$dF = -S \cdot dT - P \cdot dV + \mu \cdot dN$

$P_{liquid} = P_{gas}$

$\mu_{liquid} = \mu_{gas}$

$$P = (dF(T,V1,N1)/dV)_{T,N1} = (dF(T,V2,N2)/dV)_{T,N2} \quad (1)$$

$$\mu = (dF(T,V1,N1)/dN)_{T,V1} = (dF(T,V1,N1)/dN)_{T,V1} \quad (2)$$

$F/V = f$

$F(T,N,V)/V = f(T,N/v) = f(T,n)$

??

??

$$\mu = (dF(T,V,N)/dN)_{T,V} \cdot \frac{V}{V} = \left(\frac{d(F(T,V,N)/V)}{d(N/V)}\right)_{T,V} = (df(T,n)/dn)_{T,V}$$

$$Z = Z_{ideal} \cdot Z_{HS} \cdot Z_{disp}$$

$$Z_{ideal} = V^N \cdot \frac{1}{N!} \int \cdots \int e^{-\beta \cdot [P_1^2/2m + P_2^2/2m + \ldots]} d\vec{P_1} \cdot d\vec{P_2} \cdots d\vec{P_N}$$

$$Z_{HS} = e^{-S_{exc.\infty}/k}$$

$$Z_{disp} = \frac{Z_{interaction}}{Z_{HS}} = \frac{\sum_i \alpha \cdot D(E_i) \cdot e^{-\beta \cdot E_i}}{\lim_{T\to\infty} \sum_i \alpha \cdot D(E_i) \cdot e^{-\beta \cdot E_i}} = \frac{\sum_i D(E_i) \cdot e^{-\beta \cdot E_i}}{\sum_i D(E_i)}$$

$S_{exc.\infty} = k \cdot ln(P_{success})$

$P_{success}$

$S_{exc.\infty}$

$$Z = \frac{1}{N!} \sum_i e^{-\beta \cdot E_i} Z = \frac{1}{N!} \int \cdots \int e^{-\beta \cdot [\{P_1^2/2m + P_2^2/2m + \ldots\} + V(\vec{R_1}, \vec{R_2}, \ldots)]} d\vec{P_1} \cdot d\vec{P_2} \cdots d\vec{P_N} \cdot d\vec{R_1} \cdot d\vec{R_2} \cdots d\vec{R_N}$$

V^N/V^N

$$Z = Z_{ideal} \cdot \frac{1}{V^N} \cdot \int \cdots \int e^{-\beta \cdot V(\vec{R_1}, \vec{R_2}, \ldots)} d\vec{R_1} \cdot d\vec{R_2} \cdots d\vec{R_N}$$

$$Z_{ideal} = V^N \cdot \frac{1}{N!} \int \cdots \int e^{-\beta \cdot [P_1^2/2m + P_2^2/2m + \ldots]} d\vec{P_1} \cdot d\vec{P_2} \cdots d\vec{P_N}$$

Z_{HS}/Z_{HS}

$Z = Z_{ideal} \cdot Z_{HS} \cdot \frac{1}{Z_{HS}} \cdot \frac{1}{V^N} \cdot \int \cdot\cdot \cdot \int e^{-\beta \cdot V(\vec{R_1}, \vec{R_2}, \ldots)} d\vec{R_1} \cdot d\vec{R_2} \cdot \cdot\cdot d\vec{R_N}$

$Z_{HS} = \frac{1}{V^N} \int \cdot\cdot \cdot \int e^{-\beta \cdot V_{HS}(\vec{R_1}, \vec{R_2}, \ldots)} d\vec{R_1} \cdot d\vec{R_2} \cdot \cdot\cdot d\vec{R_N}$

$Z = Z_{ideal} \cdot Z_{HS} \cdot \frac{Z_{interaction}}{Z_{HS}} = Z_{ideal} \cdot Z_{HS} \cdot$

$F_{exc} = -k \cdot T \cdot ln(Z_{exc}) = -k \cdot T \cdot ln(Z_{HS}) - k \cdot T \cdot ln(Z_{disp}) \Rightarrow$

$S_{exc.\infty} = \lim_{T\to\infty} - \left(\frac{\partial F_{exc}}{\partial T}\right)_{V,N} but \lim_{T\to\infty} Z_{exc} = constant \Rightarrow$

