynamics there is no Dynamics, so we must resort to alternative methods.

We will determine the stability coefficients $U_{\alpha,\beta}$ as linear response coefficients. The idea is as follows. At an equilibrium E_0^α, the conjugate thermodynamic variables $i_\alpha(E_0)$ have well-defined values. If we move to a nearby equilibrium with extensive coordinates $E^\alpha = E_0^\alpha + \Delta E^\alpha$, the intensive parameters will change as well, to

$$
\begin{aligned}
i_\alpha(E_0 + \Delta E) &= \frac{\partial U}{\partial E^\alpha}(E_0 + \Delta E) = \frac{\partial U}{\partial E^\alpha}(E_0) + \sum_\beta \frac{\partial^2 U(E_0)}{\partial E^\alpha \partial E^\beta} \Delta E^\beta \\
i_\alpha(E_0) + \Delta i_\alpha &= i_\alpha(E_0) + \sum_\beta U_{\alpha,\beta} \Delta E^\beta \\
\Delta i_\alpha &= \sum_\beta U_{\alpha,\beta} \Delta E^\beta
\end{aligned}
\tag{26}
$$

As a result, the matrix elements $U_{\alpha,\beta}$ have two important interpretations:

1. They are linear response coefficients relating changes in intensive thermodynamic variables produced by changes in the extensive variables under equilibrium conditions:

$$
\frac{\partial i_\alpha}{\partial E^\beta} = U_{\alpha,\beta} = U_{\beta,\alpha} = \frac{\partial i_\beta}{\partial E^\alpha}
\tag{27}
$$

   (Maxwell Relations).

2. They are stability coefficients in the positive-definite matrix of mixed second partial derivatives $U_{\alpha,\beta} = \partial^2 U/\partial E^\alpha \partial E^\beta$ which guarantees the stability of thermodynamic systems at their equilibria.

We can measure these linear response coefficients. Therefore we can measure the matrix elements of the thermodynamic stability matrix.

Example: For the simple single component fluid with fixed number of particles, $U = U(S, V)$, $T = \partial U/\partial S$ and $-P = \partial U/\partial V$. The second derivatives can be expressed in terms of four pairs of linear response functions:

Susceptibility	Definition	Constraint
Specific Heat	$C = T\left(\dfrac{\partial S}{\partial T}\right)_X$	$X = (V, P)$
Thermal Expansion Coefficient	$\alpha = \dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_X$	$X = (S, P)$
Compressibility	$\beta = -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial P}\right)_X$	$X = (S, T)$
Heat of Pressure Variation	$\Gamma = T\left(\dfrac{\partial S}{\partial P}\right)_X$	$X = (V, T)$

The linear relationship is specifically

$$
\left[\begin{array}{c} dT \\ -dP \end{array} \right] = \left[\begin{array}{cc} \dfrac{T}{C_V} & \dfrac{1}{V\alpha_S} \\ -\dfrac{T}{\Gamma_V} & \dfrac{1}{V\beta_S} \end{array} \right] \left[\begin{array}{c} dS \\ dV \end{array} \right] \tag{28}
$$

These relations are determined as follows. By holding V constant, we find $-dP = U_{V,S}dS$, so that $\frac{1}{U_{V,S}} = -\left(\frac{\partial S}{\partial P}\right)_V = -\frac{1}{T}\Gamma_V$. The others are computed similarly.

The four matrix elements use only four of the eight susceptibilities: those four in which an extensive variable is held constant. The remaining four can be conveniently placed into a matrix describing changes in extensive variables due to changes in intensive variables:

$$
\left[\begin{array}{c} dS \\ dV \end{array} \right] = \left[\begin{array}{cc} \dfrac{C_P}{T} & -\dfrac{\Gamma_T}{T} \\ V\alpha_P & V\beta_T \end{array} \right] \left[\begin{array}{c} dT \\ -dP \end{array} \right] \tag{29}
$$

These two matrices have a certain symmetry:

$$
\begin{aligned}
U_{\alpha,\beta} &\rightarrow \left(\frac{\partial i_\alpha}{\partial E^\beta}\right)_E &=& \quad 1/(\text{Susceptibility})_E \\
U^{\beta,\alpha} &\rightarrow \left(\frac{\partial E^\beta}{\partial i_\alpha}\right)_i &=& \quad (\text{Susceptibility})_i
\end{aligned}
$$

For example, $U_{S,V} = \partial(\partial U/\partial S)/\partial V = (\partial T/\partial V)_S = 1/V\alpha_S$ while $U^{V,S} = (\partial V/\partial T)_i = V\alpha_P$. Corresponding symmetry-related off-diagonal matrix elements of the inverse and direct matrices $U^{\alpha,\beta}$ and $U_{\beta,\alpha}$ involve a susceptibility measured at constant i and its inverse measured at constant E. This applies also to the diagonal matrix elements.

