15

Extremum Principles

All correct reasoning is a grand system of tautologies, but only God can make direct use of that fact.

Herbert Simon, political scientist, economist, and psychologist (1916–2001),
Nobel Prize in Economics, 1978

In Part I we defined the entropy, derived a formal expression for it in classical statistical mechanics, and established that it is a maximum in equilibrium for an isolated composite system with constant total energy, volume, and particle number. This last result is important for many reasons, including providing us with a systematic way of calculating the equilibrium values of quantities when a constraint is released.

There are several alternative principles, called extremum principles, that also allow us to calculate equilibrium properties under different thermodynamic conditions. The derivation of these principles is the main purpose of this chapter.

> In this chapter, we derive extremum principles with respect to internal variables in a composite system. For example, energy could be exchanged through a diathermal wall, and the extremum condition would tell us how much energy was in each subsystem in equilibrium.
>
> All extremum principles in this chapter are with respect to extensive variables; that is, variables that describe how much of something is in a subsystem: for a simple system, these are just the values of U_α, V_α, or N_α for subsystem α.
>
> This chapter does not contain any extremum principles with respect to the intensive variables, such as T, P, or μ.
>
> In Chapter 16 we will examine thermodynamic stability between subsystems, which will lead to conditions on second derivatives with respect to the total volume or number of particles of the subsystems.

To begin with, corresponding to the principle that the entropy is maximized when the energy is constant, there is an 'energy minimum' principle, which states that the energy is minimized when the entropy is held constant.

15.1   Energy Minimum Principle

To derive the energy minimum principle, start with the entropy maximum principle.

Consider the entropy, S, of a composite system as a function of its energy, U, and some other parameter, X, which describes the distribution of the amount of something in the composite system. For example, X could be the number of particles in a subsystem, N_A. When a hole is made in the wall between subsystems A and B, the value of $X = N_A$ at equilibrium would maximize the entropy. In other examples we have looked at, X could be the energy of a subsystem or the volume of a subsystem that might vary with the position of a piston. It could not be the temperature, pressure, or chemical potential of a subsystem, because they are not extensive; that is, they do not represent the amount of something.

In equilibrium, the entropy is at a maximum with respect to variations in X, holding U constant. This means that the first partial derivative must vanish, and the second partial derivative must be negative

$$\left(\frac{\partial S}{\partial X}\right)_U = 0 \tag{15.1}$$

$$\left(\frac{\partial^2 S}{\partial X^2}\right)_U < 0. \tag{15.2}$$

Near equilibrium, a small change in the entropy can be represented to leading order by changes in U and X

$$dS \approx \frac{1}{2}\left(\frac{\partial^2 S}{\partial X^2}\right)_U (dX)^2 + \left(\frac{\partial S}{\partial U}\right)_X dU. \tag{15.3}$$

Let us first consider the case of $T > 0$. We know that

$$\left(\frac{\partial S}{\partial U}\right)_X = \frac{1}{T} > 0, \tag{15.4}$$

so eq. (15.3) can be written as

$$dS \approx \frac{1}{2}\left(\frac{\partial^2 S}{\partial X^2}\right)_U (dX)^2 + \left(\frac{1}{T}\right) dU. \tag{15.5}$$

Now comes the subtle part.

For the analysis of the entropy maximum principle, we isolated a composite system and released an internal constraint. Since the composite system was isolated, its total

energy remained constant. The composite system went to the most probable macro-scopic state after release of the internal constraint, and the total entropy went to its maximum. Because of the increase in entropy, the process was irreversible.

Now we are considering a quasi-static process without heat exchange with the rest of the universe, so that the entropy of the composite system is constant. However, for the process to be quasi-static we cannot simply release the constraint, as this would initiate an irreversible process, and the total entropy would increase. Outside forces are required to change the constraints slowly to maintain equilibrium conditions. This means that the energy of the composite system for this process is *not* constant.

The distinction between the entropy maximum and energy minimum principles can be illustrated by considering two experiments with a thermally isolated cylinder containing a piston that separates two volumes of gas. The two experiments are illustrated in Fig. 15.1.

