

### 13. Statistical Mechanics and Thermodynamics

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.

$$Z_1 = \sum_E e^{-\beta E} = e^{-\beta E} + e^{-\beta(E+\Delta)} = e^{-\beta E} + e^{-\beta E} e^{-\beta \Delta}$$

$$= e^{-2\beta E - \beta \Delta}$$

$$Z = \frac{(Z_1)^N}{N!} \quad \ln Z = N(\ln Z_1 - \ln N + 1)$$

$$= N(-2\beta E - \beta \Delta - \ln N + 1)$$

$$F = -kT \ln Z = -kTN(1 - 2\beta E - \beta \Delta - \ln N)$$

$$a) \quad \mu = \left( \frac{\partial F}{\partial N} \right)_{V,T} = -kT(1 - 2\beta E - \beta \Delta - \ln N) - kTN \left( -\frac{1}{N} \right)$$

$$= kT(2\beta E + \beta \Delta + \ln N - 1) + kT$$

$$= kT(2\beta E + \beta \Delta + \ln N)$$

$$b) \quad F = -kT \ln Z$$

$$c) \quad S = - \left( \frac{\partial F}{\partial T} \right)_{V,N} = kN(1 - 2\beta E - \beta \Delta - \ln N) + kTN \left( \frac{2E}{kT^2} \right)$$

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$$= kN(1 - \beta \Delta - \ln N)$$

$kN/2\beta E$

$$d) \quad p = \left( \frac{\partial F}{\partial V} \right)_{T,N} = 0$$

$$e) \quad C_p = Nk \left( 1 + \frac{f}{R} \right) \text{ degrees of freedom} \Rightarrow C_p = Nk \left( 1 + \frac{3}{R} \right)$$