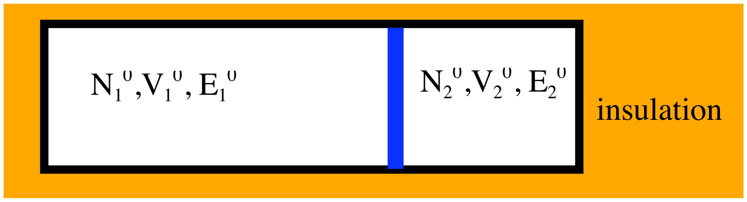
Lecture 16: Maximum/Minimum principles and what happens when you remove internal constraints.

Reading Assignment for Lectures 15--18: PKT Chapter 7
Midterm coming up Friday, Oct 29.
Problem Set 3 coming up next week.

Energy contact, thermometry, and entropy increase.

Thermodynamics describes the properties of equilibrium states.
When some "process" takes place and the system goes from one equilibrium state to another, the intermediate states may or may not be equilibrium states. The condition that they be equilibrium states is that the process takes place very slowly (i.e., *quasistatically*) , so all the states intermediate between the initial (equilibrium) state and the final (equilibrium) state are also effectively at equilibrium.
If the process is NOT quasistatic, then thermodynamics can say nothing about the intermediate states but may still be able to place restrictions on the possible final state arising from a given initial state.

I want to talk now about an important class of processes, those in which an "internal constraint" is removed and the system readjusts spontaneously. Best to do this by example, so I will consider a fluid system with variables E,V,N (but there is no assumption that this is an ideal gas).



Consider a system composed of two subsystems 1+2. Initially these subsystems are at equilibrium, isolated from one another and from the external world (indicated by the yellow box). In this situation, I claim that they have a combined entropy which is additive,

$$S_{1+2}\left(E_1^0,V_1^0,N_1^0;E_2^0,V_2^0,N_2^0\right)=S_1\left(E_1^0,V_1^0,N_1^0\right)+S_2\left(E_2^0,V_2^0,N_2^0\right).$$

The reason is that the microstates of 1 and 2 are independent, so

$$W_{1+2}\left(E_1^0,V_1^0,N_1^0;E_2^0,V_2^0,N_2^0\right)=W_1\left(E_1^0,V_1^0,N_1^0\right)\cdot W_2\left(E_2^0,V_2^0,N_2^0\right),$$

and taking $k_B \ln W$ makes the entropy additive.

Comment:
You may want to unpack this a little more carefully:

Suppose the initial ensemble is specified by saying that $E_{1,2}^0 < E_{1,2} < E_{1,2}^0 + \frac{\Delta E}{2}$.

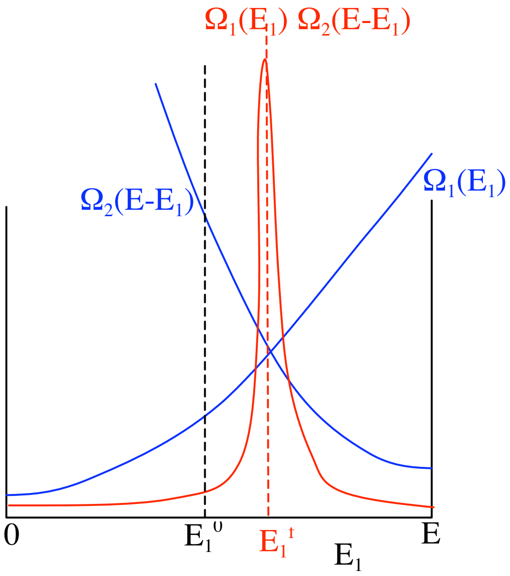
Then $W_{1,2}^0 = \Omega_{1,2}\left(E_{1,2}^0\right)\frac{\Delta E}{2}$, so $W_{1+2}^0 = \Omega_1^0\Omega_2^0\left(\frac{\Delta E}{2}\right)^2$