9 Inner Products

For many purposes it is useful to use the matrix $U_{\alpha,\beta}$ to define an inner product on the space of displacements $(\Delta E^\alpha, \Delta i_\beta, \cdots)$ near an equilibrium. This space is actually the tangent space to the surface $U = U(E^\alpha)$ at equilibrium. This can be done since $U_{\alpha,\beta}$ is positive-definite (and therefore invertible). The inverse matrix $U^{\alpha,\beta}$ relates changes in extensive variables to changes in intensive variables:

$$
\begin{aligned}
\Delta i_\alpha &= \sum_\beta U_{\alpha,\beta}\Delta E^\beta \\
\Delta E^\beta &= \sum_\alpha U^{\beta,\alpha}\Delta i_\alpha
\end{aligned} \tag{30}
$$

The two matrices are defined by

$$
U_{\alpha,\beta} = \left(\frac{\partial i_\alpha}{\partial E^\beta}\right)_E \qquad U^{\beta,\alpha} = \left(\frac{\partial E^\beta}{\partial i_\alpha}\right)_i \tag{31}
$$

The inner product is defined by any one of the three equivalent relations

$$
\begin{aligned}
(\Delta E^\alpha, \Delta E^\beta) &= U^{\alpha,\beta} \\
(\Delta E^\alpha, \Delta i_\beta) &= \delta^\alpha{}_\beta \\
(\Delta i_\alpha, \Delta i_\beta) &= U_{\alpha,\beta}
\end{aligned} \tag{32}
$$

The Schwartz inequality $(u, u)(v, v) \geq (u, v)^2$ can then be applied to vector displacements. Using $u = \Delta E^\alpha$ and $v = \Delta i_\beta$ we find

$$U^{\alpha,\alpha} U_{\beta,\beta} \geq \delta^\alpha{}_\beta \tag{33}$$

10 Equalities and Inequalities

With the structure so far developed, it is possible to exhibit a number of thermodynamic equalities and inequalities. There are four types.

10.1 Maxwell Relations

The stability coefficients are symmetric: $U_{\alpha,\beta} = U_{\beta,\alpha}$. Therefore, there must be symmetry relations among the linear response functions. These are called Maxwell Relations. Both the original matrix $U_{\alpha,\beta}$ and its inverse $U^{\beta,\alpha}$ generate Maxwell Relations. For the simple single component fluid, these two relations are

$$
\begin{aligned}
\frac{-\Gamma_V}{T} &= V\alpha_S &\text{From} \quad U_{S,V} = U_{V,S} \\
\frac{-\Gamma_T}{T} &= V\alpha_P &\text{From} \quad U^{S,V} = U^{V,S}
\end{aligned}
\tag{34}
$$

10.2 Additional Thermodynamic Equalities

There are additional equalities. This can be seen in the case of the simple single component fluid: there are three independent elements of the stability matrix but eight linear response coefficients. The Maxwell Relations reduce this number by two. There must therefore be three additional equalities among these eight susceptibilities.

The additional set of equalities is forced by the relation between the original matrix and its inverse: $\sum_\beta U_{\alpha,\beta} U^{\beta,\gamma} = \delta_\alpha{}^\gamma$. For the simple single component fluid these relations assume the form

$$
\begin{bmatrix} \dfrac{T}{C_V} & \dfrac{1}{V\alpha_S} \\ -\dfrac{T}{\Gamma_V} & \dfrac{1}{V\beta_S} \end{bmatrix}
\begin{bmatrix} \dfrac{C_P}{T} & -\dfrac{\Gamma_T}{T} \\ V\alpha_P & V\beta_T \end{bmatrix}
=
\begin{bmatrix} \dfrac{C_P}{C_V} + \dfrac{\alpha_P}{\alpha_S} & \dfrac{\beta_T}{\alpha_S} - \dfrac{\Gamma_T}{C_V} \\ \dfrac{\alpha_P}{\beta_S} - \dfrac{C_P}{\Gamma_V} & \dfrac{\beta_T}{\beta_S} + \dfrac{\Gamma_T}{\Gamma_V} \end{bmatrix}
=
\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}
\tag{35}
$$

Alternatively, either of the matrices can be inverted and equated to the other. This results in the following equivalent set of equalities

$$
\begin{aligned}
C_P - C_V &= -\frac{\alpha_P \Gamma_T}{\beta_T} \\
\beta_T - \beta_S &= -\frac{\alpha_P \Gamma_T}{C_P} \\
\alpha_P - \alpha_S &= -\frac{C_P \beta_T}{\Gamma_T} \\
\Gamma_T - \Gamma_V &= -\frac{C_P \beta_T}{\alpha_P}
\end{aligned}
\tag{36}
$$

10.3 Thermodynamic Inequalities Describing Stability

None of the equalities above depend in any way on the positive-definiteness of the matrices $U_{\alpha,\beta}$ or $U^{\beta,\alpha}$. In fact, positive-definiteness produces thermodynamic *inequalities*. These inequalities are in fact stability conditions. One basic set of inequalities is a direct consequence of the Schwartz inequality (33). For the simple single component fluid the "diagonal" inequalities are

$$
\begin{aligned}
\frac{C_P}{C_V} &\geq 1 \qquad \text{From} \quad U^{S,S}U_{S,S} \geq 1 \\
\frac{\beta_T}{\beta_S} &\geq 1 \qquad \text{From} \quad U^{V,V}U_{V,V} \geq 1
\end{aligned}
\tag{37}
$$

The "off-diagonal" inequalities come from correlations among off-diagonal matrix elements in the direct and inverse matrices: $U_{\alpha,\beta}U^{\beta,\alpha} \geq 0$ (no sum, and $\alpha \neq \beta$). For the example above, these are

$$
\begin{aligned}
\frac{\Gamma_T}{\Gamma_V} &\geq 0 \qquad \text{From} \quad U^{S,V}U_{V,S} \geq 0 \\
\frac{\alpha_P}{\alpha_S} &\geq 0 \qquad \text{From} \quad U^{V,S}U_{S,V} \geq 0
\end{aligned}
\tag{38}
$$

For $n > 2$ independent variables, there are more off-diagonal inequalities than diagonal inequalities.

