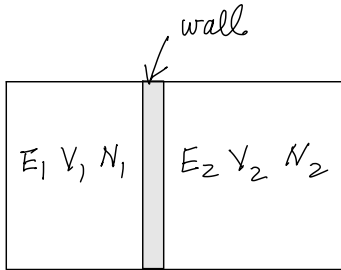


Unit 1-2: Conditions for Equilibrium, Concavity of the Entropy

Thermal Equilibrium

Consider a system that is divided into two pieces by a wall.



$$E = E_1 + E_2$$

$$S = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2)$$

The wall is immovable, impermeable (no particles can pass through it), and thermally insulating (no heat can pass through it).

A thermally insulating wall is often called an *adiabatic* wall – no heat can flow across it. A *diathermal* wall is a wall that can conduct heat.

As long as the wall is in place, the two subsystems cannot exchange energy, volume, or number of particles.

Suppose now that the wall is changed to a thermally conducting wall, so that the two subsystems can exchange energy. What will be the new E_1 and E_2 after the system reaches the new equilibrium?

$E = E_1 + E_2$ is a fixed constant by conservation of the energy – system as a whole cannot exchange energy with the external world.

But E_1 and $E_2 = E - E_1$ can change.

$$E = E_1 + E_2 \text{ fixed} \Rightarrow dE = dE_1 + dE_2 = 0 \Rightarrow dE_1 = -dE_2.$$

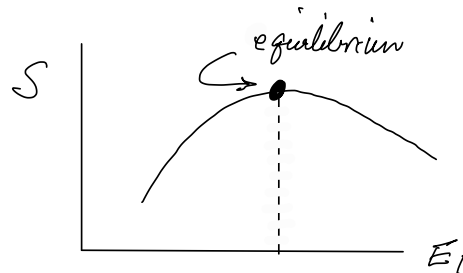
The change in entropy $S = S_1 + S_2$ as the system equilibrates is then,

$$dS = \left(\frac{\partial S_1}{\partial E_1} \right)_{V_1, N_1} dE_1 + \left(\frac{\partial S_2}{\partial E_2} \right)_{V_2, N_2} dE_2 = \frac{1}{T_1} dE_1 + \frac{1}{T_2} dE_2 = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 \quad (1.2.1)$$

Now, by postulate II, equilibrium is achieved when S reaches its *maximum*. Viewing S as a function of E_1 (with $E_2 = E - E_1$), at the maximum we must have $dS = 0$, i.e., S will not change for small changes in dE_1 . By Eq. (1.2.1) we then have,

$$dS = 0 \Rightarrow \boxed{T_1 = T_2} \quad (1.2.2)$$

The system will be in equilibrium when the two subsystems have the same temperature.



Note: $dS = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 \Rightarrow$ if $T_1 > T_2$, then since the system evolves so that one always has $dS > 0$ (entropy must increase as the system approaches equilibrium), then we must have $dE_1 < 0$. So energy flows from subsystem (1) to subsystem (2) (i.e. $dE_1 < 0$ means E_1 decreases, while $dE_2 = -dE_1 > 0$ means E_2 increases). Thus energy flows from the subsystem with higher temperature T_1 to the subsystem with lower temperature T_2 . This agrees with our expectation about temperature, that heat flows from hot to cold.

Mechanical Equilibrium

Now suppose the wall separating the two subsystems is both thermally conducting *and* it is allowed to slide so that the volumes V_1 and V_2 can change.

Still the total volume $V = V_1 + V_2$ is fixed, so $V_2 = V - V_1$ and $dV_2 = -dV_1$. We have,

$$E = E_1 + E_2 \quad \text{fixed} \quad \Rightarrow \quad dE_2 = -dE_1$$

$$V = V_1 + V_2 \quad \text{fixed} \quad \Rightarrow \quad dV_2 = -dV_1$$

We will also assume that the wall moves *slowly* so that no energy is dissipated in the friction of the moving wall.