$S_{exc.\infty} = -k \cdot ln(Z_{HS.\infty}) - k \cdot ln(Z_{disp.\infty})$

$but Z_{HS} is constant and Z_{disp.\infty} = Z_{interaction.\infty}/Z_{HS} = Z_{HS}/Z_{HS} = 1 \Rightarrow$

$S_{exc.\infty} = -k \cdot ln(Z_{HS}) - k \cdot ln(1) = -k \cdot ln(Z_{HS}) \Rightarrow$

$Z_{HS} = e^{-S_{exc.\infty}/k}$

$T \rightarrow \infty$

$F = U - T \cdot S \Rightarrow S = (U - F)/T \approx -F/T = k \cdot ln(Z)$

$let Z_{small} = partition function of the smaller box$

$let Z_{big} = partition function of the bigger box$

$\Delta S = S_{small} - S_{big} = k \cdot ln(Z_{small}) - k \cdot ln(Z_{big}) = k \cdot ln(Z_{small}/Z_{big})$

Z_{big}
ΔS
Z_{small}
Z_{valid}

$let Z_{big} = Z_{valid} + Z_{invalid}$

$but Z_{small} maps into Z_{valid} \Rightarrow Z_{small} = \alpha \cdot z_{valid} for some constant \alpha$

α
α
Z_{small}
Z_{big}

$$Z_{small} = \frac{1}{N!} \int \cdots \int e^{-\beta \cdot [\{P_1^2/2m + P_2^2/2m + \ldots\} + V(\vec{R_1}, \vec{R_2}, \ldots)]} d\vec{P_1} \cdot d\vec{P_2} \cdots d\vec{P_N} \cdot d\vec{R_1} \cdot d\vec{R_2} \cdots d\vec{R_N}$$

$$Z_{small} \propto \frac{1}{N!} \int \cdots \int e^{-\beta \cdot [V(\vec{R_1}, \vec{R_2}, \ldots)]} d\vec{R_1} \cdot d\vec{R_2} \cdots d\vec{R_N}$$

α

$$Z_{small} \propto \frac{1}{N!} \int \cdots \int e^{-\beta \cdot [V(\vec{R_1}, \vec{R_2}, \ldots)]} d\vec{R_1} \cdot \left(\frac{L_{big}}{L_{small}}\right)^3 \cdot d\vec{R_2} \cdot \left(\frac{L_{big}}{L_{small}}\right)^3 \cdots d\vec{R_N} \cdot \left(\frac{L_{big}}{L_{small}}\right)^3 \cdot \left(\frac{L_{small}}{L_{big}}\right)^{3N}$$

$$Z_{small} = \left(\frac{L_{small}}{L_{big}}\right)^{3N} \cdot Z_{big} = \left(\frac{V_{small}}{V_{big}}\right)^{N} \cdot Z_{big} \doteq \alpha \cdot Z_{big} \Rightarrow$$

$\alpha = (V_{small}/V_{big})^N$

α

$\Delta S = k \cdot ln(Z_{small}/Z_{big}) = k \cdot ln(\alpha \cdot Z_{valid}/Z_{big})$

$$\Delta S = k \cdot ln(\frac{V_{small}^N}{V_{big}^N} \cdot Z_{valid}/Z_{big})$$

$but Z_{valid}/Z_{big} = probability of success when scaling = P_{success} \Rightarrow$

$$\Delta S = k \cdot ln(\frac{V_{small}^N}{V_{big}^N} \cdot P_{success})$$

ΔS

$\Delta S_{exc.\infty} = \Delta S_{\infty} - \Delta S_{ideal.\infty}$

$but \Delta S_{ideal.\infty} = k \cdot N \cdot ln(V_{small}/V_{big}) \Rightarrow$

$$\Delta S_{exc.\infty} = k \cdot ln(\frac{V_{small}^N}{V_{big}^N} \cdot P_{success}) - k \cdot N \cdot ln(V_{small}/V_{big})$$

$\Delta S_{exc.\infty} = k \cdot ln(P_{success})$

$$Z = \sum_i D(E_i) \cdot e^{-\beta \cdot E_i}$$