

1 Macroscopic Equilibrium Thermodynamics

Macroscopic thermodynamics can be formalized in a simple, compact way which makes the relations between different thermodynamic potentials particularly easy. This handout is based on the discussions in Refs. [1, 2, 3].

1.1 Axioms and Basic Definitions

Axiom 1:

There exist special states of macroscopic physical systems, called *equilibrium states*, which can be fully described by the internal energy, E , and a set of extensive parameters, X_0, X_1, \dots, X_c .

Definition: *Extensive parameter.* A system A is composed of two subsystems, A' and A'' , which are described by X_j' and X_j'' , respectively. Then this parameter is extensive iff A is described by $X_j = X_j' + X_j''$.

Examples: *Extensive parameters.*

Internal energy E (unless the subsystems are strongly interacting).

Hydrostatic system: Volume, V . Number of particles, N .

Magnetic system: Total magnetic moment, M , parallel to applied magnetic field, H .

Dielectric system: Total polarization, P , parallel to applied electric field, \mathcal{E} .

Axiom 2:

For all systems in equilibrium there exists a function of the extensive parameters, called the *entropy*, S . If there are no internal constraints on the system, the extensive parameters take those values that *maximize* S over all possible states with internal constraints.

Definition: The functional relation between S and the extensive parameters give the *fundamental equation* for the system:

$$S = S(E, X_0, X_1, \dots, X_c) \quad (1)$$

NOTE: Since the extensive parameters describe the system completely, the fundamental equation contains *all* macroscopically relevant information about the system.

Axiom 3:

(i). S is extensive.

(ii). S is continuously differentiable and is a strictly increasing function of E .

Axiom 3 immediately gives the following useful consequences.

a. S is a first-order homogeneous function of the extensive parameters:

$$S(\lambda E, \lambda X_0, \lambda X_1, \dots, \lambda X_c) = \lambda S(E, X_0, X_1, \dots, X_c) \quad (2)$$

b.

$$\left(\frac{\partial S}{\partial E} \right)_{X_j} \geq 0, \quad (3)$$

with equality restricted to a set of measure zero at most.

c. S is invertible as a function of E , so the fundamental equation can be written on the equivalent form:

$$E = E(S, X_0, X_1, \dots, X_c) \quad (4)$$

This second formulation of the fundamental equation is the one most commonly used. We shall see that it gives rise to the commonly known thermodynamic potentials. Obviously, E is also a first-order homogeneous function of its variables:

$$E(\lambda S, \lambda X_0, \lambda X_1, \dots, \lambda X_c) = \lambda E(S, X_0, X_1, \dots, X_c). \quad (5)$$

Axiom 4:

“Third Law of Thermodynamics.” Not always obeyed.

$$S \rightarrow 0 \quad \text{when} \quad \left(\frac{\partial E}{\partial S} \right)_{X_j} \rightarrow 0$$

1.2 Intensive Parameters and Equilibrium Conditions

1.2.1 Intensive Parameters

In this section we concentrate on hydrostatic c -component systems with extensive variables E, V, N_1, \dots, N_c . Corresponding results for other kinds of systems are easily obtained by substituting other extensive parameters.

Differentiate the fundamental equation in the energy representation:

$$dE = \left(\frac{\partial E}{\partial S} \right)_{V, N_j} dS + \left(\frac{\partial E}{\partial V} \right)_{S, N_j} dV + \sum_{k=1}^c \left(\frac{\partial E}{\partial N_k} \right)_{S, V, N_{j \neq k}} dN_k \quad (6)$$

and define the following *intensive parameters*:

$$\begin{aligned} \text{Temperature :} \quad & T = \left(\frac{\partial E}{\partial S} \right)_{V, N_j} \\ \text{Pressure :} \quad & P = - \left(\frac{\partial E}{\partial V} \right)_{S, N_j} \quad \text{Note the sign!} \\ \text{Chemical potential :} \quad & \mu_k = \left(\frac{\partial E}{\partial N_k} \right)_{S, V, N_{j \neq k}} \\ \text{In general :} \quad & \\ \text{“Pressure of } k \text{ - th kind” :} \quad & P_k = \left(\frac{\partial E}{\partial X_k} \right)_{X_{j \neq k}} \end{aligned} \quad (7)$$