I now imagine that one or more of the "constraints" that keep the subsystems separated are removed. For example, let's keep the system as a whole insulated (*"adiabatic change"*) but let the piston no longer be insulated, so that heat can flow freely between 1 and 2.
Question: What is the final distribution of energy between the two subsystems?
Energy overall is conserved, so $E_1^f + E_2^f = E_1^0 + E_2^0 \equiv E$ but what are the individual final-state energies?
According to the principle of equal a priori probability the new equilibrium ensemble is supposed to weight equally all the microstates of the composite system. The new density of states of the composite system Ω_{1+2} has the form,

$$e^{\frac{1}{k_B}S_{1+2}(E)} \equiv \Omega_{1+2}\left(N_1^0,V_1^0;N_2^0,V_2^0;E\right)$$

$$= \int_0^E dE_1\,\Omega_1\left(N_1^0,V_1^0,E_1\right)\Omega_2\left(N_2^0,V_2^0,\underset{E-E_1=E_2}{E-E_1}\right) = \int_0^E dE_1\, e^{\frac{1}{k_B}\left(S_1(E_1)+S_2(E-E_1)\right)}$$

Note that $E_1 + E_2 = E_1^0 + E_2^0 = E$.



I am now going to argue that this integral is very sharply peaked, so when both subsystems are large it gets essentially all its weight from some intermediate value $E_1 = E_1^f(E)$ for which,

$$\left.\frac{\partial S_1}{\partial E_1}\right|_{E_1=E_1^f} = \left.\frac{\partial S_2}{\partial E_2}\right|_{E_2=E-E_1^f=E_2^f},$$ so that

$$S_{1+2}\left(N_1^0,V_1^0;N_2^0,V_2^0;E\right) = S_1\left(N_1^0,V_1^0,E_1^f\right) + S_2\left(N_2^0,V_2^0,E_2^f = E-E_1^f\right)$$

and, furthermore, that

$$S_{1+2}\left(N_1^0,V_1^0;N_2^0,V_2^0;E\right) \geq S_1\left(N_1^0,V_1^0,E_1^0\right) + S_2\left(N_2^0,V_2^0,E_2^0\right).$$

What this means is that:

- the condition of final equilibrium is $T_1 = T_2$ (temperatures agree after thermal contact).
- the final energy partition between the subsystems is E_1^f, E_2^f, and
- there is an increase of entropy unless $E_1^0, E_2^0 = E_1^f, E_2^f$, i.e., initial temperatures were (accidentally) equal.

This kind of argument has come up several times before:

Let the exponent $F(E_1) \equiv \frac{1}{k_B}\left(S_1(E_1) + S_2(E-E_1)\right)$. Note that S_1 and S_2 are extensive.

I claim that this function has a maximum, i.e., at some point $E_1 = E_1^f$ in $0 < E_1 < E$,

$$0 = \frac{dF}{dE_1} = \frac{1}{k_B}\left(\frac{\partial S_1(E_1)}{\partial E_1} + \frac{\partial S_2(E-E_1)}{\partial E_1}\right) = \frac{1}{k_B}\left(\left.\frac{\partial S_1}{\partial E_1}\right|_{E_1=E_1^f} - \left.\frac{\partial S_2(E_2)}{\partial E_2}\right|_{E_2=E-E_1^f}\right).$$

Let's Taylor expand about this point: Note that $F''\sim 1/N$, $F'''\sim 1/N^2$, etc.

$$F(E_1) = F\left(E_1^f\right) + 0 + \frac{1}{2}F''\left(E_1^f\right)\left(E_1 - E_1^f\right)^2 + \frac{1}{3!}F'''\left(E_1^f\right)\left(E_1 - E_1^f\right)^3 + \ldots$$

Claim: The coefficient of the second-order term is negative and goes as 1/N: (see p. 15.1)

$$\left.\frac{\partial S_1}{\partial E_1}\right|_{N_1^0,V_1^0} = \frac{1}{T_1}$$

$$\left.\frac{\partial^2 S_1}{\partial E_1^2}\right|_{N_1^0,V_1^0} = \frac{\partial}{\partial E_1}\left(\frac{1}{T_1}\right) = -\frac{1}{T_1^2}\left.\frac{\partial T_1}{\partial E_1}\right|_{N_1^0,V_1^0} = -\frac{1}{T_1^2}\frac{1}{\left.\frac{\partial E_1}{\partial T_1}\right|_{N_1^0,V_1^0}} = -\frac{1}{T_1^2}\frac{1}{C_{N_1^0,V_1^0}}$$

and similarly for S_2.

