

- (a) Consider the following approximate model of a liquid. Interactions between molecules are neglected except that all molecules experience a constant ^{binding} energy $-\eta$ that confines its motion to a volume V_0 per particle, and fixed. Show that for a large chemical liquid of N indistinguishable molecules, the partition function is:

$$Z_L = \frac{1}{N_L!} \left[N_L v_0 e^{\beta \eta} Z_p \right]^{N_L}$$

where Z_p denotes the ideal gas contribution arising from the integral over momenta:

$$Z_p = \frac{1}{h^3} \int d^3 p e^{-\beta p^2 / 2m}$$

- (b) ~~Ass.~~ Assume now that this liquid coexists with its vapor (an ideal gas). Calculate the chemical potential of the liquid μ_L and of the vapor μ_G , ^{assumed an ideal gas}
- (c) At coexistence between liquid and vapor phases: $\mu_L = \mu_G$. Find the pressure (vapor pressure as it is called) as a function of temperature at coexistence.

(a) For a single particle $Z_1 = \frac{1}{h^3} \int d^3 r d^3 p e^{-\beta p^2 / 2m} e^{\beta \eta}$

$$= \cancel{\frac{1}{h^3}} e^{\beta \eta} (N_L v_0) Z_p$$

$$\Rightarrow Z_L = \frac{1}{N_L!} \left[e^{\beta \eta} (N_L v_0) Z_p \right]^{N_L}$$

For the ideal gas $\eta = 0$ and $N_L v_0$ is V_G , the volume of the gas phase (not fixed).

$$Z_G = \frac{1}{N_G!} \left[V_G Z_p \right]^{N_G}$$

(5)

$$\mu = \frac{\partial F}{\partial N} = -k_B T \frac{\partial \ln Z}{\partial N}$$

$$\mu_G = -k_B T \quad F_G = -k_B T \ln Z_G = -k_B T \left[N_G \ln(V_G Z_p) - N_G \ln N_G + N_G \right]$$

$$\mu_G = -k_B T \left[\ln(V_G Z_p) - \ln N_G - \cancel{N_G \frac{1}{N_G} + 1} \right]$$

$$\boxed{\mu_G = -k_B T \left[\ln(V_G Z_p) - \ln N_G \right]}$$

$$F_L = -k_B T \left[N_L \ln(V_0 Z_p) + N_L \beta \gamma + \cancel{N_L \ln N_L} - \cancel{N_L \ln N_L} + N_L \right]$$

$$\boxed{\mu_L = -k_B T \left[\ln(V_0 Z_p) + \beta \gamma + 1 \right]}$$

(c) At coexistence $\mu_L = \mu_G$

$$\ln(V_G Z_p) - \ln N_G = \ln(V_0 Z_p) + \beta \gamma + 1$$

$$\ln\left(\frac{V_G}{N_G}\right) = \ln(V_0) + \beta \gamma + 1 \quad \Rightarrow \quad \frac{V_G}{N_G} = e^{\ln V_0} e^{\beta \gamma + 1} = V_0 e^{\beta \gamma + 1}$$

$$\underbrace{\frac{V_G}{N_G}}_{\text{Ideal gas}} = \frac{P}{k_B T} = \frac{N_G}{V_G}$$

$$\Rightarrow \boxed{\frac{P}{k_B T} = \frac{e^{-(\beta \gamma + 1)}}{V_0}}$$

this is the vapor pressure as a function of temperature.