With these definitions, the differential of E becomes:

$$dE = TdS - PdV + \sum_{k=1}^c \mu_k dN_k \quad (8)$$

The intensive parameters are functions of S, V , and N_k . These functional relationships are the *equations of state*:

$$\begin{aligned} T &= T(S, V, N_1, \dots, N_c) \\ P &= P(S, V, N_1, \dots, N_c) \\ \mu_k &= \mu_k(S, V, N_1, \dots, N_c) \end{aligned} \quad (9)$$

The term “*intensive* parameters” refer to the fact that these quantities are independent of the system size. (In other words: they are *homogeneous functions of zeroth order*.) Here we show this explicitly only for the temperature. The other proofs are entirely analogous.

$$\begin{aligned} T(S, V, N_1, \dots, N_c) &= \left(\frac{\partial E(S, V, N_1, \dots, N_c)}{\partial S} \right)_{V, N_j} = \left(\frac{\partial \lambda E(S, V, N_1, \dots, N_c)}{\partial (\lambda S)} \right)_{V, N_j} \\ &= \left(\frac{\partial E(\lambda S, \lambda V, \lambda N_1, \dots, \lambda N_c)}{\partial (\lambda S)} \right)_{V, N_j} = T(\lambda S, \lambda V, \lambda N_1, \dots, \lambda N_c) . \end{aligned}$$

1.2.2 Some useful theorems from the calculus of scalar fields.

Most of classical thermodynamics consists of simple applications of the theory of scalar fields. Here are some of the most useful relations.

Let $\psi = \psi(x_0, \dots, x_t)$ be a scalar field of $t+1$ scalar variables. Then

$$d\psi = \sum_{j=0}^t \frac{\partial \psi}{\partial x_j} dx_j .$$

If $x_j = x_j(u, v)$, where u and v are scalars, then:

$$d\psi = \sum_{j=0}^t \frac{\partial \psi}{\partial x_j} \frac{\partial x_j}{\partial u} du + \sum_{j=0}^t \frac{\partial \psi}{\partial x_j} \frac{\partial x_j}{\partial v} dv .$$

These relations are simply examples of the chain rule. They are trivially extended to any number of variables.

The contour surfaces of ψ define an implicit functional relationship between the x_j :

$$\psi = \text{constant} \Rightarrow \sum_{j=0}^t \frac{\partial \psi}{\partial x_j} dx_j = 0 .$$

If all x_j except for two (call them x and y) are held constant, then

$$\left(\frac{\partial y}{\partial x} \right)_{\psi, \dots} = - \left(\frac{\partial \psi}{\partial x} \right)_{y, \dots} / \left(\frac{\partial \psi}{\partial y} \right)_{x, \dots}$$

and

$$\left(\frac{\partial x}{\partial y} \right)_{\psi, \dots} = 1 / \left(\frac{\partial y}{\partial x} \right)_{\psi, \dots} .$$

For three variables, but valid in general, we have the cyclic rule:

$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1 .$$

1.2.3 Equilibrium Conditions

Using the above results we obtain the differential for S (again specifically for hydrostatic systems):

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \sum_{k=1}^c \frac{\mu_k}{T}dN_k \quad (10)$$

From this one obtains the equations of state in the entropy representation:

$$\begin{aligned} \frac{1}{T} &= \frac{1}{T}(E, V, N_1, \dots, N_c) \\ \frac{P}{T} &= \frac{P}{T}(E, V, N_1, \dots, N_c) \\ \frac{\mu_k}{T} &= \frac{\mu_k}{T}(E, V, N_1, \dots, N_c) \end{aligned} \quad (11)$$

Axiom 2 requires that $dS=0$ for a system in equilibrium. We can use this to derive equilibrium conditions for composite systems. For example: consider an isolated system composed of two subsystems which are separated from each other by a rigid, impenetrable, diathermal wall (i.e., the two systems can only exchange energy in the form of heat, but not particles or work). Then, $dE^{(2)} = -dE^{(1)}$ and $dV^{(2)}=dV^{(1)}=dN_k^{(2)}=dN_k^{(1)}=0$. Thus,

$$\text{Equilibrium} \Leftrightarrow \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right) dE^{(1)} = 0$$

so the system is in equilibrium with respect to energy flow without particle exchange or volume change iff $T^{(1)} = T^{(2)}$.