10.4 Additional Inequalities

There are additional inequalities determined by the requirement that the inner product of any nonzereo displacement with itself must be positive. One simple way to address these "nondiagonal inequalities" is to renormalize the stability matrix by multiplying each row and column by the inverse of the square root of the diagonal matrix element in that row/column. This produces the substitution

$$
U_{\alpha,\beta} \rightarrow \frac{U_{\alpha,\beta}}{\sqrt{U_{\alpha,\alpha}U_{\beta,\beta}}}
$$

The resulting matrix will have entries $+1$ along the diagonal and nonzero values elsewhere. For example, for the simple single component fluid with non-fixed number of particles this produces the result

$$
\begin{bmatrix} U_{S,S} & U_{S,V} & U_{S,N} \\ U_{V,S} & U_{V,V} & U_{V,N} \\ U_{N,S} & U_{N,V} & U_{N,N} \end{bmatrix} = \begin{bmatrix} U_{S,S} & 0 & 0 \\ 0 & U_{V,V} & 0 \\ 0 & 0 & U_{N,N} \end{bmatrix}^{1/2} \begin{bmatrix} 1 & x & y \\ x & 1 & z \\ y & z & 1 \end{bmatrix} \begin{bmatrix} U_{S,S} & 0 & 0 \\ 0 & U_{V,V} & 0 \\ 0 & 0 & U_{N,N} \end{bmatrix}^{1/2}
\tag{39}
$$

The parameters x, y, z (*i.e.*, $x = U_{S,V}/\sqrt{U_{S,S}U_{V,V}}$) then obey relations required to guarantee that the canonical matrix with $+1$ on the diagonal is positive-definite. These relations have not yet been written down even for 3×3 matrices. In the 2×2 case the result is $-1 < x < +1$, which translates to

$$
\begin{aligned}
-1 &< \frac{1/V\alpha_S}{\sqrt{(T/C_V)(1/V\beta_S)}} < +1 \qquad \text{From} \quad U_{\alpha,\beta} \\
-1 &< \frac{V\alpha_P}{\sqrt{(C_P/T)(V\beta_T)}} < +1 \qquad \text{From} \quad U^{\alpha,\beta}
\end{aligned}
\tag{40}
$$

11 Change of Variables

If the thermodynamic potential U is a function of n independent variables, their displacements ΔE^α span the tangent plane to the potential surface at an equilibrium. The displacements Δi_α constitute another set of n vectors in this plane. Additional vectors can be introduced into this linear vector space, such as $\Delta U = T\Delta S - P\Delta V$, and additional thermodynamic potentials to be introduced below (*e.g.*, $\Delta G = -S\Delta T + V\Delta P$). Of this ensemble, only n can be linearly independent and chosen as a basis set of vector displacements for this plane. One often chooses all extensive variables or all intensive variables. However, other choices are often motivated by experimental conditions.

There is a systematic procedure for choosing a convenient set of independent variables and expressing all others in terms of this basis set. The coefficients in these expansions are thermodynamic partial derivatives with respect to the new basis set.

The procedure for changing the basis set is represented in the equation

$$
\left[
\begin{array}{c|c|c}
U_{\alpha,\beta} & -I_n & 0 \\
\hline
k \times n & k \times n & k \times k
\end{array}
\right]
\left[
\begin{array}{c}
dE^1 \\
\vdots \\
dE^n \\
\hline
di_1 \\
\vdots \\
di_n \\
\hline
dU \\
\vdots \\
dG
\end{array}
\right] = 0
\tag{41}
$$

The first n equations are simply $di_\alpha = \sum_\beta U_{\alpha,\beta} dE^\beta$. The remaining k equations describe any k additional potentials, displacements, dualities, or constraints that are useful. The $2n + k$ displacements in the column vector are partitioned into n independent displacements, which constitute the coordinate system of choice, and the remaining $n + k$ dependent displacements:

$$
\left[(n+k) \times (n+k) \right]
\left[
\begin{array}{c}
(n+k) \times 1 \\
\text{Dep.}
\end{array}
\right]
+
\left[(n+k) \times n \right]
\left[
\begin{array}{c}
n \times 1 \\
\text{Indep.}
\end{array}
\right] = 0
\tag{42}
$$

As long as the square matrix is nonsingular, simple matrix operations can then be used to expand each of the dependent displacements in terms of the choice of independent displacements:

$$
\left[
\begin{array}{c}
(n+k) \times 1 \\
\text{Dep.}
\end{array}
\right]
=
\left[(n+k) \times (n+k) \right]^{-1}
\left[(n+k) \times n \right]
\left[
\begin{array}{c}
n \times 1 \\
\text{Indep.}
\end{array}
\right]
\tag{43}
$$

12 Thermodynamic Partial Derivatives

The darkest hour in any thermodynamics course always occurs when it comes time to compute thermodynamic partial derivatives. The simple algorithm presented above can be used to compute any thermodynamic partial derivative systematically in a finite number of steps.

It is possible to implement this algorithm on a computer. Appendix A contains a brief and complete description of a computer implementation of this algorithm.