As the system equilibrates, the change in entropy is,

$$dS = \left(\frac{\partial S_1}{\partial E_1} \right)_{V_1, N_1} dE_1 + \left(\frac{\partial S_1}{\partial V_1} \right)_{E_1, N_1} dV_1 + \left(\frac{\partial S_2}{\partial E_2} \right)_{V_2, N_2} dE_2 + \left(\frac{\partial S_2}{\partial V_2} \right)_{E_2, N_2} dV_2 \quad (1.2.3)$$

$$= \frac{1}{T_1} dE_1 + \frac{p_1}{T_1} dV_1 + \frac{1}{T_2} dE_2 + \frac{p_2}{T_2} dV_2 \quad (1.2.4)$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2} \right) dV_1 \quad (1.2.5)$$

At equilibrium S is maximized so $dS = 0 \Rightarrow$ $T_1 = T_2$ and $p_1 = p_2$.

When the volume can change, equilibrium is reached when the pressures of the two subsystems are equal.

Chemical Equilibrium

Now suppose the wall is thermally conducting, can slide, and is also permeable to particles (particles can pass through it). The total number of particles $N = N_1 + N_2$ remains fixed, but N_1 and $N_2 = N - N_1$ may vary. We have,

$$E = E_1 + E_2 \quad \text{fixed} \quad \Rightarrow \quad dE_2 = -dE_1$$

$$V = V_1 + V_2 \quad \text{fixed} \quad \Rightarrow \quad dV_2 = -dV_1$$

$$N = N_1 + N_2 \quad \text{fixed} \quad \Rightarrow \quad dN_2 = -dN_1$$

As the system equilibrates, the change in entropy is,

$$dS = \left(\frac{\partial S_1}{\partial E_1} \right)_{V_1, N_1} dE_1 + \left(\frac{\partial S_1}{\partial V_1} \right)_{E_1, N_1} dV_1 + \left(\frac{\partial S_1}{\partial N_1} \right)_{E_1, V_1} dN_1 + \left(\frac{\partial S_2}{\partial E_2} \right)_{V_2, N_2} dE_2 + \left(\frac{\partial S_2}{\partial V_2} \right)_{E_2, N_2} dV_2 + \left(\frac{\partial S_2}{\partial N_2} \right)_{E_2, V_2} dN_2 \quad (1.2.6)$$

$$= \frac{1}{T_1} dE_1 + \frac{p_1}{T_1} dV_1 - \frac{\mu_1}{T_1} dN_1 + \frac{1}{T_2} dE_2 + \frac{p_2}{T_2} dV_2 - \frac{\mu_2}{T_2} dN_2 \quad (1.2.7)$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2} \right) dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) dN_1 \quad (1.2.8)$$

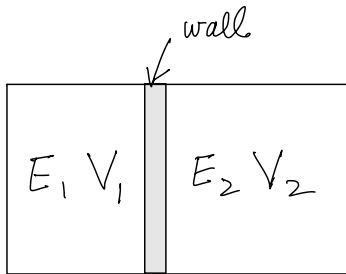
At equilibrium S is maximized so $dS = 0 \Rightarrow$ $T_1 = T_2$ and $p_1 = p_2$ and $\mu_1 = \mu_2$.

When particles can be exchanged between the two subsystems, equilibrium is reached when the subsystems have the same chemical potential.

The role of statistical mechanics is to calculate the entropy from the microscopic details of the system. Once the entropy is known, then all thermodynamic properties follow.

Mechanical Equilibrium Revisited

For another way to look at the problem of thermal and mechanical equilibrium, consider again a system divided into two subsystems by a wall. We will take the number of particles N_1 and N_2 to stay fixed, so we ignore them in the calculation below



Initially the wall is adiabatic and immovable. The subsystems are in equilibrium with energy and volume E_1 and V_1 on the left, and E_2 and V_2 on the right.

