1.3-9 isothermal – isobaric ensemble: N, p, T constant

$$\sum_V \sum_j a_{Vj} = \mathcal{A}$$

$$\sum_V \sum_j a_{Vj} E_{Vj} = \mathcal{E}$$

$$\sum_V \sum_j a_{Vj} V = \mathcal{V}$$

$$\frac{\partial}{\partial a_{Vj}} \left\{ \ln W(\bar{a}) - \alpha \sum_V \sum_j a_{Vj} - \beta \sum_V \sum_j a_{Vj} E_{Vj} - \delta \sum_V \sum_j a_{Vj} V \right\} = 0$$

$$\Rightarrow \quad a^*_{Vj} = e^{-\alpha} e^{-\beta E_{Vj}} e^{-\delta V}$$

$$P_{Vj}(N,p,T) = \frac{a^*_{Vj}}{\mathcal{A}} = \frac{e^{-\beta E_{Vj}} e^{-\delta V}}{\sum_V \sum_j e^{-\beta E_{Vj}} e^{-\delta V}}$$

$$\Delta(N,p,T) = \sum_V \sum_j e^{-\beta E_{Vj}} e^{-\delta V}$$

sum over states

Change to sum over levels; need degeneracy $\Omega(N,V,E)$

$$\Delta(N,p,T) = \sum_V \sum_E \Omega(N,V,E) e^{-\beta E(V)} e^{-\delta V}$$

2. 3-15 $\Xi(V,T,\mu) = \sum_N Q(N,V,T)\, e^{+\beta\mu N} \longrightarrow Q(\bar N,V,T)\, e^{+\beta\mu\bar N}$

$$= \Omega(\bar N, V, \bar E)\, e^{-\bar E/kT}\, e^{\mu\bar N/kT}$$

$$\ln\Xi = \ln\Omega - \frac{\bar E}{kT} + \frac{\mu\bar N}{kT} = \frac{S}{k} - \frac{E}{kT} + \frac{\mu N}{kT}$$

$$\ln\Xi = -\frac{(E-TS-\mu N)}{kT} = \frac{pV}{kT}$$

$pV = kT\ln\Xi$ $\quad$ pV is characteristic fn of Ξ

$$\Delta(N,p,T) = \sum_V Q(\cancel{N},V,T)\, e^{-\beta pV} \Rightarrow Q(N,\bar V,T)\, e^{-\beta p\bar V}$$

$$= \Omega(\cancel{N},\bar V,E)\, e^{-\bar E/kT}\, e^{-\beta p\bar V}$$

$$\ln\Delta = \ln\Omega - \frac{\bar E}{kT} - \frac{p\bar V}{kT} = \frac{S}{k} - \frac{E}{kT} - \frac{pV}{kT}$$

$$\ln\Delta = -\frac{(E-TS+pV)}{kT} = -\frac{G}{kT}$$

$-G = kT\ln\Delta$ $\quad$ $-G$ is characteristic fn of Δ

$$\Phi(V,E,\beta\mu) = \sum_N \Omega(N,V,E)\, e^{+\beta\mu N} \to \Omega(\bar N,V,E)\, e^{+\beta\mu\bar N}$$

$$\ln\Phi = \ln\Omega + \beta\mu N = \frac{S}{k} + \frac{\mu N}{kT} = \frac{(TS+\mu N)}{kT}$$

$\mu N = G \Rightarrow TS+\mu N = TS + G = TS + (E-TS+pV) = E+pV = H$

$\Rightarrow H = kT\ln\Phi$ $\quad$ H is characteristic fn of Φ

3-20 We will treat volume as discrete.

$$\Delta = \sum_{vj} e^{-\beta E_{vj}} e^{-\beta p v} \qquad P_{vj} = \frac{e^{-\beta E_{vj}} e^{-\beta p v}}{\Delta}$$

$$\bar{V} = \sum_{vj} V P_{vj} = -\left(\frac{\partial \ln \Delta}{\partial \beta p}\right)_{v,j}$$

$$\overline{V^2} = \sum_{vj} V^2 P_{vj} = \frac{1}{\Delta} \sum V^2 e^{-\beta E_{vj}} e^{-\beta p v}$$

$$= -\frac{1}{\Delta} \frac{\partial}{\partial \beta p} \sum V e^{-\beta E_{vj}} e^{-\beta p v}$$

$$= -\frac{1}{\Delta} \frac{\partial}{\partial \beta p} (\bar{V} \Delta) = -\frac{\partial \bar{V}}{\partial \beta p} - \bar{V} \underbrace{\frac{\partial \ln \Delta}{\partial \beta p}}_{-\bar{V}}$$

$$\sigma_v^2 = \overline{V^2} - \bar{V}^2 = -\frac{\partial \bar{V}}{\partial \beta p} + \bar{V}^2 - \bar{V}^2 = -\frac{\partial \bar{V}}{\partial \beta p}$$

$$= -kT \frac{\partial \bar{V}}{\partial p} = kT \bar{V} \kappa$$

$$\boxed{\sigma_v = (kT \bar{V} \kappa)^{1/2}}$$

$$\frac{\sigma_v}{\bar{V}} = \left(\frac{kT\kappa}{\bar{V}}\right)^{1/2}$$

For ideal gas, $\kappa = \frac{1}{p}$

$$\frac{\sigma_v}{\bar{V}} = \left(\frac{kT}{p\bar{V}}\right)^{1/2} = \left(\frac{1}{N}\right)^{1/2} \qquad Q.E.D.$$

We have shown that relative fluctuation in V get very small as N gets large.