Under the integral, the first term limits relevant values of E_1 to those within $\sqrt{N}$ of E_1^f.

In this range, the third term goes as $\frac{1}{\sqrt{N}}$, so it and all higher terms make no contribution to the integral when N is large.

Thus, the final form of the integral is $e^{F\left(E_1^f\right)}\int_0^E dE_1\, e^{-\frac{1}{2}|F''|\left(E_1-E_1^f\right)^2+\text{small}}$, i.e., it is a Gaussian integral which is very narrow. Thus, we can extend the limits to infinity with negligible error, finding, $e^{F\left(E_1^f\right)}\int_0^E dE_1\, e^{-\frac{1}{2}|F''|\left(E_1-E_1^f\right)^2} = \sqrt{\frac{2\pi}{|F''|}}e^{F\left(E_1^f\right)}$.

In the end it is the logarithm of this integral, which gives S_{1+2}. The prefactor gives a contribution of order lnN which is irrelevant compared to the main extensive term ($\ln N << N$), so

$S_{1+2}\left(N_1^0,V_1^0;N_2^0,V_2^0;E\right) = S_1\left(N_1^0,V_1^0,E_1^f\right) + S_2\left(N_2^0,V_2^0,E_2^f = E - E_1^f\right)$, as claimed.

Since this is just the value of the integrand at the maximum, it is clearly larger than the initial entropy (unless, of course, we happened to start out at the maximum). QED

Q: Why has entropy of states increased?

A: As we have seen, the final state "finds" the highest possible density of states of the composite system. More states gnerally available when the internal constraint is removed.

Comments:

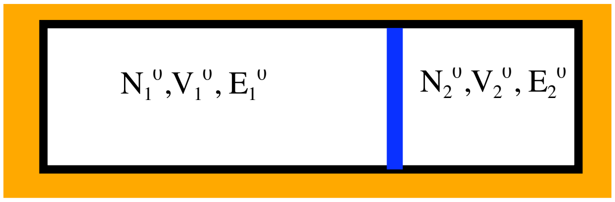
1. Thermometry: $\frac{\partial \ln\Omega(E,V,N)}{\partial E} = \frac{1}{k_B T}$

The significance of this derivative is that it is the quantity which subsystems share when they come to equilibrium in energy contact. This derivative is the "thermodynamic" definition of temperature. The choice of k_B is arbitrary and simply sets the temperature scale.

Alternatively, you can use the ideal monatomic gas as a "thermometer" to define temperature with $k_B T \equiv \frac{PV}{N}$. Quantities on the right are measurable. Again, k_B is a convention. All gases become ideal in the limit of low-enough density. Thus, equality of temperature allows us to use "ideal gas thermometer."

2. Other kinds of contact: Similar arguments (which I will not do here) apply to different kinds of "contact."

(a) Energy *plus* volume contact: Pressure equality.
In addition to removing piston insulation, now allow piston to move, so now:



$$\begin{aligned} E_1 + E_2 &= E_1^0 + E_2^0 = E \text{ and} \\ V_1 + V_2 &= V_1^0 + V_2^0 = V. \end{aligned} \quad (\text{ both fixed}).$$

With

$$e^{\frac{1}{k_B} S_{1+2}(E,V)} \equiv \Omega_{1+2}\left(E, V; N_1^0; N_2^0\right)$$

$$= \int_0^E dE_1 dV_1 \Omega_1\left(E_1, V_2, N_1^0\right) \Omega_2\left(V - V_1, E - E_1, N_2^0\right) = \int_0^E dE_1 dV_1\, e^{\frac{1}{k_B}\left(S_1(E_1,V_1) + S_2(E - E_1, V - V_1)\right)}$$

The (now-two-dimensional) integral is sharply peaked at values of $E_1 = E_1^f, V_1 = V_1^f$ such that

$$\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2}, \text{i.e.,} \frac{1}{T_1} = \frac{1}{T_2}, \text{and}$$

$$\frac{\partial S_1}{\partial V_1} = \frac{\partial S_2}{\partial V_2}, \text{i.e.,} \frac{P_1}{T_1} = \frac{P_2}{T_2}.$$

That is the conditions for equilibrium are $T_1 = T_2, P_1 = P_2$. And, again, the entropy of the final state is larger than the entropy of the initial state.