Now the wall is allowed to both slide and to conduct heat.

$$E = E_1 + E_2 \quad \text{stays fixed} \quad \Rightarrow \quad E_2 = E - E_1$$

$$V = V_1 + V_2 \quad \text{stays fixed} \quad \Rightarrow \quad V_2 = V - V_1$$

The total entropy can thus be written as a function of E_1 and V_1 ,

$$S = S_1(E_1, V_1) + S_2(E - E_1, V - V_1) \quad (1.2.9)$$

This entropy S is maximized when the system reached equilibrium. Thus equilibrium is when,

$$0 = \left(\frac{\partial S}{\partial E_1} \right)_{V_1} = \left(\frac{\partial S_1}{\partial E_1} \right)_{V_1} + \left(\frac{\partial S_2}{\partial E_2} \right)_{V_2} \frac{\partial E_2}{\partial E_1} = \frac{1}{T_1} - \frac{1}{T_2} \quad (1.2.10)$$

$$0 = \left(\frac{\partial S}{\partial V_1} \right)_{E_1} = \left(\frac{\partial S_1}{\partial V_1} \right)_{E_1} + \left(\frac{\partial S_2}{\partial V_2} \right)_{E_2} \frac{\partial V_2}{\partial V_1} = \frac{p_1}{T_1} - \frac{p_2}{T_2} \quad (1.2.11)$$

$\Rightarrow T_1 = T_2$ and $p_1 = p_2$. More specifically, since T and p are functions of E and V , we have,

$$T_1(E_1, V_1) = T_2(E - E_1, V - V_1) \quad \text{and} \quad p_1(E_1, V_1) = p_2(E - E_1, V - V_1) \quad (1.2.12)$$

The above are two equations for the two unknowns E_1 and V_1 . In principle one can therefore solve them to find the new values of E_1 and V_1 (and hence also $E_2 = E - E_1$ and $V_2 = V - V_1$) in the new equilibrium state.

Now, however, consider the same initial situation, but now the wall is free to slide but still stays adiabatic. Since no heat can be transported across the wall, we have $dQ_1 = T_1 dS_1 = 0$ and $dQ_2 = T_2 dS_2 = 0$. Thus $dS_1 = dS_2 = 0$. The entropy of each subsystem stays fixed and cannot change. So,

$$dS_1 = \left(\frac{\partial S_1}{\partial E_1} \right)_{V_1} dE_1 + \left(\frac{\partial S_1}{\partial V_1} \right)_{E_1} dV_1 = \frac{1}{T_1} dE_1 + \frac{p_1}{T_1} dV_1 = 0 \quad \Rightarrow \quad dE_1 = -p_1 dV_1 \quad (1.2.13)$$

Similarly,

$$dS_2 = \left(\frac{\partial S_2}{\partial E_2} \right)_{V_2} dE_2 + \left(\frac{\partial S_2}{\partial V_2} \right)_{E_2} dV_2 = \frac{1}{T_2} dE_2 + \frac{p_2}{T_2} dV_2 = 0 \quad \Rightarrow \quad dE_2 = -p_2 dV_2 \quad (1.2.14)$$

The energy of each side can change only by doing mechanical work in moving the wall.

The total energy is still conserved, so $E = E_1 + E_2$ is fixed, and so $dE_2 = -dE_1$.

The total volume is still fixed, so $V = V_1 + V_2$ is fixed, and so $dV_2 = -dV_1$.

From $dS_1 = 0$ we concluded $dE_1 = -p_1 dV_1$. From $dS_2 = 0$ we concluded $dE_2 = -p_2 dV_2 \Rightarrow (-dE_1) = -p_2(-dV_1) \Rightarrow dE_1 = -p_2 dV_1$. We thus conclude that equilibrium is achieved when $p_1 = p_2$, or when

$$p_1(E_1, V_1) = p_2(E - E_1, V - V_1) \quad (1.2.15)$$

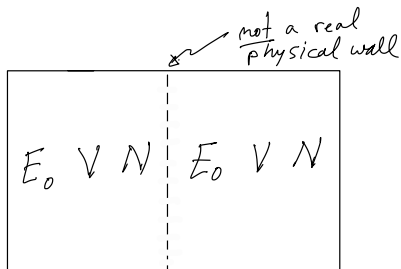
In equilibrium, the pressures of the two subsystems must be equal, so that the net force on the sliding wall is zero.

But the above is just *one* equation for *two* unknowns, E_1 and V_1 . Therefore, thermodynamics alone does *not* give enough information to determine the new equilibrium state. The postulate about maximizing the entropy does not help us here since the total entropy does not change, $dS = dS_1 + dS_2 = 0$, when the wall is adiabatic.