Entropy maximum experiment: Here the piston is simply released, as illustrated in the upper picture in 15.1. The total energy is conserved, so that entropy is maximized at constant energy.

Energy minimum experiment: Here the piston is connected by a rod to something outside the cylinder, as illustrated in the lower picture in 15.1. The piston is moved quasi-statically to a position at which the net force due to the pressure from the gas in the two
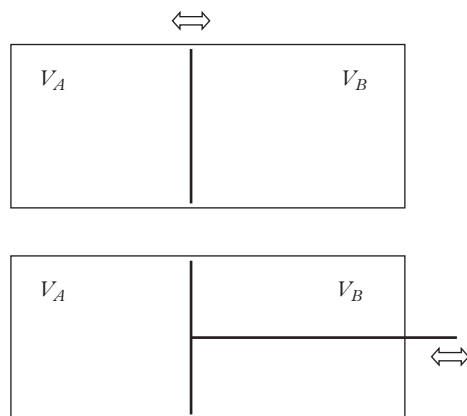

Fig. 15.1 *Piston experiments. The two diagrams each represent a cylinder that is sealed at both ends and is divided into two subvolumes by a moveable piston. Both systems are thermally isolated, and cannot exchange heat energy with the rest of the universe. When the piston in the upper cylinder is released it will move freely until it comes to an equilibrium position that maximizes the entropy. In the lower cylinder, the piston is attached to a rod that can be pushed or pulled from outside the cylinder. The piston is moved to a position at which there is no net force on the piston from the gas in the two subvolumes of the cylinder, minimizing the energy.*

subvolumes is zero. The total energy of the cylinder has been reduced. However, since the process is quasi-static and there has been no heat exchange between the cylinder and the rest of the universe, the total entropy of the system is unchanged. Energy is minimized at constant entropy.

To determine the change in energy for the process in which the piston is held and moved quasi-statically to the equilibrium position, we can turn eq. (15.5) around to find the leading behavior of dU as a function of dS and dX,

$$dU \approx -\frac{T}{2}\left(\frac{\partial^2 S}{\partial X^2}\right)_U (dX)^2 + TdS. \qquad (15.6)$$

Eq. (15.6) gives us a new way of expressing the equilibrium conditions:

$$\left(\frac{\partial U}{\partial X}\right)_S = 0, \qquad (15.7)$$

and

$$\left(\frac{\partial^2 U}{\partial X^2}\right)_S = -\frac{T}{2}\left(\frac{\partial^2 S}{\partial X^2}\right)_U > 0. \qquad (15.8)$$

Since the first partial derivative vanishes, and the second partial derivative is positive, the energy is a minimum at equilibrium for constant entropy (still assuming that the temperature is positive). This is another consequence of the Second Law of Thermodynamics. Indeed, it is equivalent to the maximization of the entropy in an isolated system as an expression of the Second Law.

A consequence of eq. (15.8) is that the maximum work that you can extract from a system in a process with fixed entropy is given by the change in energy of the system. To see this, note that maximum efficiency is always achieved by quasi-static processes. The differential form of the fundamental relation is valid for quasi-static processes

$$dU = TdS - PdV + \mu dN = TdS + đW + \mu dN. \qquad (15.9)$$

We can see that if the entropy and the number of particles are held constant, the change in the energy of the system is equal to the work done on it,

$$dU = đW. \qquad (15.10)$$

If the temperature is negative, the equations are unchanged, but the sign of $\partial^2 U/\partial X^2$ becomes negative. This is a reflection of the upper limit of the energy for systems that can support negative temperatures.

For the rest of the chapter, we will limit the discussion to positive temperatures.

15.2   Minimum Principle for the Helmholtz Free Energy

Both the entropy maximum principle and the energy minimum principle apply to a situation in which the composite system is thermally insulated from the rest of the universe. Now consider a different situation, in which the composite system (and its constituent subsystems) are in contact with a thermal reservoir, so that the temperature of the composite system is held constant. The entropy maximum and energy minimum principles no longer apply, because we can transfer energy and entropy in and out of the thermal reservoir. Nevertheless, we can find an extremum principle under these conditions.