13 Covariance and Contravariance

The original extensive displacements ΔE^α can be expressed in terms of the new basis set ΔB^γ: $\Delta E^\alpha = \sum_\gamma M^\alpha{}_\gamma \Delta B^\gamma$. In this new coordinate system the stability matrix is

$$
\sum_{\alpha,\beta} U_{\alpha,\beta} \Delta E^\alpha \Delta E^\beta \quad \rightarrow \quad \sum_{\alpha,\beta} \sum_{\delta,\gamma} U_{\alpha,\beta} M^\alpha{}_\gamma M^\beta{}_\delta \Delta B^\gamma \Delta B^\delta
$$
$$
U' \;=\; M^t U M \tag{44}
$$

The transformed matrix U' is positive definite whenever U is. This is a consequence of Sylvester's Theorem, which states that the index of a symmetric matrix S (number of positive eigenvalues $-$ number of negative eigenvalues) is unchanged under a transformation of the type $M^t S M$, where M is nonsingular.

The duality between the intensive variables i_α and the extensive variables E^α carries over to a duality between the new variables B^γ and their conjugate variables f_γ. The duality is determined by the usual methods

$$
f_\gamma = \frac{\partial U}{\partial B^\gamma} = \sum_\alpha \frac{\partial U}{\partial E^\alpha} \frac{\partial E^\alpha}{\partial B^\gamma} = \sum_\alpha i_\alpha M^\alpha{}_\gamma \tag{45}
$$

The First Law of Thermodynamics and the Gibbs-Duhem duality are invariant under the change of basis:

$$
\sum_\gamma f_\gamma dB^\gamma = dU \qquad\qquad \sum_\gamma B^\gamma df_\gamma = 0 \tag{46}
$$

14 Useful Change of Basis

One particularly useful change of basis involves replacing one or more extensive variables by the corresponding conjugate intensive variables. We will compute the change of basis matrix and the matrix $U_{*,*}$ for this new coordinate system.

We represent the first k extensive displacements by ΔX and the remaining $n - k$ extensive displacements by ΔY. The corresponding conjugate intensities are represented by Δp and Δq. The linear response matrix relating these displacements is partitioned into blocks

$$
\begin{bmatrix} \Delta p \\ \Delta q \end{bmatrix} = \begin{bmatrix} A & B \\ B^t & C \end{bmatrix} \begin{bmatrix} \Delta X \\ \Delta Y \end{bmatrix} \tag{47}
$$

The new coordinate system consists of displacements $[\Delta p, \Delta Y]^t$. It is a simple matter to show that the change of basis matrix M is

$$
\begin{bmatrix} \Delta X \\ \Delta Y \end{bmatrix} = \begin{bmatrix} A^{-1} & -A^{-1}B \\ 0 & I_{n-k} \end{bmatrix} \begin{bmatrix} \Delta p \\ \Delta Y \end{bmatrix} \tag{48}
$$

The metric in the new coordinate system is computed from $U' = M^t U M$:

$$
\Delta^{(2)} U = \frac{1}{2} \begin{bmatrix} \Delta X & \Delta q \end{bmatrix} \begin{bmatrix} \Delta p \\ \Delta Y \end{bmatrix} = \frac{1}{2} \begin{bmatrix} \Delta p & \Delta Y \end{bmatrix} \begin{bmatrix} A^{-1} & 0 \\ 0 & c^{-1} \end{bmatrix} \begin{bmatrix} \Delta p \\ \Delta Y \end{bmatrix} \tag{49}
$$

Here c is the $(n-k) \times (n-k)$ submatrix of U^{-1}:

$$
\begin{bmatrix} A & B \\ B^t & C \end{bmatrix}^{-1} = \begin{bmatrix} a & b \\ b^t & c \end{bmatrix}
\tag{50}
$$

The attractive feature of such coordinate systems is the zero off-diagonal blocks in the metric matrix.
For the simple single component fluid the four metrics of interest are

$$
\begin{bmatrix} \Delta S & \Delta V \end{bmatrix} \begin{bmatrix} \frac{T}{C_V} & \frac{1}{V\alpha_S} \\ \frac{T}{\Gamma_V} & \frac{1}{V\beta_S} \end{bmatrix} \begin{bmatrix} \Delta S \\ \Delta V \end{bmatrix} \qquad \begin{bmatrix} \Delta T & \Delta V \end{bmatrix} \begin{bmatrix} \frac{C_V}{T} & 0 \\ 0 & \frac{1}{V\beta_T} \end{bmatrix} \begin{bmatrix} \Delta T \\ \Delta V \end{bmatrix}
\tag{51}
$$

$$
\begin{bmatrix} -\Delta P & \Delta S \end{bmatrix} \begin{bmatrix} V\beta_S & 0 \\ 0 & \frac{T}{C_P} \end{bmatrix} \begin{bmatrix} -\Delta P \\ \Delta S \end{bmatrix} \qquad \begin{bmatrix} \Delta T & -\Delta P \end{bmatrix} \begin{bmatrix} \frac{C_P}{T} & \frac{-\Gamma_T}{T} \\ V\alpha_P & V\beta_T \end{bmatrix} \begin{bmatrix} \Delta T \\ -\Delta P \end{bmatrix}
\tag{52}
$$

15   Legendre Transformations

For some purposes it is even more useful to construct a new potential function than simply to choose a new basis. The Gibbs', Helmholtz, and Free Energy potentials are examples of such useful efforts.

