Gibbs canonical Ensemble: (N, P, T)

Eg: Classical Ideal gas : $\mu = \{\vec{q}_i, \vec{p}_i\} \in V_\mu$

Fluctuating quantities are — $\mathcal{H}(\mu)$ (T const)

(i) $H(\nu) = \mathcal{H}(\mu) + PV_\mu$

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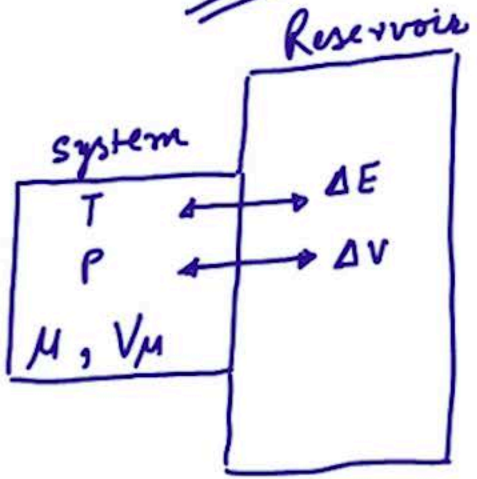
Fluctuating quantities are — Energy & Volume

(i) $H_\mu = \mathcal{H}(\mu) + PV_\mu$ "Enthalpy"

(ii) V_μ "Volume"

Probability density function (PDF) : $\rho(\mu, V_\mu) = \dfrac{e^{-\beta[\mathcal{H}(\mu) + PV_\mu]}}{Z(N,P,T)} \cdot \dfrac{1}{N!}$.

$V_0 \equiv$ volume scale

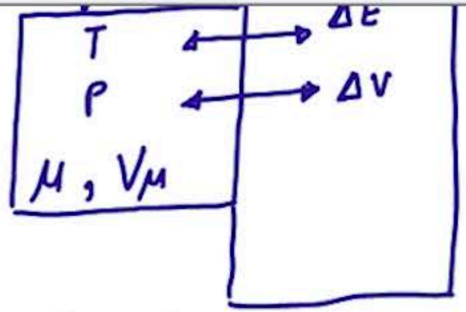


Phase space : $\mu \in \{\vec{q}_i, \vec{p}_i\}$

& Volume of box V_μ

Partition function : $Z(N,P,T) = \frac{1}{h^{3N}} \cdot \frac{1}{N!} \cdot \frac{1}{V_0} \int_{V=0}^{\infty} dV \int \cdots \int \prod_{j=1}^{3N} dq_j \, dp_j \, e^{-\beta[}$

& Volume of box V_μ



Partition function : $Z(N,P,T) = \frac{1}{h^{3N}} \cdot \frac{1}{N!} \cdot \frac{1}{V_0} \int_{V=0}^{\infty} dV \int \cdots \int \prod_{j=1}^{3N} dq_j \, dp_j \, e^{-\beta\left[\sum_{\alpha=1}^{3N} p_\alpha^2/2m + PV\right.}$

$$= \frac{1}{h^{3N}} \cdot \frac{1}{N!} \cdot \frac{1}{V_0} \int_{V=0}^{\infty} dV \; V^N \left(\int_{p_1=-\infty}^{+\infty} dp_1 \, e^{-\beta p_1^2/2m} \right)^{3N} \qquad \ldots\ldots \quad V^N = \left(\int_{q \in \text{box}} d^3q \right)^N$$

Partition function :
$$Z(N,P,T) = \frac{1}{h^{3N}} \cdot \frac{1}{N!} \cdot \frac{1}{V_0} \int_{V=0}^{\infty} dV \int \cdots \int \prod_{j=1}^{3N} dq_j \, dp_j \, e^{-\beta\left[\sum_{\alpha=1}^{3N} p_\alpha^2/2m + PV\right]}$$

$$= \frac{1}{h^{3N}} \cdot \frac{1}{N!} \cdot \frac{1}{V_0} \int_{V=0}^{\infty} dV \; V^N \left(\int_{p_1=-\infty}^{+\infty} dp_1 \, e^{-\beta p_1^2/2m} \right)^{3N} e^{-\beta P V}$$

