Lecture 17:
Entropy increase: “entropy maximization” and its relation to Free energy minimization, etc.

Reading Assignment for Lectures 15--18: PKT Chapter 7
Midterm coming up Friday, Oct 29.
Problem Set 3 due Oct. 22 (accepted up thru Oct. 25) now available at the website.
Graded papers for Problem Set 1 will be available Tuesday.

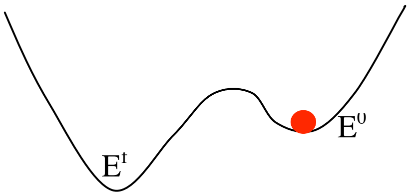
We have seen how, when internal constraints are removed, an isolated system will always increase its entropy, unless it is already accidentally equilibrated. This comes about because constraints always decrease the number of available states, so their removal leads to more available states and, through $S = k_B \ln W$, to higher entropy.

Note:
The “process” involved here is one which starts at equilibrium and ends at equilibrium, so that the initial and final “entropies” S^0 and S^f are well defined. (you can’t define the entropy for a non-equilibrium state).
The process takes place “spontaneously”, i.e., it occurs as a natural equilibration, without outside interference.
The intermediate states through which the system passes in going from 0 to f may or may not be equilibrium states. They will, in general be equilibrium states, if the process occurs slowly (quasistatically), however, if the process is abrupt, they will not be.

This statement becomes in thermodynamics the statement that, for any isolated thermodynamic system at equilibrium, when an internal constraint is removed and the system re-equilibrates,

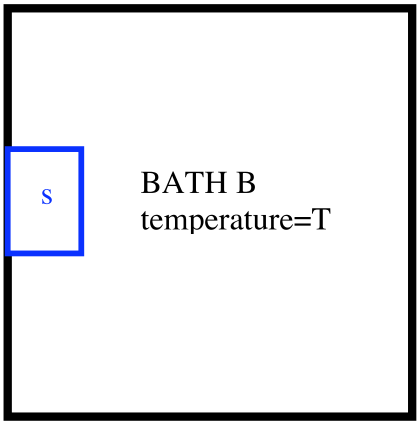
$\boxed{\Delta S = S^f - S^0 \ge 0.}$ “Second Law of Thermodynamics” includes this property.

(note that the ΔS here refers to the *entire* process and is not generally infinitesimal)
“An isolated thermodynamic system maximizes its entropy”
Note: I want you to think of this statement as like the mechanical statement that “an isolated mechanical system minimizes its energy.”
The ball is only stable at a local minimum E^0.
That minimum may or may not be global.
Removal of constraint allows ball to move to lower minimum E^f.



From this most basic thermodynamic extremum principle, a number of other principles follow:
Claim:
A thermodynamic system at constant temperature (but otherwise isolated) minimizes its Helmholtz free energy F(T,V,N).

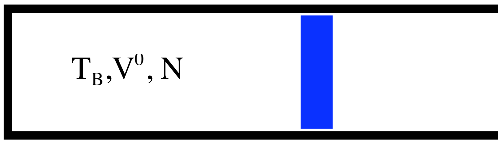
Proof:
Both the system s and the bath B are thermodynamically large.
But, the bath is much larger than the system, so the temperature T is determined by the bath.
Suppose some constraint inside the system is removed.
We know from the second law that
$\Delta S = \Delta S_{s+B} = \Delta S_s + \Delta S_B \ge 0$.
In the equilibration, some heat ΔQ will in general flow from the bath into the system.
ΔQ can be negative; I’m not saying which way the heat flows.
I am simply defining ΔQ so that it is “into” the “system.”
The corresponding heat flow into the bath is –ΔQ.



the bath is so large that it is never out of equilibrium, so $-\Delta Q = T\Delta S_B$ and we can then write the second law entirely in terms of quantities belonging to the system (the bath disappears):
$T\Delta S_s - \Delta Q \ge 0$.
But, what the first law says for the system is $\Delta Q = \Delta E_s + \Delta W$, where ΔW is the work (if any) done by the system on the external world.
It follows that $T\Delta S_s - \Delta E_s \ge \Delta W$ or (since F=E-TS) $\boxed{F_s^0 - F_s^f \ge W.}$

Thus,
1. If the system does not do work, its Helmholz free energy can only decrease in a spontaneous isothermal process.

2. If work is done, then the maximum work possible is not the energy difference $E^0 - E^f$ but rather the free energy difference. It is for this reason that F is called the "available" or "free" energy.



