13. *Statistical Mechanics and Thermodynamics* (Fall 2002)

Consider an ideal monoatomic gas in which each atom has two internal energy states, one an energy $\Delta$ above the other. There are $N$ atoms in a volume $V$ at temperature $T$.

Find the a) chemical potential, b) free energy, c) entropy, d) pressure and e) heat capacity at constant pressure.

$$z = \sum_r e^{-\beta\epsilon_r} = \sum_r e^{-\beta(p^2/2m + \epsilon_{int})}$$
$$= \sum_i e^{-\beta\epsilon_{int}} \sum_n e^{-\beta p^2/2m}$$
$$= (e^{-\beta\epsilon} + e^{-\beta(\epsilon+\Delta)}) \sum_n e^{-\beta p^2/2m}$$
$$\cong (e^{-\beta\epsilon} + e^{-\beta(\epsilon+\Delta)}) \left[\int_0^\infty e^{-\beta p_x^2/2m} dn_x\right]^3$$
$$= (e^{-\beta\epsilon} + e^{-\beta(\epsilon+\Delta)}) \left[\int_0^\infty e^{-\beta\hbar^2\pi^2 n^2/2mL^2} dn\right]^3 \quad \text{since } p_x = \hbar\frac{n_x\pi}{L}$$
$$= (e^{-\beta\epsilon} + e^{-\beta(\epsilon+\Delta)}) \left[\sqrt{\frac{2mL^2}{\beta\hbar^2\pi^2}}\,\frac{\sqrt{\pi}}{2}\right]^3 \quad \text{by letting } u = \sqrt{\frac{\beta\hbar^2\pi^2}{2mL^2}}\,n$$
$$= (e^{-\beta\epsilon} + e^{-\beta(\epsilon+\Delta)})\, V \left(\frac{2\pi m}{\beta h^2}\right)^{3/2}$$

$$Z = \frac{z^N}{N!} = \frac{1}{N!}(e^{-\beta\epsilon} + e^{-\beta(\epsilon+\Delta)})^N V^N \left(\frac{2\pi m}{\beta h^2}\right)^{3N/2}$$
$$\ln(Z) = N\ln(e^{-\beta\epsilon} + e^{-\beta(\epsilon+\Delta)}) + N\ln(V) + \frac{3}{2}N\ln\left(\frac{2\pi m}{\beta h^2}\right) - N\ln(N) + N$$

a. $$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = \left(\frac{\partial}{\partial N}\right)_{V,T}(-kT\ln(Z))$$
$$= -kT\left[\ln(e^{-\beta\epsilon} + e^{-\beta(\epsilon+\Delta)}) + \ln(V) + \frac{3}{2}\ln\left(\frac{2\pi m}{\beta h^2}\right) - \ln(N)\right]$$
$$= -kT\left[-\beta\epsilon + \ln(1+e^{-\beta\Delta}) + \ln(V) + \frac{3}{2}\ln\left(\frac{2\pi m}{\beta h^2}\right) - \ln(N)\right]$$
$$= \epsilon - kT\ln(1+e^{-\beta\Delta}) - kT\ln(V) - \frac{3}{2}kT\ln\left(\frac{2\pi m}{\beta h^2}\right) + kT\ln(N)$$

b. $$F = -kT\ln(Z) = N\epsilon - NkT\ln(1+e^{-\beta\Delta}) - NkT\ln(V)$$
$$- \frac{3}{2}NkT\ln\left(\frac{2\pi m}{\beta h^2}\right) + NkT\ln(N) - NkT$$

c. $$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk\ln(1+e^{-\beta\Delta}) + N\cancel{k}T\frac{1}{1+e^{-\beta\Delta}}e^{-\beta\Delta}\left(\frac{\Delta}{\cancel{k}T^2}\right)$$
$$+ Nk\ln(V) + \frac{3}{2}Nk\ln\left(\frac{2\pi m}{\beta h^2}\right) + \frac{3}{2}N\cancel{kT}\frac{\cancel{\beta h^2}}{\cancel{2\pi m}}\frac{\cancel{2\pi m}}{\cancel{h^2}}k$$
$$- Nk\ln(N) + Nk$$
$$= Nk\ln(1+e^{-\beta\Delta}) + N\frac{\Delta}{T}\frac{1}{e^{\beta\Delta}+1} + Nk\ln(V) + \frac{3}{2}Nk\ln\left(\frac{2\pi m}{\beta h^2}\right) - Nk\ln(N) + \frac{5}{2}Nk$$

d. $$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{NkT}{V}$$

e. $$C_p = C_v + Nk = \left(\frac{\partial E}{\partial T}\right)_v + Nk = T\left(\frac{\partial S}{\partial T}\right)_v + Nk$$
$$= Nk + T\left[\cancel{\frac{Nk}{1+e^{-\beta\Delta}}e^{-\beta\Delta}\left(\frac{\Delta}{kT^2}\right)} + \frac{N\Delta}{T}\frac{\left(\frac{\Delta}{kT^2}\right)e^{\beta\Delta}}{(e^{\beta\Delta}+1)^2} - \cancel{\frac{N\Delta}{T^2}\frac{1}{e^{\beta\Delta}+1}} + \frac{3}{2}Nk\frac{1}{T}\right]$$
$$= \frac{N\Delta^2}{kT^2}\frac{e^{\beta\Delta}}{(e^{\beta\Delta}+1)^2} + \frac{5}{2}Nk$$