Under constant temperature conditions, it is natural to use the Helmholtz free energy, which is the Legendre transform of U with respect to T:

$$F = U[T] = U - TS. \tag{15.11}$$

To analyze the new situation at constant temperature, consider the explicit case of the composite system of interest in contact with a thermal reservoir at temperature T_R, but thermally isolated from the rest of the universe. At equilibrium with respect to some thermodynamic variable X (subsystem volume, number of particles, and so on), the total energy is a minimum. This gives us the equations

$$\frac{\partial}{\partial X} (U + U_R) = 0 \tag{15.12}$$

and

$$\frac{\partial^2}{\partial X^2} (U + U_R) > 0 \tag{15.13}$$

subject to the condition that the entropy is constant (called the 'isentropic' condition)

$$\frac{\partial}{\partial X} (S + S_R) = 0. \tag{15.14}$$

The only energy exchange between the reservoir and the system is in the form of heat. The differential form of the fundamental relation for the reservoir simplifies to $dU_R = T_R dS_R$, which gives us an equation for the partial derivatives,

$$\frac{\partial U_R}{\partial X} = T_R \frac{\partial S_R}{\partial X}. \tag{15.15}$$

The partial derivative of the Helmholtz free energy of the system can now be transformed to show that it vanishes in equilibrium

$$\frac{\partial F}{\partial X} = \frac{\partial}{\partial X}(U - TS) \tag{15.16}$$

$$= \frac{\partial}{\partial X}(U - T_R S)$$

$$= \frac{\partial U}{\partial X} - T_R\frac{\partial S}{\partial X}$$

$$= \frac{\partial U}{\partial X} + T_R\frac{\partial S_R}{\partial X}$$

$$= \frac{\partial U}{\partial X} + \frac{\partial U_R}{\partial X}$$

$$= \frac{\partial}{\partial X}(U + U_R)$$

$$= 0.$$

A similar derivation shows that F is a minimum at equilibrium

$$\frac{\partial^2 F}{\partial X^2} = \frac{\partial^2}{\partial X^2}(U - TS) \tag{15.17}$$

$$= \frac{\partial^2}{\partial X^2}(U - T_R S)$$

$$= \frac{\partial^2 U}{\partial X^2} - T_R\frac{\partial^2 S}{\partial X^2}$$

$$= \frac{\partial^2 U}{\partial X^2} + T_R\frac{\partial^2 S_R}{\partial X^2}$$

$$= \frac{\partial^2 U}{\partial X^2} + \frac{\partial^2 U_R}{\partial X^2}$$

$$= \frac{\partial^2}{\partial X^2}(U + U_R)$$

$$> 0.$$

The maximum work that can be obtained from a system in contact with a thermal reservoir is not given by the change in U for the system, because energy can be extracted from the reservoir. However, the maximum work is given by the change in Helmholtz free energy.

As in the previous section, we note that maximum efficiency is always obtained with quasi-static processes. The differential form of the fundamental relation in the Helmholtz free energy representation is valid for quasi-static processes at constant temperature:

$$dF = -SdT - PdV + \mu dN = -SdT + \dbar W + \mu dN. \tag{15.18}$$

We can see that if the temperature and the number of particles are held constant, the change in the Helmholtz free energy of the system is equal to the work done on it,

$$dF = \dbar W. \tag{15.19}$$

As was the case for the corresponding eq. (15.10), the work referred to in eq. (15.19) is more general than $-PdV$ for a composite system.

> As was the case for the energy minimum principle, the minimum principle for the Helmholtz free energy refers to processes in which a constraint on the amount of something in a subsystem is released quasi-statically. It is therefore not valid to substitute the temperature or pressure of a subsystem for X in eq. (15.17), even though it might be tempting. We will discuss second derivatives with respect to temperature, pressure, and chemical potential in Chapter 16.

15.3   Minimum Principle for the Enthalpy

When the pressure is held constant, minimizing the enthalpy gives us the condition of equilibrium. The proof is similar to those in the previous sections.