$$\ldots\ldots \; V^N = \left(\int_{q \in \text{box}} d^3 q \right)^N$$

$$= \frac{1}{h^{3N}} \cdot \frac{1}{N!} \frac{1}{V_0} \int_{V=0}^{\infty} dV \; V^N \left(\frac{2\pi m}{\beta}\right)^{3N/2} e^{-\beta P V}$$

$$= \frac{1}{h^{3N} V_0 N!} \left(\frac{2\pi m}{\beta}\right)^{3N/2} \underbrace{\int_0^{\infty} dV \; V^N \; e^{-\beta P V}}$$

$$= \frac{1}{N! \, V_0} \left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} \mathcal{L}\left[V^N\right]$$

$\mathcal{L}[V^N]$ = Laplace transform of V^N.

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$$\mathcal{L}[f(x)] = \int_0^{\infty} e^{-sx} f(x)\, dx = F(s)$$

$$\mathcal{L}[V^N] = \int_0^{\infty} e^{-\beta P V}\, V^N\, dV$$

$$= \cancelto{0}{\frac{V^N e^{-\beta P V}}{(-\beta P)}\Bigg|_0^{\infty}} - \int_0^{\infty} \frac{N V^{N-1} e^{-\beta P V}}{(-\beta P)}\, dV$$

$$= \frac{N}{\beta P} \cdot \mathcal{L}[V^{N-1}]$$

$$h^{3N} V_0 N! \left(\quad \beta \quad \right) \quad \int_0$$

$$= \frac{1}{N!\, V_0}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} \mathcal{L}\left[V^N\right]$$

$\mathcal{L}[V^N]$ = Laplace transform of V^N

$$= \frac{1}{N!\, V_0}\left(\frac{1}{\lambda(T)}\right)^{3N} \cdot \frac{N!}{(\beta P)}$$

$$= \frac{N!}{(\beta P)^{N+1}} = F(\beta P)$$

$$\mathcal{L}[f(x)] = \int_0^\infty e^{-sx} f(x)\, dx = F(s)$$

$$\mathcal{L}[V^N] = \int_0^\infty e^{-\beta P V}\, V^N\, dV$$

$$-\beta P V \Big/ \infty \qquad \infty \qquad N-1 \quad -\beta P$$

$$Z(N,P,T) = \frac{1}{\lambda(T)^{3N}} \cdot \frac{1}{(\beta P)^{N+1}}$$

$\lambda(T)$: De Broglie scale $= \dfrac{h}{\sqrt{2\pi m k_B T}}$

$$\lambda_n \; : \; n^{-1/3}$$

$$\lambda(T)/\lambda$$

$$\mathcal{L}[f(x)] = \int_0^{\infty} e^{-sx} f(x)\, dx = F(s)$$

$$\mathcal{L}[V^N] = \int_0^{\infty} e^{-\beta P V} V^N \, dV$$

$$= \cancel{\frac{V^N e^{-\beta P V}}{(-\beta P)}\Bigg|_0^{\infty}}^{\,0} - \int_0^{\infty} \frac{N V^{N-1} e^{-\beta P V}}{(-\beta P)} dV$$

$$= \frac{N}{\beta P} \cdot \mathcal{L}[V^{N-1}]$$

$\vdots \qquad \vdots$

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$$Z(N,P,T) = \frac{1}{\lambda(T)^{3N}} \cdot \frac{1}{(\beta P)^{N+1}} \qquad (1)$$

$\lambda(T)$: De Broglie scale $= \dfrac{h}{\sqrt{2\pi m k_B T}}$

λ_n : $n^{-1/3}$ "Density length scale"

$\lambda(T)/\lambda_n \gg 1$ "Quantum effects"

