Isobaric Ensemble

$$\omega = F(V,T,N) \rightarrow G(P,T,N) = \bar{\omega}$$

Constant volume — Constant pressure

$$G = F + PV$$ thermodynamic

$$A = V \qquad P = \bar{A}$$

$$\mathcal{Z}_{ib}(P,TN) = \int_0^\infty dV\, e^{-\beta[F(V,T,N)+PV]}$$

which defines the distribution of volumes at constant pressure

$$P(V) \propto e^{-\beta[F(V)+PV]}$$

$$\frac{\partial}{\partial V}(F(V)+PV)\Big|_{V^*} = 0 \Rightarrow \underbrace{\left(\frac{\partial F}{\partial V}\right)_{V^*}}_{-P_{\text{system}}} = -P_{\text{bath}}$$

$$\frac{\partial^2}{\partial V^2}(F+PV) > 0$$

$$-\frac{\partial P}{\partial V} = +\frac{1}{V\kappa_T} > 0$$

$$\sigma_V^2 = k_B T\, V \kappa_T > 0$$ volume fluctuations

Perfect gas in the Isobaric Ensemble (2)

$$Z_{con} = \int \frac{d^{3N}p \, d^{3N}q}{h^{3N} N!} e^{-\beta \sum_i \frac{p_i^2}{2m}} =$$

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

$$= \frac{V^N}{h^{3N} N!} \left(\sqrt{2\pi m k_B T} \right)^{3N} = \frac{V^N}{\lambda^{3N} N!}$$

$$\boxed{\lambda = \frac{h}{\sqrt{2\pi m k_B T}}}$$

De Broglie Thermal Wave lenght

$$Z_{ib} = \int_0^\infty dV \, e^{-\beta P V} Z_{con}(V) =$$

Normalization

$$= \int \frac{dV}{\lambda^3} e^{-\beta P V} \frac{V^N}{\lambda^{3N} N!} = \frac{1}{(\beta P)^{N+1}} \frac{1}{\lambda^{3N} N!} \underbrace{\int_0^\infty dx \, e^{-x} x^N}_{N!}$$

normalization

$$Z_{ib} = \cancel{\frac{1}{\beta P}} \frac{1}{(\beta P \lambda^3)^{N+1}} = \frac{\cancel{\lambda^3}}{(\cancel{\beta} P \lambda^3)^{N+1}}$$

$$G = -\frac{1}{\beta} \ln Z_{ib} = \frac{N+1}{\beta} \ln(\beta P \lambda^3) = \mu N$$

definition of chemical potential

for large N

$$\boxed{\mu = k_B T \ln\left(\frac{P \lambda^3}{k_B T} \right)}$$

chemical potential of perfect gas

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

$$\frac{\partial G}{\partial P} = \frac{\partial}{\partial P} N k_B T \ln P = \frac{N k_B T}{P} \Rightarrow \text{gas' law}$$

$$\left(\frac{\partial^2 G}{\partial P^2}\right) = \left(\frac{\partial V}{\partial P}\right)_T = -\frac{N k_B T}{P^2}$$

$$-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{N k_B T}{P^2 V} = \frac{1}{P} > 0$$ isothermal compressibility of perfect gas

fugacity of perfect gas

$$z = e^{\beta\mu} = \frac{P\lambda^3}{k_B T}$$

for classical approximation to be true

$$\left(\frac{V}{N}\right) \gg \lambda^3$$

interparticle distance

for a perfect gas

$$V = \frac{N k_B T}{P} \qquad \frac{V}{N} = \frac{k_B T}{P} \gg \lambda^3 \Rightarrow z \ll 1$$

the limit $z \to 0$ is the classical low density limit