Let the system of interest be in contact with a constant pressure reservoir at pressure P_R. At equilibrium with respect to some thermodynamic variable X, the total energy is again a minimum, subject to the constant total volume condition

$$\frac{\partial}{\partial X}(V + V_R) = 0. \tag{15.20}$$

The only energy exchange between the reservoir and the system is in the form of work. The differential form of the fundamental relation for the reservoir simplifies to $dU_R = -P_R dV_R$, which gives us an equation for the partial derivatives:

$$\frac{\partial U_R}{\partial X} = -P_R \frac{\partial V_R}{\partial X}. \tag{15.21}$$

The partial derivative of the enthalpy of the system can now be transformed to show that it vanishes in equilibrium:

$$\begin{aligned}
\frac{\partial H}{\partial X} &= \frac{\partial}{\partial X}(U + PV) \qquad\qquad\qquad (15.22)\\
&= \frac{\partial}{\partial X}(U + P_R V)\\
&= \frac{\partial U}{\partial X} + P_R \frac{\partial V}{\partial X}\\
&= \frac{\partial U}{\partial X} - P_R \frac{\partial V_R}{\partial X}\\
&= \frac{\partial U}{\partial X} + \frac{\partial U_R}{\partial X}\\
&= \frac{\partial}{\partial X}(U + U_R)\\
&= 0.
\end{aligned}$$

A similar derivation shows that H is a minimum at equilibrium:

$$\frac{\partial^2 H}{\partial^2 X} = \frac{\partial^2}{\partial^2 X}\left(U + PV\right) \tag{15.23}$$

$$= \frac{\partial^2}{\partial X^2}\left(U + P_R V\right)$$

$$= \frac{\partial^2 U}{\partial X^2} + P_R \frac{\partial^2 V}{\partial X^2}$$

$$= \frac{\partial^2 U}{\partial X^2} - P_R \frac{\partial^2 V_R}{\partial X^2}$$

$$= \frac{\partial^2 U}{\partial X^2} + \frac{\partial^2 U_R}{\partial X^2}$$

$$= \frac{\partial^2}{\partial X^2}\left(U + U_R\right)$$

$$> 0.$$

Changes in the enthalpy can be related to the heat added to a system. For reversible processes holding both P and N constant, $TdS = \dbar Q$, and

$$dH = TdS + VdP + \mu dN \tag{15.24}$$

becomes

$$dH = \dbar Q. \tag{15.25}$$

Because of eq. (15.25), the enthalpy is often referred to as the 'heat content' of a system. Although this terminology is common in chemistry, I do not recommend it. It can be quite confusing, since you can add arbitrarily large amounts of heat to a system without altering its state, as long as you also remove energy by having the system do work. Heat is not a state function and $\dbar Q$ is not an exact differential. Eq. (15.25) equates an exact and an inexact differential only with the restrictions of $dN = 0$ and $dP = 0$, which makes variations in the system one-dimensional.

15.4   Minimum Principle for the Gibbs Free Energy

If a system is in contact with both a thermal reservoir and a pressure reservoir, the Gibbs free energy is minimized at equilibrium,

$$\frac{\partial G}{\partial X} = 0 \tag{15.26}$$

$$\frac{\partial^2 G}{\partial X^2} > 0. \tag{15.27}$$

The proof of these equations is left as an exercise.

For a composite system in contact with both a thermal reservoir and a pressure reservoir, the Gibbs free energy also allows us to calculate the maximum work that can be obtained by a reversible process. If a composite system can do work on the outside world through a rod, as in the bottom diagram in Fig. 15.1, the differential form of the fundamental relation will be modified by the addition of a term $đW_X$,

$$dG = -SdT + VdP + đW_X + \mu dN. \tag{15.28}$$

For a reversible process with no leaks $(dN = 0)$, constant pressure $(dP = 0)$, and constant temperature $(dT = 0)$, the change in the Gibbs free energy is equal to the work done on the system,

$$dG = đW_X. \tag{15.29}$$

15.5 Exergy

In engineering applications it is common to introduce another thermodynamic potential called the 'exergy', E, which is of considerable practical value.[1] Exergy is used in the common engineering situation in which the environment provides a reversible reservoir at temperature, T_o, and pressure, P_o, which are usually taken to be the atmospheric temperature and pressure.

> In engineering textbooks, the exergy is often denoted by the letter E, which could lead to confusion with the energy. This is especially true for books in which the energy is denoted by E, making the distinction rely on a difference in font. Reader beware!