Example: Isothermal expansion of an ideal gas
Suppose there is a process in which the piston is released and moves (spontaneously) to the right, so the volume expands from V^0 to V^f.
According to the minimum principle, $F_s^0 - F_s^f \ge W$.

But, for the ICMG we found (Lect. 14.4) $F(T,V,N) = -Nk_BT\ln\left(\frac{T^{3/2}V}{N}\right) - Nk_BT\cdot const$.

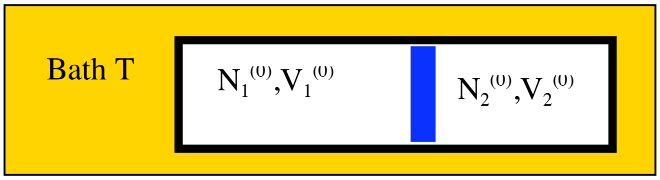
Only V is changing, so $F_s^0 - F_s^f = Nk_BT\ln\frac{V^f}{V^0} \ge W$.

Compare that with the two situations we discussed earlier (Lect. 13.2):

(a) Quasistatic expansion: $W = \int_{V^0}^{V^f} dV\,P = \int_{V^0}^{V^f} dV\,\frac{Nk_BT}{V} = Nk_BT\ln\frac{V^f}{V^0}$. Limit is achieved.

(b) Very-rapid expansion: No work done, W=0. Limit is respected.
Note that both processes have the same initial and final states.
Q: Where does the "extra" energy come from in case (a)?
A: For the ideal gas (only) the rapid expansion is adiabatic (there is no heat flow from or to the thermal bath, since E(T) only). In case (a) but without the thermal bath, the gas would cool, since it is doing work. In the presence of the bath, that cooling is averted by heat flow in from the bath to the system. The energy from the heat flowing in is the source of the work done in case (a), since the (internal) energy of the gas only depends on T and, therefore, does not change in the process. Thus quasistatic expansion is the maximally "efficient" process (in the sense that it allows the system to do the most work) simply because it guarantees the largest possible flow of energy into the system from the bath.
What the second law guarantees is that there is no way of getting more work out than the quasistatic process.
Comment: You can derive the "minimum" property of the Helmholtz free energy (at fixed T) directly by a "convolution" argument analogous to that used for the entropy:
Consider a composite system (1+2) both systems thermodynamically large. Since T is fixed, the only constraints that can be "released" are volume and volume+number. Let me do volume:

When the partition is free to move,
$Z_{1+2}\left(V = V_1^0 + V_2^0\right) = \int dV_1 Z_1(V_1) Z_2(V - V_1)$.



But, $F = -k_B T \ln Z \Leftrightarrow Z = e^{-\frac{1}{k_B T}F}$, so

$$Z_{1+2}\left(V = V_1^0 + V_2^0\right) = e^{-\frac{1}{k_B T}F_{1+2}(V)} = \int dV_1 e^{-\frac{1}{k_B T}\left(F_1(V_1)+F_2(V-V_1)\right)}.$$

In a way that should be familiar now, the exponent has a maximum at

$$\frac{\partial}{\partial V_1}\left[-\frac{1}{k_B T}\left(F_1(V_1)+F_2(V-V_1)\right)\right] = 0 \Rightarrow \frac{\partial F_1}{\partial V_1} = \frac{\partial F_2}{\partial V_2}$$ (i.e., $P_1=P_2$).

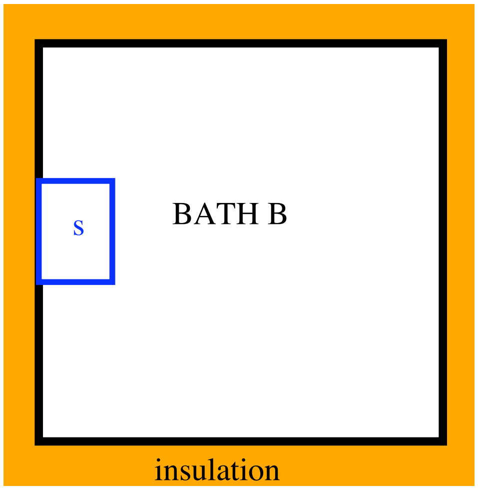
The second derivative is negative (so that it is a maximum) and goes as N (so that fluctuations are small), $\frac{\partial^2}{\partial V_1^2}\left[-\frac{1}{k_B T}F_1(V_1)\right] = \frac{\partial}{\partial V_1}\left(\frac{P}{k_B T}\right) = \frac{1}{k_B T}\cdot\frac{1}{\frac{\partial V}{\partial P}}\cdot\frac{1}{\frac{V}{V}} = -\frac{1}{k_B T V \kappa_T}$, where

$\kappa_T \equiv -\frac{1}{V}\frac{\partial V}{\partial P}\Big|_{T,N}$ is the "isothermal compressibility," which is intrinsically positive for any stable system.

