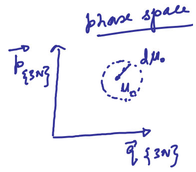
Canonical Ensemble (N,V,T)

Classical ideal gas $\quad \underbrace{\mu : \{\vec{q}_i, \vec{p}_i\}}_{\text{Microstates}} \in \underbrace{N,V,T}_{\text{Macrostate}}$

Probability density function (PDF): $p(\mu) = p(\{\vec{q}_i, \vec{p}_i\}) = \dfrac{1}{h^{3N}} \cdot \dfrac{1}{N!} \dfrac{e^{-\beta H(\mu)}}{Z(N,V,T)}$

Probability of finding system in neighborhood of some point in phase space : $\mu_0 : \{\vec{q}_i, \vec{p}_i\}$ & $\mu_0 + d\mu_0$ $\quad = p(\mu)\, d\mu \Big|_{\mu=\mu_0}$



Canonical partition function:

$$Z(N,V,T) = \frac{1}{h^{3N}} \cdot \frac{1}{N!} \cdot \int \cdots \int d^3\vec{q}_1\, d^3\vec{q}_2 \cdots d^3\vec{q}_N\, d^3\vec{p}_1\, d^3\vec{p}_2 \cdots d^3\vec{p}_N\, e^{-\beta \sum_{i=1}^{N} p_i^2/2m}$$

$$= \frac{1}{h^{3N}} \cdot \frac{1}{N!} \left(\int d^3\vec{q}_1 \right)^N \int \cdots \int d^3\vec{p}_1\, d^3\vec{p}_2 \cdots d^3\vec{p}_N\, e^{-\beta (p_1^2 + p_2^2 + \cdots p_N^2)/2m}$$

.... $\vec{p}_i$ & $\vec{q}_i$ are independent.

$$= \frac{1}{h^{3N}} \cdot \frac{1}{N!} \cdot V^N \left(\int d^3\vec{p}_1\, e^{-\beta p_1^2/2m} \right)^N$$

$$= \frac{1}{h^{3N}} \cdot \frac{1}{N!} \cdot V^N \Big(\underbrace{\iiint dp_x\, dp_y\, dp_z\, e^{-\beta (p_x^2 + p_y^2 + p_z^2)/2m}}_{1^{st} \text{ particle only}} \Big)^N$$

$$= \frac{1}{h^{3N}} \cdot \frac{1}{N!} V^N \left(\int dp_x\, e^{-\beta p_x^2/2m} \right)^{3N}$$

.... p_x, p_y, p_z are independent.

$$= \frac{1}{h^{3N}} \cdot \frac{1}{N!} V^N \left(\frac{2\pi m}{\beta} \right)^{\frac{3N}{2}}$$

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

$$Z(N,V,T) = \frac{V^N}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} \quad \ldots \text{ is dimensionless}$$

$$= \frac{V^N}{N!}\underbrace{\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}\cdot N}}_{V^{-1}}$$

This tells us $\left(\frac{2\pi m k_B T}{h^2}\right)^{1/2} = \lambda^{-1}$ "Inverse length scale"

this gives: $\lambda = \dfrac{h}{\sqrt{2\pi m k_B T}} \xrightarrow[T\to\infty]{} 0$

λ tells us the onset of Quantum Mechanics

$n = N/V$ "density"

Construct $\lambda_n = n^{-1/3}$ "density scale length"

Ratio: λ/λ_N decides if Q.M. are present!

$\lambda/\lambda_N \ll 1$ "Classical limit" High T, low n

$\lambda/\lambda_N \gg 1$ "Quantum limit" Low T, high n

Recall, Partition function: $Z(N,V,T) = \frac{V^N}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}}$

Build connection to thermodynamics: $F = -k_B T \ln Z$

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

$$F = -Nk_B T\left[\ln\left(\frac{eV}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right)\right] \quad \text{—— (1)}$$

Recall from thermodynamics: $F = E - TS$

$dF = dE - Tds - sdT$

$dF = -Pdv + \mu dN - sdT$ .... 1st law: $Tds = Pdv - \mu dN + dE$

Hence entropy: $S = -\frac{\partial F}{\partial T}\Big|_{N,V} = \frac{\partial (-F)}{\partial T}\Big|_{N,V}$

$$= Nk_B\left[\ln\left(\frac{eV}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right)\right] + Nk_B\cancel{T}\left[\frac{3}{2}\cdot\frac{\cancel{h^2}}{\cancel{2\pi m k_B T}}\cdot\frac{\cancel{2\pi m k_B}}{\cancel{h^2}}\right]$$

$$= Nk_B\left[\ln\left(\frac{eV}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right)\right] + \frac{3}{2}Nk_B \qquad (2)$$

For pressure: $P = -\frac{\partial F}{\partial V}\Big|_{N,T} = \frac{\partial (-F)}{\partial V}\Big|_{N,T}$

$$= \cancel{N}k_BT\cdot\left(\frac{N}{\cancel{e}V}\right)(\cancel{e}/\cancel{N})$$

$$= \frac{Nk_BT}{V}$$

Equation of state: $\boxed{PV = Nk_BT}$

Internal Energy: $E = F + TS = -Nk_BT\left[\cancel{\ln\left(\frac{eV}{N}\right)} + \frac{3}{2}\cancel{\ln\left(\frac{2\pi m k_B T}{h^2}\right)}\right] +$

$$TNk_B\left[\cancel{\ln\left(\frac{eV}{N}\right)} + \frac{3}{2}\cancel{\ln\left(\frac{2\pi m k_B T}{h^2}\right)}\right] + \frac{3}{2}Nk_BT$$

$\therefore \boxed{E = \frac{3}{2}Nk_BT}$

From thermodynamics: $\frac{\partial F}{\partial N}\Big|_{V,T} = \mu$ "Chemical Potential"

Recall, $F = -Nk_BT\left[\ln\left(\frac{eV}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right)\right]$

$$\mu = -\cancel{N}k_BT\left[\frac{\cancel{N}}{\cancel{eV}}\cdot\cancel{eV}\cdot\left(\frac{-1}{\cancel{N^2}}\right)\right] + \left[\ln\left(\frac{eV}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right)\right](-k_BT)$$

$$= k_BT\left[1 - \ln\left(\frac{eV}{N}\cdot\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right)\right]$$

$$= k_BT\left[\ln e - \ln\left(\frac{eV}{N}\cdot\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right)\right]$$

$$= k_B T \ln\left(\frac{N}{V}\cdot\left(\frac{h^2}{2\pi m k_B T}\right)^{3/2}\right)$$

$$\boxed{\mu = k_B T \ln\left(n\lambda^3\right)} \qquad \because n = N/V$$

Meaning of these derivatives:

$$dF = -PdV + \mu dN - SdT$$

$$P = -\left.\frac{\partial F}{\partial V}\right|_{N,T}$$

$$S = -\left.\frac{\partial F}{\partial T}\right|_{V,N}$$

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{V,T}$$

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Computation of Pressure: