ENTROPY COMPUTATION IN THE MICROCANONICAL ENS.

$S = k \ln W$ W = number of states
k = Boltzmann's constant

$$W = \int_{\substack{E<H<E+\Delta \\ q \text{ in volume } V}} \frac{d^{3N}p \, d^{3N}q}{h^{3N} N!}$$

$E < H < E+\Delta$ defines a shell in phase space

NOTE: $\begin{cases} E \text{ prop. to } N \text{ (extensive)} \\ \Delta \text{ is of order } 1 \end{cases}$

Factor $1/N!$: it guarantees extensivity

IDEAL GAS $\quad H = \frac{1}{2m} \sum_i p_i^2$ [NOTE: <u>MONOATOMIC</u> GAS]

$$E<H<E+\Delta \implies 2mE < \sum_i p_i^2 < 2m(E+\Delta)$$

$$W = \frac{V^N}{h^{3N} N!} \int_{E<H<E+\Delta} d^{3N}p$$

$\longrightarrow$ change to hypersferical coordinates $P = \sqrt{\sum_i p_i^2}$

$$= \frac{V^N}{h^{3N} N!} S_{3N} \int_{\sqrt{2mE}}^{\sqrt{2m(E+\Delta)}} P^{3N-1} \, dP$$

S_{3N}: sphere in 3N-dimensions
This is the result of the integration over the solid angle.

$$= \frac{V^N}{h^{3N} N!} S_{3N} \frac{1}{3N} \left[(2m)^{3N/2} (E+\Delta)^{3N/2} - (2m)^{3N/2} E^{3N/2} \right]$$

$$= \left(\frac{(2m)^{3/2}}{h^3} V \right)^N \frac{S_{3N}}{N!} \frac{1}{3N} E^{3N/2} \left[\left(1 + \frac{\Delta}{E}\right)^{3N/2} - 1 \right]$$

For $N \to \infty$, $E = N\epsilon$

$$\left(1+\frac{\Delta}{E}\right)^{3N/2} = \left(1+\frac{\Delta}{N\epsilon}\right)^{3N/2} = e^{3\Delta/2\epsilon} \Rightarrow \text{number of order } 1$$

$$\ln W = N \ln\left(\frac{(2m)^{3/2}}{h^3} V\right) + \log\left(\frac{S_{3N}}{N!}\right) +$$

$$+ \underbrace{\log\left(\frac{1}{3N}\right)}_{\substack{\text{negligible} \\ O(\ln N)}} + \frac{3N}{2}\ln E + \underbrace{\ln\left(e^{3\Delta/2\epsilon} - 1\right)}_{\substack{\text{negligible} \\ O(1)}}$$

Now

$$\frac{S_{3N}}{N!} = \frac{2\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)} \frac{1}{N!}$$

$$\ln \frac{S_{3N}}{N!} = \underbrace{\ln 2}_{\text{negligible}} + \frac{3N}{2}\ln \pi - \ln N! - \ln \Gamma\left(\frac{3N}{2}\right)$$

negligible [we only keep terms $O(N), O(N \ln N)$]

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

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

$$= \frac{3N}{2}\ln N + \frac{3N}{2}\ln\frac{3}{2} - \frac{3N}{2}$$

sum $\Rightarrow \frac{5N}{2}\ln N - \frac{5N}{2} + \frac{3N}{2}\ln\frac{3}{2}$

$$\ln \frac{S_{3N}}{N!} = \frac{3N}{2}\ln \pi - \frac{5N}{2}\ln N + \frac{5N}{2} - \frac{3N}{2}\ln\frac{3}{2}$$

$$= -\frac{5N}{2}\ln N + \frac{5N}{2} + \frac{3N}{2}\ln\frac{2\pi}{3}$$

We get

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

$$+ \frac{3N}{2}\ln E$$

$$= N \ln\left[\left(\frac{4\pi m}{3h^2}\right)^{3/2} \underbrace{\frac{V}{N}}_{\text{intensive}} \underbrace{\left(\frac{E}{N}\right)^{3/2}}_{\text{intensive}}\right] + \frac{5N}{2}$$

MAIN RESULT: $\ln W$ is extensive AS IT SHOULD BE

Computation of T, p

$$dE = T\,dS - p\,dV + \mu\,dN \Longrightarrow dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{3}{2}k\frac{N}{E} \Longrightarrow \boxed{E = \frac{3}{2}NkT} \Longrightarrow E = c_V kTN$$

$$c_V = \frac{3}{2}$$

$$p = T\left(\frac{\partial S}{\partial V}\right)_{E,N} = Tk\frac{N}{V} \qquad \boxed{p = \frac{NkT}{V}}$$

Can we obtain the Helmholtz free energy or the Gibbs free energy from the microcanonical results?

THE ANSWER IS YES: all ensembles are equivalent.

For example, we compute $F(T,V,N)$, Helmholtz free energy : $F = E - TS$

We rewrite S in terms of T

$$S = Nk \ln\left[\left(\frac{4\pi m}{3h^2}\right)^{3/2} \frac{V}{N}\left(\frac{3}{2}kT\right)^{3/2}\right] + \frac{5Nk}{2}$$

$$= Nk \ln\left[\left(\frac{2\pi m k T}{h^2}\right)^{3/2} \frac{V}{N}\right] + \frac{5Nk}{2}$$

Define $\lambda = \dfrac{h}{\sqrt{2m\pi kT}}$ de Broglie wave length

$$S = Nk \ln\left(\frac{V}{N\lambda^3}\right) + \frac{5Nk}{2}$$

$$F = \frac{3}{2}NkT - NkT\ln\left(\frac{V}{N\lambda^3}\right) - \frac{5NkT}{2}$$

$$= NkT\ln\left(\frac{N\lambda^3}{V}\right) - NkT =$$

$$= NkT\ln(\rho\lambda^3) - NkT$$

This is consistent with the general result

$$F = NkT \ln \rho + N g(T)$$

here $g(T) = kT \ln \lambda^3 - kT$ $\quad$ (remember: λ depends on T, $\lambda \propto T^{-1/2}$)

$$\downarrow$$

$$T \ln T^{-3/2}$$