The exergy is defined as the amount of useful work that can be extracted from the system and its environment. If we use X to denote the internal variable (or variables) that change when work is done by the system, we can write the exergy as

$$\mathrm{E}(T_o, P_o, X) = -W(X) \tag{15.30}$$

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[1] The concept of exergy was first introduced in the nineteenth century by the German chemist Friedrich Wilhelm Ostwald (1853–1932), who in 1909 was awarded the Nobel Prize in Chemistry. Ostwald divided energy into 'Exergie' (exergy = useful energy) and 'Anergie' (anergy = wasted energy).

where W is the work done *on* the system. (Note that engineering textbooks often use the opposite sign convention for W.)

Clearly, exergy is used in essentially the same situation described in the previous section on the Gibbs free energy, so it is not surprising that the exergy and the Gibbs free energy are closely related. The main difference is that the exergy is defined so that it is zero in the 'dead state', in which G takes on its minimum value and X takes on the corresponding value X_o. The dead state is characterized by the impossibility of extracting any more useful work. If we subtract the value taken on by the Gibbs free energy in the dead state, we can make explicit the connection to the exergy,

$$\mathrm{E}(T_o, P_o, X) = G(T_o, P_o, X) - G(T_o, P_o, X_o). \tag{15.31}$$

The equation for the exergy in engineering texts is usually written without reference to the Gibbs free energy,

$$\mathrm{E}(T_o, P_o, X) = (U - U_o) + P_o(V - V_o) - T_o(S - S_o) + KE + PE. \tag{15.32}$$

Note that the kinetic energy, KE, and the potential energy, PE, are included explicitly in this equation, while they are implicit in eq. (15.31).

> It is a common engineering convention that although the kinetic and potential energy are included in the exergy, they are not included in the internal energy of the system, as we have done in the rest of this book. Note that the zero of potential energy is also assumed to be determined by the environment.

Since the exergy is the maximum amount of work that can be obtained from a system exposed to the atmospheric temperature and pressure, it is an extremely useful concept in engineering. An engineer is concerned with how much work can be obtained from a machine in a real environment, and this is exactly what the exergy provides.

15.6 Maximum Principle for Massieu Functions

Just as minimization principles can be found for F, H, and G, which are Legendre transforms of U, maximization principles can be found for the Massieu functions, which are Legendre transforms of the entropy.

The maximization principles can be seen most quickly from the relations

$$S[1/T] = -F/T \tag{15.33}$$

and

$$S[1/T, P/T] = -G/T \tag{15.34}$$

and a comparison with the minimization principles for F and G.

15.7   Summary

The extremum principles derived in this chapter are central to the structure of thermo-dynamics for several reasons.

1. We will use them immediately in Chapter 16 to derive stability conditions for general thermodynamic systems.
2. When stability conditions are violated, the resulting instability leads to a phase transition, which is the topic of Chapter 17.
3. Finally, in Parts III and IV, we will often find that the most direct calculations in statistical mechanics lead to thermodynamic potentials other than the energy or the entropy. The extremum principles in the current chapter are essential for finding equilibrium conditions directly from such statistical mechanics results.

15.8   Problems

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PROBLEM 15.1
Extremum conditions

1. Helmholtz free energy for the ideal gas
   From the expression for the Helmholtz free energy of the ideal gas, calculate ΔF for an isothermal expansion from volume V_A to V_B when the system is in equilibrium with a thermal reservoir at temperature T_R. Compare this to the work done on the system during the same expansion.
2. Gibbs free energy minimum principle
   Consider a composite system with a property X that can be varied externally. [For example, X could be the volume of a subsystem, as discussed in class.]
   Prove that at equilibrium,

$$\left(\frac{\partial G}{\partial X}\right)_{T,P,N} = 0$$

   and

$$\left(\frac{\partial^2 G}{\partial X^2}\right)_{T,P,N} > 0.$$

3. Let $đW$ be the work done on the system by manipulating the property X from outside the system.
   Prove that $dG = đW$, when the system is in contact with a reservoir that fixes the temperature at T_R and the pressure at P_R.