CANONICAL ENSEMBLE

We start from the partition function

$$Q(N,V,T) = \int \frac{d^{3N}p\, d^{3N}q}{h^{3N} N!} e^{-\beta H} \qquad \boxed{\beta = \frac{1}{kT}}$$

The connection with thermodynamics is given by

$$F = -kT \ln Q$$

↑ free energy (Helmholtz f. energy)

Now we have $\quad H = \sum_i \frac{p_i^2}{2m} + U(q_1 \cdots q_N)$

Now Q factorizes:

$$Q(N,V,T) = \frac{1}{h^{3N} N!} \int d^{3N}p\, e^{-\beta \sum_i \frac{p_i^2}{2m}} \int d^{3N}q\, e^{-\beta U}$$

$$Z = \int d^{3N}q\, e^{-\beta U}$$ ≡ configurational partition function [the interesting part!]

$$\int d^{3N}p\, e^{-\beta \sum_i \frac{p_i^2}{2m}} = \left[\int_{-\infty}^{+\infty} dp\, e^{-\beta p^2/2m} \right]^{3N} \qquad \left(\int dx\, e^{-\alpha x^2} = \sqrt{\frac{\pi}{\alpha}} \right)$$

$$= \left(\frac{2m\pi}{\beta} \right)^{3N/2} = (2m\pi kT)^{3N/2}$$

$$Q = \frac{1}{h^{3N} N!} (2m\pi kT)^{3N/2} Z = \frac{1}{\lambda^{3N} N!} Z$$

λ is the same as before $\quad \lambda = \frac{h}{(2m\pi kT)^{1/2}}$

The Helmholtz free energy is therefore

$$F = -kT \ln \left[\frac{Z}{\lambda^{3N} N!} \right]$$

The ideal gas case [<u>monoatomic</u> gas]:

$$Z = \int d^{3N}q \, e^{-\beta U} \underset{\substack{(U=0) \\ \text{no interactions}}}{=} \int d^{3N}q = V^N$$

$$\begin{aligned}
F^{(id)} &= -kT \ln \left(\frac{V^N}{\lambda^{3N} N!} \right) \\
&= -kT \ln \left(\frac{V^N}{\lambda^{3N}} \right) + kT \ln N! \\
&= -NkT \ln \left(\frac{V}{\lambda^3} \right) + NkT \ln N - NkT \\
&= NkT \ln \left(\frac{\lambda^3 N}{V} \right) - NkT = NkT \ln (\rho \lambda^3) - NkT
\end{aligned}$$

<u>General case</u>

$$F = -kT \ln \left(\frac{Z}{\lambda^{3N} N!} \right) = -kT \ln \left(\frac{V^N}{\lambda^{3N} N!} \right) - kT \ln \frac{Z}{V^N}$$

$$= \underbrace{F^{(id)}}_{\text{ideal gas contribution}} - kT \ln \left(\frac{Z}{V^N} \right)$$

the interesting part that encodes the interaction
"excess free energy"

Chemical potential

$$dF = -SdT - pdV + \mu dN \quad \text{(differential of } F\text{)}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial F^{id}}{\partial N}\right)_{T,V} + \left(\frac{\partial F^{exc}}{\partial N}\right)_{T,V}$$

$$\left(\frac{\partial F^{id}}{\partial N}\right)_{T,V} = \frac{\partial}{\partial N}\left[NkT \ln \frac{\lambda^3 N}{V} - NkT\right]_{T,V \text{ fixed}}$$

$$= kT \ln \frac{\lambda^3 N}{V} + kT - kT = kT \ln \frac{\lambda^3 N}{V} = kT \ln \rho\lambda^3$$

$$\mu = kT \ln \rho\lambda^3 + \left(\frac{\partial F^{exc}}{\partial N}\right)_{T,V}$$

ideal contribution $\mu^{(id)}$

excess contribution $\mu^{(exc)}$