Modern

Day 24

Today

0. Last time
I Entropy & the 2nd law
II Summary of feedback
   In class-exam vote: Fri. Nov 6th
III Statistical Mechanics
IV Binary Model Example

(Fix links to Mercury Spectrum)

I Second Law:

$$\boxed{\Delta S_{tot} \geq 0}$$

for any physical process

Remember: 2nd law tells you the direction in which heat flows — from hot to cold.

In a reversible process:

$$\boxed{\Delta S_{tot} = 0}$$ (can go either way)

0. We studied the free expansion of an ideal gas.

This is an irreversible process!

Gas is isolated ⇒ process is adiabatic $đQ = 0$

$đW = 0$ (nothing to push on)

So,

$$dU = 0 \Rightarrow dT = 0$$

Replace by an isothermal expansion between same initial and final volumes.

Irreversible process: process can only go one way:

$$\boxed{\Delta S_{tot} > 0}$$

How is the reversible result possible? In a reversible process, heat goes into the system and comes out of the environment at same T. So,

$$\Delta S_{system} = -\Delta S_{environment}$$

II The pace

too slow 4 5 6 7 too fast

\# of people: 2 2 5 2

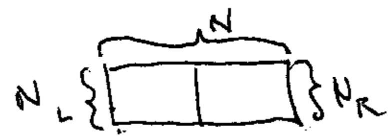
III Statistical Mechanics is the study of systems with many particles.

Let's introduce some terminology:

Microstate: describe every particle

Macrostate: characterized by thermodynamic variables $(N, V, P, T, U, S, \ldots)$

IV Binary Model



N molecules assigned to two chambers

Microstate: a particular assignment of the molecules — 2^N ways to do this.

Macrostate: Specification of N and N_L (it follows that $N_R = N - N_L$)

Multiplicity: $\Omega(N, N_L)$

To figure this out, let's do some

Multiplicity: (of a macrostate)

Ω = # of microstates corresponding to a given macrostate.

Entropy: $S = k \ln \Omega$

(k is Boltzmann's constant)

Let's study an example of these ideas

Special cases

$\Omega(1,1) = 1 \quad \Omega(1,0) = 1$

$\Omega(2,2) = 1, \; \Omega(2,1) = 2, \; \Omega(2,0) = 1$

$\boxed{\cdot \mid \times}$ or $\boxed{\times \mid \cdot}$

$\Omega(3,3) = 1, \; \Omega(3,2) = 3, \; \Omega(3,1) = 3, \; \Omega(3,0) = 1$

(e.g. $\boxed{{}^{R}{}_{G} \mid B}$, $\boxed{{}^{R}{}_{B} \mid G}$, $\boxed{{}^{B}{}_{G} \mid R}$)

Keep working cases until you see the pattern. Here it is

$$\Omega(N, N_L) = \underbrace{\binom{N}{N_L}}_{\text{choose function}} \underset{\text{defined by}}{\equiv} \frac{N!}{N_L!\,(N-N_L)!}$$

Factorials can be cumbersome, so

$$\Omega(N,s) = \frac{N!}{\left(\frac{N}{2}+s\right)!\left(\frac{N}{2}-s\right)!}$$

Suppose: N is large, and the "imbalance" is a small fraction of N:

$$N_L = \frac{N}{2}+s, \quad \text{with} \quad \frac{2s}{N} \equiv x \ll 1$$

Introduce Stirling's Approximation:

$$n! \approx \sqrt{2\pi n}\, e^{-n}\, n^n \quad (\text{for large } n)$$

We'll use this to simplify Ω (after some effort in calculation.).

$$\approx \frac{\sqrt{3\pi N}\; e^{-N}\, N^N}{\sqrt{2\pi\left(\frac{N}{2}+s\right)}\, e^{-\frac{N}{2}-s}\left(\frac{N}{2}+s\right)^{\frac{N}{2}+s}\sqrt{2\pi\left(\frac{N}{2}-s\right)}\, e^{-\frac{N}{2}+s}\left(\frac{N}{2}-s\right)^{\frac{N}{2}-s}}$$

$$= \sqrt{\frac{N}{2\pi}}\;\frac{N^N}{\sqrt{\left(\frac{N}{2}\right)^2-s^2}\;\underbrace{\left[\left(\frac{N}{2}+s\right)\left(\frac{N}{2}-s\right)\right]^{N/2}}_{=\left[\frac{N}{2}(1+x)\frac{N}{2}(1-x)\right]^{N/2}=\left(\frac{N}{2}\right)^N\left(1-x^2\right)^{\frac{N}{2}}}}\;\frac{\left(\frac{N}{2}-s\right)^s}{\left(\frac{N}{2}+s\right)^s}$$

$$= \sqrt{\frac{N}{2\pi}}\;\frac{2^N}{\left(\frac{N}{2}\right)\sqrt{1-x^2}\left(1-x^2\right)^{\frac{N}{2}}}\left(\frac{1-x}{1+x}\right)^s$$

Next time we will use Taylor expansion to prove that

$$\Omega(N,s) \approx \sqrt{\frac{2}{\pi N}}\; 2^N\, e^{-\frac{2s^2}{N}}.$$