The procedure is as follows. We subtract $\sum_{\alpha=1}^{k} i_\alpha E^\alpha$ from the internal energy U to create a new potential K:

$$
K = U - \sum_{\alpha=1}^{k} i_\alpha E^\alpha
\tag{53}
$$

Its differential is

$$
\begin{aligned}
dK &= dU - \sum_{\alpha=1}^{k} i_\alpha dE^\alpha - \sum_{\alpha=1}^{k} E^\alpha di_\alpha \\
&= -\sum_{\alpha=1}^{k} E^\alpha di_\alpha + \sum_{\alpha=k+1}^{n} i_\alpha dE^\alpha
\end{aligned}
\tag{54}
$$

The function K is homogeneous of degree $+1$. There is therefore a Gibbs-Duhem duality:

$$
-\sum_{\alpha=1}^{k} E^\alpha di_\alpha + \sum_{\alpha=k+1}^{n} i_\alpha dE^\alpha = dK \qquad -\sum_{\alpha=1}^{k} i_\alpha dE^\alpha + \sum_{\alpha=k+1}^{n} E^\alpha di_\alpha = 0
\tag{55}
$$

The four standard potentials are summarized below:

Name	Potential	Differential	Duality
U	Internal Energy	$dU = TdS - PdV$	$SdT - VdP = 0$
$F = U - TS$	Helmholtz Free Energy	$dF = -SdT - PdV$	$-TdS - VdP = 0$
$H = U + PV$	Enthalpy	$dH = TdS + VdP$	$SdT + PdV = 0$
$G = U - TS + PV$	Gibbs Free Energy	$dG = -SdT + VdP$	$-TdS + PdV = 0$

The second variation of K can be computed easily

$$
\Delta^{(2)}K = \frac{1}{2}\left(-\sum_{\alpha=1}^{k} \Delta E^\alpha \Delta i_\alpha + \sum_{\alpha=k+1}^{n} \Delta i_\alpha \Delta E^\alpha \right)
\tag{56}
$$

This differs in sign from the corresponding expression in (49) in the first k places. The metric matrix for $\Delta^{(2)}K$ is then easily obtained from (49): identify Δi_α ($\alpha = 1 \cdots k$) with Δp and ΔE^α ($\alpha = k+1 \cdots n$) with ΔY

$$\Delta^{(2)}K = \frac{1}{2} \begin{bmatrix} \Delta p & \Delta Y \end{bmatrix} \left[\begin{array}{c|c} -A^{-1} & 0 \\ \hline 0 & c^{-1} \end{array} \right] \begin{bmatrix} \Delta p \\ \Delta Y \end{bmatrix} \tag{57}$$

This matrix is

- Negative definite in the subspace spanned by its natural intensive variables.

- Positive definite in the subspace spanned by its natural extensive variables.

It is in general indefinite ($k \neq 0, n$).

The second variations of the Helmholtz potential $F = U - TS$ and the enthalpy $H = U + PV$ are

$$\Delta^{(2)}F = \frac{1}{2} \begin{bmatrix} \Delta T & \Delta V \end{bmatrix} \begin{bmatrix} \frac{-C_P}{T} & 0 \\ 0 & \frac{T}{V\beta_T} \end{bmatrix} \begin{bmatrix} \Delta T \\ \Delta V \end{bmatrix} \qquad \Delta^{(2)}H = \frac{1}{2} \begin{bmatrix} -\Delta P & \Delta S \end{bmatrix} \begin{bmatrix} -V\beta_S & 0 \\ 0 & \frac{T}{C_P} \end{bmatrix} \begin{bmatrix} -\Delta P \\ \Delta S \end{bmatrix}$$
$$\tag{58}$$

We discuss the Gibbs Potential in the case that two chemical species are present and $U = U(S, V, N_1, N_2)$. Then $G = U - TS - (-P)V$. The metric is defined by

$$\Delta^{(2)}G = \frac{1}{2} \begin{bmatrix} \Delta T & -\Delta P & \Delta N_1 & \Delta N_2 \end{bmatrix} \begin{bmatrix} -A^{-1} & 0 \\ 0 & c^{-1} \end{bmatrix} \begin{bmatrix} \Delta T \\ -\Delta P \\ \Delta N_1 \\ \Delta N_2 \end{bmatrix} \tag{59}$$

The 2×2 submatrices A and c are

$$A = \begin{bmatrix} \frac{T}{C_{V,N_1,N_2}} & \frac{1}{V\alpha_{S,N_1,N_2}} \\ \frac{-T}{\Gamma_{V,N_1,N_2}} & \frac{1}{V\beta_{S,N_1,N_2}} \end{bmatrix} \qquad c = \begin{bmatrix} \left(\frac{\partial N_1}{\partial \mu_1}\right)_{P,T,\mu_2} & \left(\frac{\partial N_1}{\partial \mu_2}\right)_{P,T,\mu_1} \\ \left(\frac{\partial N_2}{\partial \mu_1}\right)_{P,T,\mu_2} & \left(\frac{\partial N_2}{\partial \mu_2}\right)_{P,T,\mu_1} \end{bmatrix} \tag{60}$$

Both matrices (and their inverses) are positive-definite. At equilibrium, the Gibbs Potential is a minimum in the subspace defined by $\Delta T = \Delta P = 0$ and a maximum in the subspace defined by $\Delta N_1 = \Delta N_2 = 0$.