4.5-23 Two-component systems:

$$\Xi(V,\beta,\gamma_1,\gamma_2) = \sum_{N_1,N_2,j} e^{-\beta E_{N_1 N_2 j}} e^{-\gamma_1 N_1} e^{-\gamma_2 N_2}$$

$$\overline{N_1} = \sum_{N_1 N_2 j} N_1 P_{N_1 N_2 j} = -\frac{1}{\Xi}\left(\frac{\partial \Xi}{\partial \gamma_1}\right)_{\beta, V, \gamma_2} = -\frac{\partial \ln \Xi}{\partial \gamma_1}$$

$$\overline{N_2} = -\frac{1}{\Xi}\left(\frac{\partial \Xi}{\partial \gamma_2}\right)_{\gamma_1, V, \beta} = -\frac{\partial \ln \Xi}{\partial \gamma_2}$$

$$\overline{N_1 N_2} = \frac{1}{\Xi}\sum_{N_1 N_2 j} N_1 N_2 e^{-\beta E_{N_1 N_2 j}} e^{-\gamma_1 N_1} e^{-\gamma_2 N_2}$$

$$= -\frac{1}{\Xi}\frac{\partial}{\partial \gamma_1}\sum_{N_1 N_2 j} N_2 e^{-\beta E_{N_1 N_2 j}} e^{-\gamma_1 N_1} e^{-\gamma_2 N_2}$$

$$= -\frac{1}{\Xi}\frac{\partial}{\partial \gamma_1}(\overline{N_2}\,\Xi) = -\frac{\partial \overline{N_2}}{\partial \gamma_1} - \overline{N_2}\underbrace{\frac{\partial \ln \Xi}{\partial \gamma_1}}_{\overline{N_1}}$$

$$= -\frac{\partial \overline{N_2}}{\partial \gamma_1} + \overline{N_1}\,\overline{N_2}$$

$$\overline{N_1 N_2} - \overline{N_1}\,\overline{N_2} = -\frac{\partial \overline{N_2}}{\partial \gamma_1}$$

$$\gamma_1 = -\mu_1/kT$$

$$\Rightarrow \overline{N_1 N_2} - \overline{N_1}\,\overline{N_2} = kT\left(\frac{\partial \overline{N_2}}{\partial \mu_1}\right)_{V,T,\mu_2}$$

Analogous arguments lead to

$$\overline{N_1 N_2} - \overline{N_1}\,\overline{N_2} = kT\left(\frac{\partial \overline{N_1}}{\partial \mu_2}\right)_{V,T,\mu_1}$$

Q.E.D.

5.

3-24 $\overline{H^2} - \overline{H}^2 = \sum_{Vj} H_j^2(V)\, P_j(V) - \overline{H}^2$

where $P_j(V) = \dfrac{e^{-\beta E_j(V)} e^{-\beta pV}}{\overline{Q}(p,V,T)}$

Partition fn. for NPT ensemble $\rightarrow$ $\overline{Q}(p,V,T) \equiv \sum_{Vj} e^{-\beta E_j(V)} e^{-\beta pV}$

$H = E + pV \Rightarrow \overline{Q} = \sum_{Vj} e^{-\beta H_j}$

$$\sum_{Vj} H_j^2(V)\, P_j(V) = \frac{1}{\overline{Q}} \sum_{Vj} (E_j + pV) H_j\, e^{-\beta E_j} e^{-\beta pV}$$

$$= \frac{1}{\overline{Q}} \sum_{Vj} (E_j + pV) H_j\, e^{-\beta(E_j + pV)}$$

$$= -\frac{1}{\overline{Q}} \frac{\partial}{\partial \beta} (\overline{H}\,\overline{Q}) = -\frac{\partial \overline{H}}{\partial \beta} - \overline{H} \underbrace{\frac{\partial \ln \overline{Q}}{\partial \beta}}_{-\overline{H}}$$

$$= -\frac{\partial \overline{H}}{\partial \beta} + \overline{H}^2$$

$$\overline{H^2} - \overline{H}^2 = -\frac{\partial \overline{H}}{\partial \beta} = kT^2 \left(\frac{\partial \overline{H}}{\partial T}\right) = kT^2 C_p \qquad \text{Q.E.D.}$$