The upshot is that $F_{1+2}(V) = F_1\left(V_1^f\right) + F_2\left(V_2^f\right) \le F_1\left(V_1^0\right) + F_2\left(V_2^0\right)$, where V_1^f is the volume at the maximum of the exponent, i.e., where $P_1=P_2$, and there is a net decrease of F in the equilibration process.

"Open" Systems:

1. Deriving the Boltzmann (Canonical) Distribution:
System (s) plus thrmal bath (B) with s<<B ($N_s << N_B$)
Consider a large system (the "bath," B) and a small system (the "system," s) . s can itself be thermodynamically large as long as it is much smaller than B. But, it can also be small (just a few degrees of freedom). Assume s+B is microcanonically distributed ("equal a priori probability"). Initially s and B are isolated. They are then put into thermal contact and come to equilibrium.



Claim: The small system s will be distributed canonically, i.e., $P_n \sim e^{-\frac{E_n^{(s)}}{k_B T}}$,
where T is the temperature $\frac{1}{T} = \frac{\partial S_B}{\partial E_B} \equiv \frac{1}{T_B}$ defined by the bath. (see Lect. 11.1)

What is the observed probability of a particular microstate $E_n^{(s)}$ of s, assuming that the entire system s+B has a known total energy $E = E_s^0 + E_B^0$,

so $P_n = \dfrac{e^{-\frac{E_n^{(s)}}{k_B T}}}{Z_s}$ with normalization $Z_s(T,V_s,N_s) \equiv \sum_n e^{-\frac{E_n^{(s)}}{k_B T}}$, where n runs over the states of s.

This distribution is called the "canonical" distribution.

The point is that the system s can have a variety of energies with different probabilities.

Range of variation of the energy of s can be large on the scale of E_s but still small on the scale of E_B.

Proof:

We assume that s+B is distributed microcanonically, so, for each particular combined state s,B, the probability is

$$P_{s+B}(E) = \frac{1}{\text{total number of states of } (s+B) \text{ with } (E \text{ to } E+\Delta E)} = \frac{1}{\Omega_{s+B}(E)\Delta E}.$$

Consider now a particular state n of s with energy $E_n^{(s)}$.

$$P_n = \frac{\text{total number states of B}\left(E - E_n^{(s)} \text{ to } E - E_n^{(s)} + \Delta E\right)}{\text{total number states of } (\text{s}+\text{B})(E \text{ to } E+\Delta E)} = \frac{\Omega_B\left(E - E_n^{(s)}\right)\Delta E}{\Omega_{s+B}(E)\Delta E} \propto \Omega_B\left(E - E_n^{(s)}\right)$$

.

But, $\Omega_B\left(E - E_n^{(s)}\right) = e^{\frac{1}{k_B} S_B\left(E - E_n^{(s)}\right)}$, so, expanding around the total energy E,

$$S_B\left(E - E_n^{(s)}\right) = S_B(E) - E_n^{(s)} \left.\frac{\partial S_B}{\partial E}\right|_E + \frac{1}{2} E_n^{(s)2} \left.\frac{\partial^2 S_B}{\partial E^2}\right|_E + \dots$$

Notice that

$\left.\dfrac{\partial S_B}{\partial E}\right|_E = \dfrac{1}{T_B}$ and $\left.\dfrac{\partial^2 S_B}{\partial E^2}\right|_E = \dfrac{\partial}{\partial E}\left(\dfrac{1}{T}\right) = -\dfrac{1}{T^2 C_{N_B,V_B}} \sim \dfrac{1}{N_B}$, so the quadratic and higher terms are down by factors of $\dfrac{N_s}{N_B} << 1$ and, therefore, negligible. It follows that

$$P_s\left(E_n^{(s)}\right) \propto \Omega_B\left(E - E_n^{(s)}\right) \propto e^{-\frac{E_n^{(s)}}{k_B T_B}}.$$ QED