16 Entropy as the Thermodynamic Potential

Classical Thermodynamics can also be formulated in the entropy representation. This formulation is equivalent to the formulation in the energy representation. However, there are three reasons for which it might be preferable:

1. In this formulation, it is closer to questions involving the relation between thermodynamics and information.

2. The natural formulation of statistical mechanics (the big brother of thermodynamics) is in terms of numbers of states, which is more directly related to entropy (by the log function) than to energy.

3. The formulation of nonequilibrium thermodynamics is in terms of entropy production and dissipation, rather than energy production and dissipation.

The thermodynamic potential surface relating all the extensive variables can be written in the form $F(U, S, V, N_j, \cdots) = 0$ for some function F. An n-dimensional tangent plane to this surface can be constructed at an equilibrium. All such tangent planes lie on the same side of this surface. If we solve $F = 0$ for $U = U(S, V, \cdots)$ then U lies entirely below each surface, so that U is a minimum (subject to constraints) at an equilibrium, and $\Delta^{(2)}U$ is positive-definite. On the other hand, if we solve $F = 0$ for $S = S(U, V, \cdots)$ then S lies entirely above each surface, so that S is a maximum (subject to constraints) at an equilibrium, and $\Delta^{(2)}S$ is negative-definite.

The discussion in the early sections of this Chapter proceed in the entropy representation as they did for the energy representation. The entropy function depends naturally on extensive variables and their conjugate intensive variables. The potential is homogeneous of degree +1. The First Law statements in the two representations are

$$dU = TdS - PdV + \mu dN + \cdots \tag{61}$$

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN - \cdots \tag{62}$$

There is a duality, as before, between extensive and conjugate intensive variables. The pairs of conjugate variables in the entropy representation are shown in Table 3.2. The intensive variables have interpretations similar to those given earlier. For example, $1/T$ is the entropy cost to add one unit of energy to the system; P/T is the entropy cost to change the volume by one unit; $-\mathbf{\Omega} \cdot \mathbf{J}/T$ is the entropy cost to add one unit of angular momentum $\mathbf{J}$ to the system.

The Gibbs-Duhem duality in the entropy representation is

$$\frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu_j}{T}dN_j - \cdots = dS \qquad Ud\left(\frac{1}{T}\right) + Vd\left(\frac{P}{T}\right) - N_j d\left(\frac{\mu_j}{T}\right) - \cdots = 0 \tag{63}$$

The intensive variables are equal for two systems at equilibrium.

The stability condition at equilibirum is that entropy is a maximum, or $\Delta S^{(2)}$ is negative-definite. The negative-definite matrix $S_{\alpha,\beta} = \partial^2 S/\partial E^\alpha \partial E^\beta$ is closely related to the positive-definite stability matrix $U_{\alpha,\beta}$. We derive this connection now.

The two matrices $U_{\alpha,\beta}$ and $S_{\alpha,\beta}$ are linear response matrices as follows:

$$\begin{bmatrix} dT \\ -dP \\ d\mu \end{bmatrix} = \begin{bmatrix} & & \\ & U_{*,*} & \\ & & \end{bmatrix} \begin{bmatrix} dS \\ dV \\ dN \end{bmatrix} \qquad d\begin{bmatrix} 1/T \\ P/T \\ -\mu/T \end{bmatrix} = \begin{bmatrix} & & \\ & S_{*,*} & \\ & & \end{bmatrix} \begin{bmatrix} dU \\ dV \\ dN \end{bmatrix} \tag{64}$$

The differentials of the new intensive variables are

$$d\begin{bmatrix} 1/T \\ P/T \\ -\mu/T \end{bmatrix} = -\frac{1}{T}\begin{bmatrix} \frac{1}{T} & 0 & 0 \\ \frac{P}{T} & 1 & 0 \\ \frac{-\mu}{T} & 0 & 1 \end{bmatrix}\begin{bmatrix} dT \\ -dP \\ d\mu \end{bmatrix} \tag{65}$$

We have in addition

$$d\begin{bmatrix} S \\ V \\ N \end{bmatrix} = \begin{bmatrix} \frac{1}{T} & \frac{P}{T} & \frac{-\mu}{T} \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} dU \\ dV \\ dN \end{bmatrix} \tag{66}$$

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Putting these together, we find

$$
d \begin{bmatrix} 1/T \\ P/T \\ -\mu/T \end{bmatrix} = -\frac{1}{T} \begin{bmatrix} \frac{1}{T} & 0 & 0 \\ \frac{P}{T} & 1 & 0 \\ \frac{-\mu}{T} & 0 & 1 \end{bmatrix} \begin{bmatrix} & & \\ & U_{*,*} & \\ & & \end{bmatrix} \begin{bmatrix} \frac{1}{T} & \frac{P}{T} & \frac{-\mu}{T} \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} dU \\ dV \\ dN \end{bmatrix} \tag{67}
$$

In simple words, the result is that $S_{*,*} = -\frac{1}{T} M^t U_{*,*} M$, where M^t and M are the matrices given in (65) and (66). As a result the negative-definite matrix $S_{*,*}$ contains no information not already present in the positive-definite matrix $U_{*,*}$. The equalities and inequalities among the matrix elements of $S_{*,*}$ and its inverse $S^{*,*}$ are all immediate consequences of those obtained from $U_{*,*}$ and its inverse $U^{*,*}$. It is comforting to know there is a simple relationship between these two definite matrices.

