Back to Entropy and Free Energy

Microcanonical Ensemble

$$S = k_B \ln \Omega$$

Example: Ideal Gas

$$\sum_i \frac{\vec{p}_i^{\,2}}{2m} = E$$ constrain

the $3N$ momenta to be on a

$3N$ dimensional sphere of radius

P, so that $P^2 = \sum_i \vec{p}_i^{\,2} = 2mE$

The surface area $\sim P^{3N-1}$

So $\Omega \overset{?}{\sim} \overset{\text{momenta}}{P^{3N-1}} \; \overset{\text{Position}}{V^N}$

If we ignore the -1 in $3N-1$

$$\Omega \overset{?}{\sim} \left(\sqrt{2mE}\right)^{3N} V^N$$

The more careful approach is

$$\Omega = \frac{1}{N!}\int \frac{d^{3N}p\, d^{3N}q}{h^{3N}}\, \delta\left(\sum \frac{\vec{p}_i^{\,2}}{2m} - E\right)$$

Semiclassical counting of states

Indistinguishability of particles

$$= \frac{V^N}{h^{3N} N!}\, \frac{2\pi^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)} \int dp\, p^{3N-1}\, \delta\left(p^2 - E\right)$$

$$\int dp\, p^{3N-1}\, \delta\left(p^2 - 2mE\right) = \int dp\, p^{3N-1} (2p)^{-1}\, \delta\left(p - \sqrt{2mE}\right)$$

$$= \left(\sqrt{2mE}\right)^{3N-2} \cdot \frac{1}{2}$$

$$\left[\frac{2\pi^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)} (2mE)^{\frac{3N}{2}-1}\, \frac{V^N}{N!\, h^{3N}} \cdot \frac{1}{2}\right] = \Omega(E, V, N)$$

$$S = k_B \ln \Omega(E, V, N)$$

For entropy per perparticle

$$\frac{S}{N} = \frac{1}{N} k_B \left[\frac{3N}{2} \ln\left(\frac{2\pi m E}{h^2}\right) - \ln(2mE) \right.$$

$$\left. + N \ln V - \ln \Gamma\left(\frac{N}{2}\right) - \ln N! \right]$$

Notice $\Gamma(M+1) = M!$

$$\ln \Gamma(M+1) \simeq M \ln M - M + O(\ln M)$$

(Striling's Formula)

$$\ln \Gamma\left(\frac{3N}{2}\right) \simeq \frac{3N}{2} \ln \frac{3N}{2} - \frac{3N}{2} + O(\ln N)$$

$$\ln N! \approx N \ln N - N + O(\ln N)$$

In $\frac{S}{N}$ ignoring terms of the order of $\frac{\ln N}{N}$ (and for some order $\frac{1}{N}$).

we get

$$\frac{S}{N} = k_B \left[\frac{3}{2} \ln\left(\frac{2\pi m E}{h^2}\right) + N \ln V - \frac{3}{2} \ln N - \ln N + \frac{5}{2} \right]$$

$$= k_B \left[\frac{3}{2} \ln\left(\frac{2\pi m E}{N h^2}\right) + N \ln \frac{V}{N} + \frac{5}{2} \right]$$

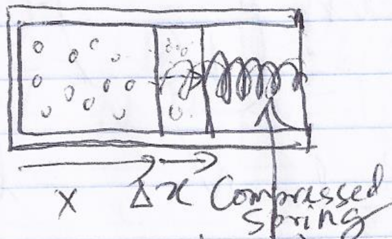
Sakur Tetrode formula

Note that, to figure [redacted] out

$$\left.\begin{aligned} \frac{1}{T} &= \frac{\partial S}{\partial E} \\ \text{and } \frac{P}{T} &= \frac{\partial S}{\partial V} \end{aligned}\right\} \text{ all we needed was } \Omega \sim E^{\frac{3N}{2}} V^N$$

We would need the rest if we [redacted] compute $\left(\frac{\partial S}{\partial N}\right)_{E,V}$ which is related to chemical potential.

Notice that gas at constant temperature could do work and apply forces



At constant temperature, the energy of ideal gas does not change.

The work is done by entropic forces. As volume increases entropy increases.

Where does the energy come from?
From the bath

$$\Omega_B(E_B)\,\Omega(E_G)$$

needs to be maximized

$$E_G \to E_G \qquad \Omega_B(E_B - \Delta V(x))\,\Omega(E_G, x)$$

$V(x)$ is the spring potential.
Ω_B goes down but Ω_G increases
Done quasistatically

$$\frac{\Delta S}{k_B} = \Delta x\, \partial_x \ln \Omega_G(E_G, x) + \Delta V(x)\, \partial_{E_B} \ln \Omega$$

$$= \Delta x \left[A \frac{\partial}{\partial V}\left(\ln \Omega_G\right)_{E_G} - \frac{f(x)}{k_B T} \right]$$

$$= \Delta x \left(\frac{A P(x)}{k_B T} - \frac{f(x)}{k_B T} \right)$$

$$= \frac{\Delta x}{k_B T}\left(AP(x) - f(x)\right)$$

As long as $AP(x) > f(x)$, it will push on, so that entropy keeps increasing.

More generally force applied would be

$$-\frac{\partial}{\partial x}(E - TS)$$

$$\underbrace{-\frac{\partial E}{\partial x}}_{\text{usual stuff}} + T\,\underbrace{\frac{\partial S}{\partial x}}_{\text{Entropic force}}$$

Entropic force depends strongly on temperature.