Pressure ensemble

$T, P, N \longrightarrow G$ free Gibbs energy.

- S system in contact with a heat reservoir and work R
- E_0, V_0 energy and total volume.
- Diatermic wall and free for moving but impermeable.

$$P_j = c\,\Omega_R(E_0 - E_j, V_0 - V_j)$$

$\Omega_R(E,R) \rightarrow$ Number of accessible states of R with E and V.

$$\ln(P_j) = \text{constant} + \left(\frac{\partial \ln(\Omega_R)}{\partial E}\right)_{E_0,V_0}(-E_j) + \left(\frac{\partial \ln(\Omega)}{\partial V}\right)_{E_0,V_0}(-V_j) + \dots$$

$$\frac{\partial \ln(\Omega_R)}{\partial E} = \frac{1}{K_B T} \qquad \frac{\partial \ln(\Omega_R)}{\partial V} = \frac{p}{K_B T}$$

then

$$\ln(P_j) = \text{constant} - \frac{E_j}{K_B T} - \frac{pV_j}{K_B T}$$

$$P_j = \frac{1}{Y}\exp(-\beta E_j - \beta p V_j)$$

$$Y := \sum_j \exp(-\beta E_j - \beta p V_j)$$ Partition function

$$Y = \underbrace{\sum_V \exp(-\beta p V) \sum_j}_{j \text{ restricted to } V} \exp[-\beta E_j(V)]$$

$$= \sum_V \exp(-\beta p V)\, Z(\beta, V)$$

$$= \sum_V \exp(-\beta p V + \ln(Z)) \sim \exp\left[-\beta \min_V(-K_B T \ln(Z) + pV)\right]$$

then, $$Y \sim \exp\left[-\beta \min_{V} \{ F + pV \}\right]$$

thus, $$Y \sim \exp(-\beta G)$$

therefore, $$G = G(T,p,N) \longrightarrow -\frac{1}{\beta} \ln(Y(T,p,N))$$

$$g(T,p) = -\frac{1}{\beta} \lim_{N\to\infty} \frac{1}{N} \ln(Y(T,p,N))$$

Fluctuations

$$\langle E_j \rangle = Y^{-1} \sum_j E_j \exp(-\beta E_j - \beta p V_j)$$

$$= -\frac{\partial}{\partial \beta} \ln(Y) + \frac{p}{\beta} \frac{\partial}{\partial p} \ln(Y)$$

$$= \frac{\partial}{\partial p} \beta G + \frac{p}{\beta} \frac{\partial}{\partial p} (-\beta G)$$

$$= \frac{\partial}{\partial \beta} \beta(U - TS + pV) - \frac{p}{V} \frac{\partial}{\partial p} \beta(U - TS + pV)$$

$$= U + pV - \frac{p}{\beta} \beta V = U$$

Finally, $$\langle E_j \rangle = U$$ intern energy

$$\langle V_j \rangle = Y^{-1} \sum_j V_j \exp(-\beta E_j - \beta p V_j)$$

$$= -\frac{1}{\beta} \frac{\partial}{\partial p} \ln(Y)$$

$$= -\frac{1}{\beta} \frac{\partial}{\partial p} - \beta G$$

$$= \frac{1}{\beta} \frac{\partial}{\partial p} \beta(U - TS + pV) = V$$

$$\langle V_j \rangle = V$$ volume of the system.

$$\langle (\Delta V)^2 \rangle = \langle (V_j - \langle V_j \rangle)^2 \rangle = \langle V_j^2 \rangle - \langle V_j \rangle^2$$

$$= Y^{-1} \sum_j V_j^2 \exp(-\beta E_j - \beta p V_j) - \left[Y^{-1} \sum_j V_j \exp(-\beta E_j - \beta p V_j) \right]^2$$

$$= \frac{1}{\beta^2} Y^{-1} \frac{\partial^2 Y}{\partial p^2} - \frac{1}{\beta^2} \left[Y^{-1} \frac{\partial Y}{\partial p} \right]^2$$

$$= \frac{1}{\beta^2} \frac{\partial}{\partial p} \left(Y^{-1} \frac{\partial Y}{\partial p} \right) = \frac{1}{\beta^2} \frac{\partial}{\partial p} \left(\frac{\partial}{\partial p} \ln(Y) \right)$$

but,

$$\frac{\partial}{\partial p} \ln(Y) \longrightarrow -\beta \frac{\partial G}{\partial p} = -\beta V$$

then,

$$\langle (\Delta V)^2 \rangle = -\frac{1}{\beta} \left(\frac{\partial V}{\partial p} \right)_{T,N} = k_B T V K_T \geq 0$$

$K_T \rightarrow$ Thermic compressibility.

$$\frac{\langle (\Delta V)^2 \rangle^{1/2}}{\langle V \rangle} = \frac{\sqrt{k_B T V K_T}}{V} \sim \frac{1}{\sqrt{V}} \xrightarrow{\text{thermodynamic limit}} 0$$

Ideal gas

$$Z = Z(T, V, N) = \frac{1}{N!} Z^N$$

$$Z_1 = \left(\frac{2\pi m}{\beta h^2} \right)^{3/2} V$$

$$Y(T, p, N) = \int_0^\infty dV \exp(-\beta p V) Z(T, V, N)$$

$$= \frac{1}{N!} \left(\frac{2\pi m}{\beta h^2} \right)^{3N/2} \int_0^\infty V^N \exp(-\beta p V) dV$$

$$\int_0^\infty x^n e^{-\alpha x} dx = (-1)^n \frac{d^n}{dx^n} \int_0^\infty e^{-\alpha x} dx = (-1)^{2N} N! \alpha^{-N-1} \quad ; \alpha > 0.$$

then,

$$Y(T,p,N) = \frac{1}{N!}\left(\frac{2\pi m}{\beta h^2}\right)^{3N/2} \frac{N!}{(\beta N)^{N+1}}$$

$$\lim_{N\to\infty} \frac{1}{N}\ln(Y) = \frac{3}{2}\ln\left(\frac{2\pi m}{\beta h^2}\right) - \ln(\beta p)$$

$$g(T,p) = -\frac{3}{2}K_B T\ln\left(\frac{2\pi m K_B T}{h^2}\right) - K_B T\ln\left(\frac{K_B T}{p}\right)$$

$$s = -\left(\frac{\partial g}{\partial T}\right) = \frac{5}{2}K_B\ln(T) - K_B\ln(p) + \text{constant.}$$

$$C_p = T\left(\frac{\partial s}{\partial T}\right)_p = \frac{5}{2}K_B$$

$$v = \left(\frac{\partial g}{\partial p}\right)_T = \frac{K_B T}{p}$$

Boyle law