The inverse $S^{*,*}$ is easily obtained by taking the inverse of $S_{*,*}$. Specifically, we find $S^{*,*} = -TM^{-1}U^{*,*}(M^t)^{-1}$. For a simple single component fluid, the covariant and contravariant entropy stability matrices are

$$
S_{\alpha,\beta} = -\frac{1}{T} \begin{bmatrix} \dfrac{1}{TC_v} & \dfrac{P}{TC_V} + \dfrac{1}{TV\alpha_S} \\[3mm] \dfrac{P}{TC_V} - \dfrac{1}{\Gamma_V} & \dfrac{P^2}{TC_V} - \dfrac{P}{\Gamma_V} + \dfrac{P}{TV\alpha_S} + \dfrac{1}{V\beta_S} \end{bmatrix} \tag{68}
$$

$$
S^{\alpha,\beta} = -T \begin{bmatrix} TC_P - PVT\alpha_P + P\Gamma_T + P^2V\beta_T & -\Gamma_T - PV\beta_T \\[3mm] TV\alpha_P - PV\beta_T & V\beta_T \end{bmatrix} \tag{69}
$$

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Table 3.1

Conjugate Variables

Energy Representation

$$dU = \sum_\alpha i_\alpha \, dE^\alpha$$

$$= T \, dS - P \, dV + \mu_j \, dN_j + F \, dX + \mathcal{T}_{\mu\nu} \, d\mathcal{S}^{\mu\nu}$$

$$+\mathbf{H} \cdot d\mathbf{M} + \mathbf{E} \cdot d\mathbf{P} + \Phi \, dQ + \mathbf{\Omega} \cdot d\mathbf{J} + \kappa \, dA$$

Intensive Variable	Symbol	Symbol	Extensive Variable
Temperature	T	S	Entropy
Pressure	$-P$	V	Volume
Chemical Potentials	μ_j	N_j	Particle Numbers
Force	F	X	Displacement
Stress Tensor	$\mathcal{T}_{\mu\nu}$	$\mathcal{S}^{\mu\nu}$	Strain Tensor
Magnetic Field	$\mathbf{H}$	$\mathbf{M}$	Magnetization
Electric Field	$\mathbf{E}$	$\mathbf{P}$	Polarization
Electric Potential	Φ	Q	Charge
Angular Velocity	$\mathbf{\Omega}$	$\mathbf{J}$	Angular Momentum
B. H. Surface Gravity	κ	A	Black Hole Surface Area

Table 3.2

Conjugate Variables

Entropy Representation

$$dS = \sum_\alpha i_\alpha \; dE^\alpha$$

$$= \frac{1}{T} \; dU + \frac{1}{T}P \; dV - \frac{1}{T}\mu_j \; dN_j - \frac{1}{T}F \; dX - \frac{1}{T}\mathcal{T}_{\mu\nu} \; d\mathcal{S}^{\mu\nu}$$

$$- \frac{1}{T}\mathbf{H}\cdot \; d\mathbf{M} - \frac{1}{T}\mathbf{E}\cdot \; d\mathbf{P} - \frac{1}{T}\Phi \; dQ - \frac{1}{T}\mathbf{\Omega}\cdot \; d\mathbf{J} - \frac{1}{T}\kappa \; dA$$

Intensive Variable	Symbol	Symbol	Extensive Variable
Temperature	$1/T$	U	Energy
Pressure	P/T	V	Volume
Chemical Potentials	$-\mu_j/T$	N_j	Particle Numbers
Force	$-F/T$	X	Displacement
Stress Tensor	$-\mathcal{T}_{\mu\nu}/T$	$\mathcal{S}^{\mu\nu}$	Strain Tensor
Magnetic Field	$-\mathbf{H}/T$	$\mathbf{M}$	Magnetization
Electric Field	$-\mathbf{E}/T$	$\mathbf{P}$	Polarization
Electric Potential	$-\Phi/T$	Q	Charge
Angular Velocity	$-\mathbf{\Omega}/T$	$\mathbf{J}$	Angular Momentum
B. H. Surface Gravity	$-\kappa/T$	A	Black Hole Surface Area

Appendix A
Simple Algorithm for Thermodynamic Partial Derivatives

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Abstract

A simple algorithm for computing arbitrary thermodynamic partial derivatives is described and a computer implementation is presented.

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Computing thermodynamic partial derivatives is the *bête noire* of a typical thermodynamics course. The purpose of the present contribution is to point out that a simple algorithm exists for computing any thermodynamic partial derivative in a fixed number of simple steps[1], and to present a short code which implements this algorithm.

The algorithm will be presented for a substance described by $n = 2$ independent extensive variables, S and V. The differentials of the extensive variables dS, dV, the differentials of the conjugate intensive variables dT, $-dP$, differentials of potentials dU, dF, dG, dH, and other differentials (*e.g.*, $d\sigma = -dP + mdT$ along coexistence curves) can be treated as vectors in a plane. In fact, they are rigorously vectors in the tangent plane to the equilibrium surface $U = U(S, V)$. Two linearly independent vectors may be chosen to span this plane. The remaining differentials (vectors) can then be solved as linear combinations of the two independent basis vectors. The desired thermodynamic partial derivative is an expansion coefficient, and can be determined by inspection. Implementation of this procedure is straightforward using methods of linear algebra[1]. We present an even simpler implementation.