The new equilibrium state will depend on details of how energy is dissipated in the system, such as the viscosity of the gases in each subsystem, or the friction associated with the sliding of the wall. Viscosity is the mechanism by which the energy added to one subsystem via the mechanical work done by the wall goes into increasing the temperature of that gas. If the gases had no viscosity, and the wall slid without any friction, the wall would just oscillate in simple harmonic motion and no new equilibrium would ever be reached.

Concavity of the Entropy and Stability of Equilibrium (Callen Chapters 3 and 5)

Consider a container of gas, that is *conceptually* divided into two equal halves (i.e. there is no physical wall).

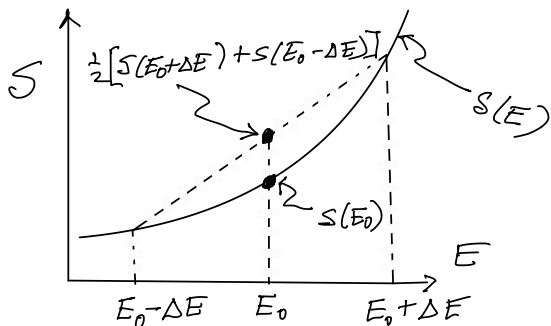


If N and V are fixed to be the same on both sides, we expect that the energy will also be equal on both sides. Call that energy E_0 . Then,

$$S^{\text{total}} = S(2E_0, 2V, 2N) = S(E_0, V, N) + S(E_0, V, N) = 2S(E_0, V, N)$$

The second term represents the entropy of the total system which has energy $2E_0$, volume $2V$, and number of particles $2N$, while the third term represents that entropy as the sum of the two half subsystems.

Consider now how S depends on E . If S were *not* a concave function of E (i.e. $S(E)$ is convex $\Rightarrow \partial^2 S / \partial E^2 > 0$), then the system would not be stable! We see this as follows. For a convex $S(E)$ we have behavior as in the sketch below.

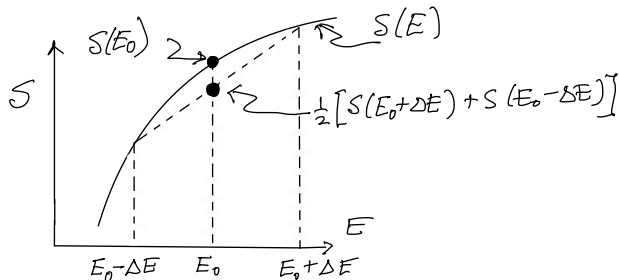


Consider that a small amount of energy ΔE is transferred from one side to the other, so that the entropy on one side is $S(E_0 + \Delta E)$ and on the other side is $S(E_0 - \Delta E)$. By the sketch on the left, we see that the total system would then have a total entropy $S^{\text{total}} = S(E_0 + \Delta E) + S(E_0 - \Delta E) > 2S(E_0)$.

Thus the system would *increase* its entropy by making this energy transfer of ΔE . Since systems in equilibrium always maximize their entropy, we would have to conclude that the original assumed state where both halves have the same energy E_0 could not be a stable equilibrium.

If $S(E)$ were convex, the system would thus prefer to have an inhomogeneous distribution of the energy. That violates our notion of an equilibrium state where constant E, V, N are the only relevant macroscopic variables. If the system preferred an inhomogeneous distribution of energy, we would have to be considering $E(\mathbf{r})$. We therefore conclude that a convex $S(E)$ cannot lead to a spatially homogeneous stable equilibrium, and so $S(E)$ must be a concave function.

If $S(E)$ is concave, then we have the situation as in the sketch below.



In this case we find $2S(E_0) > S(E_0 + \Delta E) + S(E_0 - \Delta E)$ and so transferring energy ΔE from one side of the system to the other would *decrease* the total entropy, and so it does not happen. The state with a spatially homogeneous energy E_0 will be the stable equilibrium state.

By similar arguments we can conclude that S must be a concave function of *all* its variables.

$$d^2 S < 0 \quad S \text{ is concave in all its variables} \quad (1.2.16)$$