This reasoning can also be used to show that heat flows from regions of high T to regions of low T . Consider the previous system, but with $T^{(1)} < T^{(2)}$ and an *adiabatic* (i.e., perfectly insulating) rigid and impermeable separator. Then we remove the constraint on heat flow by making the separator diathermal. According to Axiom 2, the entropy change $\Delta S > 0$. Thus,

$$\left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right) \Delta E^{(1)} > 0 \Rightarrow \Delta E^{(1)} > 0.$$

In other words: heat flows from hot to cold.

Analogously we can show that a subsystem at high pressure will expand at the expense of one at low pressure if the wall is replaced by an impenetrable and adiabatic piston, and that particles flow from subsystems of high chemical potential to subsystems of lower chemical potential.

1.2.4 Euler's and Gibbs-Duhem's Equations

The first-order homogeneity of E has some important consequences. Differentiating Eq. (5) with respect to λ and then setting $\lambda = 1$ yields a result commonly known as Euler's equation. (It is a special case of Euler's Theorem on scalar fields.)

$$E(S, X_j) = \frac{\partial E}{\partial(\lambda S)} \frac{\partial(\lambda S)}{\partial \lambda} + \sum_{k=0}^c \frac{\partial E}{\partial(\lambda X_k)} \frac{\partial(\lambda X_k)}{\partial \lambda} \Big|_{\lambda=1}$$

$$= TS + \sum_{k=0}^c P_k X_k \quad (\text{in general}) \quad (12)$$

$$= TS - PV + \sum_{k=1}^c \mu_k N_k \quad (\text{hydrostatic system}) \quad (13)$$

In the entropy representation we get analogously

$$S = \frac{1}{T}E + \frac{P}{T}V - \sum_{k=1}^c \frac{\mu_k}{T}N_k \quad (14)$$

and similarly for general systems.

Differentiating Euler's equation in the energy representation and subtracting the differential of E [Eq. (6)] we get the Gibbs-Duhem equation:

$$SdT - VdP + \sum_{k=1}^c N_k d\mu_k = 0 \quad (15)$$

\Rightarrow For a single phase of a c -component system the number of independent variables (*the number of thermodynamic degrees of freedom*) is $f = c + 1$. If the system consists of p phases in equilibrium we get p such equations, and therefore $f = c + 2 - p$. This is the famous *Gibbs Phase Rule*.

1.3 Alternative Formulations

Axiom 2 is equivalent with the Principle of Entropy Maximization in the following formulation:

The equilibrium values of the unconstrained parameters are such that S is maximum for the given value of E .

Next we show that this is equivalent with the Principle of Energy Minimization in the following formulation:

The equilibrium values of the unconstrained parameters are such that E is minimum for the given value of S .

Our argument is from Tisza [1]:

Assume a state which is *unstable* according to the energy criterion. Then we can perturb the state at constant V and X_j such that $\Delta E < 0$ while $\Delta S = 0$. If we next put the system in contact with a heat reservoir, we can return the energy lost in the first perturbation. But since $(\partial S/\partial E)_{V, X_j} = 1/T > 0$, $\Delta S > 0$ in the second perturbation. We thus have produced a composite perturbation that gives $\Delta S > 0$ with $\Delta E = 0$, which implies that the state is *unstable* according to the entropy criterion.

Analogously, if the state is unstable according to the entropy criterion, we can construct a composite fluctuation which shows that it is unstable according to the energy criterion as well.

We have shown implication in both directions, and thus equivalence. QED.

To obtain *Thermodynamic Potentials* suitable for different experimental conditions, we use Legendre transformations, starting either from the energy or the entropy formulation of

Axiom 2. The most common ones are obtained from the energy formulation, and we limit ourselves to those here.