We illustrate the algorithm by computing the thermodynamic partial derivative $(\partial G/\partial T)_U$. We introduce three classes of relations among the differentials:

1. Linear response relations among the extensive and intensive thermodynamic variables:

$$
\left[\begin{array}{c} dS \\ dV \end{array} \right] = \left[\begin{array}{cc} C_P/T & V\alpha_P \\ V\alpha_P & V\kappa_T \end{array} \right] \left[\begin{array}{c} dT \\ -dP \end{array} \right]
$$

2. Expressions relating thermodynamic potentials to extensive and intensive variables, such as $dU = TdS - PdV$, $dF = -SdT - PdV$.

3. Other constraints, such as displacements along coexistence curves: $d\sigma = -dP + mdT$.

The linear response constraints are introduced as eq[1] and eq[2] in Fig. 1, which presents a Maple worksheet solution to the problem. The four potentials have been introduced as eq[3] through eq[6]. The coexistence constraint has been introduced as eq[7].

An appropriate subset of equations is chosen, depending on the derivative desired. The desired derivative, $(\partial G/\partial T)_U$, involves the potentials U and G. Therefore we must deal with eq[3], and eq[5],

as well as eq[1] and eq[2], which are always used. The independent basis vectors are dT and dU. The dependent basis vectors are therefore dS, dV, dP, dG. The callup $solve(\{eq[1], eq[2], eq[3], eq[5]\}, \{dS, dV, dP, dG\})$ computes each of the four dependent vectors dS, dV, dP, dG as linear combinations of the two independent vectors dT and dU. Coefficients in this expansion include the desired thermodynamic partial derivative. The desired derivative can be determined by inspecting the output of the *solve* callup or exhibited by computing a derivative. In particular, $(\partial G/\partial T)_U = diff(dG, dT)$, as shown in Fig. 1.

In the event that additional thermodynamic partial derivatives are desired with dU and dT as independent variables, the entire matrix of thermodynamic partial derivatives can be output by replacing the last two steps in Fig. 1 by the steps shown in Fig. 2.

$>$ $eq[1] := dS = (C[P]/T) * dT - V * alpha[P] * dP :$
$>$ $eq[2] := dV = V * alpha[P] * dT - V * kappa[T] * dP :$
$>$ $eq[3] := dU = T * dS - P * dV :$
$>$ $eq[4] := dF = -S * dT - P * dV :$
$>$ $eq[5] := dG = -S * dT + V * dP :$
$>$ $eq[6] := dH = T * dS + V * dP :$
$>$ $eq[7] := dsigma = -dP + m * dT :$
$>$ $solve(\{eq[1], eq[2], eq[3], eq[5]\}, \{dS, dP, dV, dG\}) :$
$>$ $der[U] := diff(dG, dT);$

$$der_U := \frac{S\alpha_P T - SP\kappa_T - C_P + PV\alpha_P}{-\alpha_P T + P\kappa_T}$$

Figure 2: Maple worksheet for computing the thermodynamic partial derivative $(\partial G/\partial T)_U$.

References

[1] R. Gilmore, "Thermodynamic Partial Derivatives", J. Chem. Phys. **75**(12), 5964-5966 (1981).

```
>  #Input equations as in Fig. 1
>  equs :=  {eq[1], eq[2], eq[3], eq[5]} :
>  Variables :=  {dS, dT, dP, dV, dU, dG} :
>  DepVars :=  {dS, dP, dV, dG} :
>  IndepVars :=  {dT, dU} :
>  n_V := 6 : n_D := 4 : n_I := 2 :
>  for i from 1 to n_D do n[i] := DepVars[i] od :
    for j from 1 to n_I do d[j] := IndepVars[j] od :
    Symb := matrix(n_D, n_I, (i, j)− > n[i]/d[j]) :
>  s := solve(equs, DepVars) :
>  assign(s) :
>  for i from 1 to n_D do nn[i] := DepVars[i] od :
>  M2 := matrix(n_D, n_I, (i, j)− > diff(nn[i], d[j])) :
>  evalm(Symb) = evalm(M2);
```

$$
\begin{bmatrix}
\dfrac{dS}{dT} & \dfrac{dS}{dU} \\[2mm]
\dfrac{dP}{dT} & \dfrac{dP}{dU} \\[2mm]
\dfrac{dV}{dT} & \dfrac{dV}{dU} \\[2mm]
\dfrac{dG}{dT} & \dfrac{dG}{dU}
\end{bmatrix}
=
\begin{bmatrix}
-\dfrac{-C_P\,P\,\kappa_T + \alpha_P{}^2\,T\,P\,V}{\%1\,T} & -\dfrac{\alpha_P}{\%1} \\[3mm]
\dfrac{-C_P + P\,V\,\alpha_P}{V\,\%1} & \dfrac{1}{V\,\%1} \\[3mm]
-\dfrac{\alpha_P{}^2\,T\,V - C_P\,\kappa_T}{\%1} & -\dfrac{\kappa_T}{\%1} \\[3mm]
\dfrac{S\,\alpha_P\,T - S\,P\,\kappa_T - C_P + P\,V\,\alpha_P}{\%1} & \dfrac{1}{\%1}
\end{bmatrix}
$$

$$\%1 := -\alpha_P\,T + P\,\kappa_T$$

Figure 3: Maple worksheet for computing many thermodynamic partial derivatives with dT and dU as independent variables.