High n, low T

$$\mathcal{L}[f(x)] = \int_0 e^{\cdots} f(x)\,dx = \cdots$$

$$\mathcal{L}[V^N] = \int_0^\infty e^{-\beta P V} V^N \, dV$$

$$= \cancel{\left.\frac{V^N e^{-\beta P V}}{(-\beta P)}\right|_0^\infty}^{\,0} - \int_0^\infty \frac{N V^{N-1} e^{-\beta P V}}{(-\beta P)} dV$$

$$= \frac{N}{\beta P} \cdot \mathcal{L}[V^{N-1}]$$

$\vdots \qquad \vdots$

$\vdots$

$N!$

2/2

$\lambda(T)$ (βP)

$$G = -k_B T\left[-3N \ln \lambda(T) - (N+1)\ln(\beta P)\right] \qquad (2)$$

From thermodynamics:

$$G = \overset{\text{Enthalpy}}{H} - TS$$

$$dG = dH - Tds - sdT = \underbrace{dE + Pdv + vdP}_{dH} - Tds - sdT$$

$$= \mu dN + VdP - sdT \quad \ldots\ldots$$

1^{st} law: $Tds = Pdv + dE - \mu d$

$$dG = \mu\, dN + V dP - S dT \quad \ldots\ldots$$

Invoking

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

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

$$S = \left.\frac{\partial G}{\partial T}\right|_{N,P}$$

Compute $V = \left.\frac{\partial G}{\partial P}\right|_{N,T} = (N+1) k_B T \left.\frac{\partial}{\partial P} \ln(\beta P)\right|_{N,T}$

$$= (N+1) k_B T \frac{1}{\cancel{\beta} P} \cdot \cancel{\beta}$$

$$V \approx N k_B T / P \quad \ldots\ldots \because N \gg 1$$

$$N + 1 \approx N$$

Computing H:

$$H = \sum_{\mu, V_\mu} \left(\mathcal{H}(\mu) + P V_\mu \right) P(\mu, V_\mu)$$

$$= \frac{\sum_{\mu, V_\mu} \left(H(\mu) + P V_\mu \right) e^{-\beta [H(\mu) + P V_\mu]}}{Z(N, P, T)}$$

$$= \frac{-\frac{\partial}{\partial \beta} \sum_{\mu, V_\mu} e^{-\beta [\mathcal{H}(\mu) + P V_\mu]}}{Z(N, P, T)}$$

$$H = -\frac{1}{Z}\cdot\frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\ln Z = \frac{\partial}{\partial \beta}(-\ln Z)$$

Recalling, $Z(N,P,T) = \frac{1}{\lambda(T)^{3N}}\cdot\frac{1}{(\beta P)^{N+1}}$

$$-\ln Z = +3N\ln\lambda(T) + (N+1)\ln(\beta P)$$

$$H = \frac{\partial}{\partial \beta}\left[3N \ln \lambda(T) + (N+1)\ln(\beta P)\right]$$

$$= \frac{3N}{\lambda(T)} \cdot \frac{\partial}{\partial \beta}\lambda(T) + \frac{(N+1)}{\beta \cancel{P}} \cdot \cancel{P}$$

$$\ldots\ldots \lambda(T) = \frac{h}{(2\pi m k_B T)^{1/2}} = h\left(\frac{\beta}{2\pi m}\right)^{1/2}$$

$$= \frac{3N}{h\,\beta^{1/2}}(2\pi m)^{1/2} \cdot \frac{h}{(2\pi m)^{1/2}} \cdot \frac{1}{\cdot}$$

$$= \frac{3N\,(\cancel{2\pi m})^{1/2}}{\cancel{h}\,\beta^{1/2}} \cdot \frac{\cancel{h}}{(\cancel{2\pi m})^{1/2}} \cdot \frac{1}{2\beta^{1/2}} + \frac{N}{\beta}$$

$$\ldots\ldots\ \lambda(T) = \frac{h}{(2\pi m k_B T)^{1/2}} = h\left(\frac{\beta}{2\pi m}\right)^{1/2}$$

$N+1 \approx N$ (large N)

$$= \frac{3}{2} N k_B T + N k_B T = \frac{5}{2} N k_B T$$

$$H = \frac{5}{2} N k_B T$$

$\therefore\ C_p$ = Heat capacity at const. Pressure $= \left.\frac{\partial H}{\partial T}\right|_p = \frac{5}{2} N k_B$.