Definition:

Let $Y(X_0, \dots, X_k)$ be a scalar field of the extensive variables X_j and let $P_j = \left(\frac{\partial Y}{\partial X_j}\right)_{X_{i \neq j}}$ be the corresponding intensive variables in the “Y-representation.” Then

$$\Lambda = Y[P_0, \dots, P_i]_{i \leq k} = Y - \sum_{j=0}^i P_j X_j \quad (16)$$

is the Legendre transform of Y with respect to $X_{j \leq i}$.

By differentiation we find that

$$d\Lambda = - \sum_{j=0}^i X_j dP_j + \sum_{j=i+1}^k P_j dX_j, \quad (17)$$

so that $\Lambda = \Lambda(P_0, \dots, P_i, X_{i+1}, \dots, X_k)$ is a function of the variables indicated in the argument. Just like in classical mechanics, the Legendre transform is a method to choose the experimentally observed or controlled variables as the independent ones. The formulations connected by the Legendre transforms are equivalent.

The four most common thermodynamic potentials obtained from E (for hydrostatic systems) are:

Constant T (Canonical ensemble):

Helmholtz free energy.

$$A(T, V, N_k) = E[T] = E - TS = -PV + \sum_k \mu_k N_k$$

$$dA = -SdT - PdV + \sum_k \mu_k dN_k.$$

Constant P :

Enthalpy.

$$H(S, P, N_k) = E[P] = E + PV = TS + \sum_k \mu_k N_k$$

$$dH = TdS + VdP + \sum_k \mu_k dN_k.$$

Constant T and P :

Gibbs’ free energy.

$$G(T, P, N_k) = E[T, P] = E + PV - TS = \sum_k \mu_k N_k$$

$$dG = -SdT + VdP + \sum_k \mu_k dN_k.$$

Constant T and μ_k (Grand Canonical ensemble):

Grand Canonical potential.

$$\Phi(T, V, \mu_k) = E[T, \mu_k] = E - TS - \sum_k \mu_k N_k = -PV$$

$$d\Phi = -SdT - PdV - \sum_k N_k d\mu_k.$$

These thermodynamic potentials are all *minimized* at equilibrium for fixed values of their respective independent variables.

1.4 Response Functions

Thermodynamic response functions are derivatives of one thermodynamic parameter with respect to another under specific conditions on the remaining variables. Some examples

(specifically given only for hydrostatic systems) are:

Thermal expansivity:

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P, N_k} \quad (18)$$

Isothermal compressibility:

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T, N_k} \quad (19)$$

Under conditions of constant N_k the exact differential of E is

$$dE = TdS - PdV . \quad (20)$$

Since PdV (with sign depending on the convention used) is the infinitesimal mechanical work associated with the perturbation, TdS must be the energy transferred by thermal means, i.e. the infinitesimal *heat*. The corresponding response functions with respect to a change in temperature are the *Specific Heats*. There are several different such quantities, depending on which parameters are held fixed during the process.

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_{V, N_k} = \left(\frac{\partial E}{\partial T} \right)_{V, N_k} . \quad (21)$$

$$C_P = T \left(\frac{\partial S}{\partial T} \right)_{P, N_k} = \left(\frac{\partial H}{\partial T} \right)_{P, N_k} . \quad (22)$$

Through the equality of mixed second derivatives, the exact differentials of the thermodynamic potentials give rise to a large number of useful relations between response functions, called *Maxwell Relations*. For example, from Eq. (20) we get

$$\left(\frac{\partial T}{\partial V} \right)_{S, N_k} = - \left(\frac{\partial P}{\partial S} \right)_{V, N_k}$$

An elegant mnemonic device for these relations is the Thermodynamic Square. See Callen [2].

References

- [1] L. Tisza, *Generalized Thermodynamics* (MIT Press, Cambridge, 1966).
- [2] H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics* (Wiley, New York, 1985).
- [3] H. S. Robertson, *Statistical Thermophysics* (PTR Prentice-Hall, Englewood Cliffs, 1993).