Notes:

(i) How do you know here that the extremum is a maximum? Turns out that it involves both positivity of the heat capacity and (new) positivity of the compressibility. Both of these are "stability conditions."

(ii) When you write $\frac{\partial S}{\partial V} = \frac{P}{T}$, how do you know that P is the (mechanical) pressure? Can argue this in several ways. Easiest to use the ideal gas as a pressure gauge (like the ideal-gas thermometer), with $\frac{\partial S_1}{\partial V_1} = \frac{\partial S_2}{\partial V_2}$ to guarantee transitivity.

(b) Energy *plus* number contact: Chemical potential equality.
Semipermeable membranes and chemical potential equality.
In the simplest situation, this just means you make holes in the piston. Thus,

$$E_1 + E_2 = E_1^0 + E_2^0 = E \text{ and}$$

$$N_1 + N_2 = N_1^0 + N_2^0 = N.$$

$$\text{So,} \quad \begin{aligned} &\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2}, \text{i.e.,} \frac{1}{T_1} = \frac{1}{T_2}, \text{and} \\ &\frac{\partial S_1}{\partial N_1} = \frac{\partial S_2}{\partial N_2}, \text{i.e.,} -\frac{\mu_1}{T_1} = -\frac{\mu_2}{T_2}. \end{aligned}$$

That is the conditions for equilibrium are $T_1 = T_2, \mu_1 = \mu_2$. And, again, the entropy of the final state is larger than the entropy of the initial state.

For a single species of particle, this is not very interesting. When there are holes in the piston, everything equilibrates, i.e., when $T_1 = T_2, \mu_1 = \mu_2$, then $P_1 = P_2$.

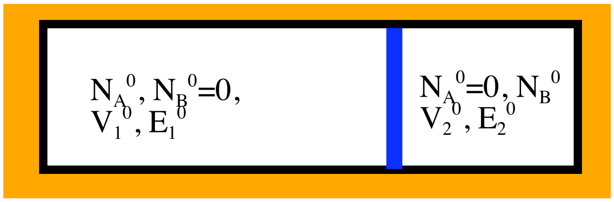
But, it becomes more interesting, when there are several species present, A, B, C,..., whose equilibration can be independently controlled by means of "semipermeable" barriers, which pass one species but not the others.

Such barriers are common in biology in the form of semipermeable membranes which may pass small molecules but not large ones or neutral molecules but not charged ones.

Examples:

1. Gases and the law of partial pressures:

Suppose now that the partition passes heat and is made semipermeable to B but remains impermeable to A.



Q: What happens?

A: B molecules move from the right to the left until $\mu_1^B = \mu_2^B$, which for ideal gases (only) means $n_1^B = n_1^B$.

Thus, the pressure in 1 increases and the pressure in 2 decreases. In general $P_1 \neq P_2$. Indeed, for ideal gases (only) $P_1 = \dfrac{\left(N_A^0 + N_{1,B}^f\right)k_B T}{V_1^0}, P_2 = \dfrac{\left(N_{2,B}^f\right)k_B T}{V_2^0}$.

(law of partial pressures: each species exerts its own pressure)

2. Semipermeable membranes and osmotic pressure:

Now make the partition permeable to water but not the solute. The water will move (to the left!) until $\mu_1^{water} = \mu_2^{water}$.

We will study this in more detail later.

Water is an incompressible fluid, so there can be a dramatic increase of pressure in 1 (and a corresponding decrease in pressure in 2 in this unrealistic closed geometry).