Chap 5,

7. $$Z = e^{aT^3V}$$

$$F = -k_BT\ln Z = -ak_BT^4V$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = +ak_BT^4$$

$$-S = \frac{\partial F}{\partial T} = -4ak_BT^3V.$$

$$S = 4ak_BT^3V$$

$$U = F + TS = 3ak_BT^4V$$

12. $$G = U_A + P_RV_A - T_RS_A$$

$$= F_A + P_RV_A + (T_A - T_R)S_A$$

$$\left(\frac{\partial G}{\partial V_A}\right)_T = 0 = \left(\frac{\partial F}{\partial V_A}\right)_T + P_R \quad \sim$$

$$= -P_A + P_R \quad \sim \quad P_R = P_A$$

$$\left(\frac{\partial G}{\partial S_A}\right)_{V,P} = \left(\frac{\partial U_A}{\partial S_A}\right)_V - T_R = T_A - T_R = 0$$

$$\sim \boxed{T_A = T_R}$$

16 One particle

$$Z_1 = \sum_i e^{-\beta\epsilon_i}$$

$$= 1 + 3e^{-\beta\epsilon} + 3e^{-2\beta\epsilon} + e^{-3\beta\epsilon}$$

$$= \left(1 + e^{\beta\epsilon}\right)^3$$

N particles

$$Z_N = \left(Z_1\right)^N = \left(1 + e^{-\beta\epsilon}\right)^{3N}$$

$$F = -k_BT \ln Z_N = -3Nk_BT \ln\left(1 + e^{-\epsilon/k_BT}\right)$$

17.

$$Z = \left(\frac{V-Nb}{N}\right)^N \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{\frac{3N}{2}} e^{N^2a^2/(Vk_BT)}$$

$$-F = k_BT\left\{ N\ln\left(\frac{V-Nb}{N}\right) + \frac{3N}{2}\left[\ln T + \ln\frac{mk_B}{2\pi\hbar^2}\right] + \frac{N^2a^2}{Vk_BT}\right\}$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$= k_BTN\left(\frac{1}{V-Nb}\right) - \frac{N^2a^2}{V^2}$$

or $$\boxed{\left(P + \frac{N^2a^2}{V^2}\right)\left(V-Nb\right) = Nk_BT}$$

17 contd. $U = k_B T^2 \left(\frac{\partial \ln Z}{\partial T}\right)$

$$= k_B T^2 \left\{ \frac{3N}{2} \cdot \frac{1}{T} - \frac{N^2 a^2}{V k_B T^2} \right\}$$

$$U = \frac{3}{2} N k_B T - \frac{N^2 a^2}{V}$$

$\longrightarrow$

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$$U = -\frac{\partial}{\partial\beta}\ln Z$$

$$Z = \sum_i e^{-\beta\epsilon_i}$$

$$\frac{\partial}{\partial\beta}\ln Z = \frac{-\sum_i e^{-\beta\epsilon_i}\cdot\epsilon_i}{Z} = -\sum_i p_i\epsilon_i = \underline{-U}$$

Harmonic Oscillator

$$E_n = \left(n + \tfrac{1}{2}\right)\hbar\omega$$

$$Z = \sum_n e^{-\beta E_n}$$

$$= e^{-\beta\hbar\omega/2}\sum_{n=0}^{\infty} e^{-\beta n\hbar\omega}$$

$$= e^{-\beta\hbar\omega/2}\cdot\frac{1}{1-e^{-\beta\hbar\omega}}$$

$$\ln Z = -\frac{\beta\hbar\omega}{2} - \ln\left(1-e^{-\beta\hbar\omega}\right)$$

$$\frac{\partial\ln Z}{\partial\beta} = -\frac{\hbar\omega}{2} - \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}$$

$$U = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}$$