

## M17T.2 (Surface Adsorption)

For a free boson in 3D, we can treat it as a classical ideal gas w/ 3 translational degrees of freedom.

For an adsorbed boson in 2D, we treat it as a Bose gas w/ 2 translational degrees of freedom.

$$E_{3D} = \frac{p^2}{2m} = \frac{p_x^2 + p_y^2 + p_z^2}{2m}$$

$$E_{2D} = -\epsilon_0 + \frac{p_x^2 + p_y^2}{2m}$$

$\bar{\epsilon}$  2D Bose gas can also neglect condensate phenomena, so we cannot neglect quantum statistics.

Treat  $\bar{\epsilon}$  3D gas as a grand canonical ensemble,  $\bar{\epsilon}$  2D gas as another. At equilibrium, we only have

$\bar{\epsilon}$  requirement  $\mu_{3D} = \mu_{2D} = \mu$ .

We know  $\bar{\epsilon}$  canonical partition function for  $\bar{\epsilon}$  classical ideal gas is:  $Q(T, V) = \frac{V}{\lambda^3}$

Thus,  $\bar{\epsilon}$  grand partition function is:  $Z(T, V, \mu) = \sum_{N=0}^{\infty} e^{\beta \mu N} \frac{1}{N!} \frac{V^N}{\lambda^{3N}}$ , w/  $\lambda = \sqrt{\frac{2\pi\hbar^2}{m k_B T}}$  is  $\bar{\epsilon}$  thermal wavelength.  
 $= \exp\left(\frac{Vz}{\lambda^3}\right)$ , where  $z = e^{\beta \mu}$  is  $\bar{\epsilon}$  fugacity.

$$\text{We can write } \Phi = \log Z = \frac{Vz}{\lambda^3} = \frac{PV}{k_B T} \Rightarrow e^{\beta \mu} = \frac{P}{k_B T} \lambda^3 \Rightarrow \mu = k_B T \log\left(\frac{P \lambda^3}{k_B T}\right)$$

For  $\bar{\epsilon}$  2D gas, we can write  $\bar{\epsilon}$  total particle number as:

$$\begin{aligned} N &= \int d\epsilon g(\epsilon) n_{BE}(\epsilon) \\ &= \int d\epsilon g(\epsilon) \frac{1}{\exp(\beta(\epsilon - \mu)) - 1} \\ &= \int d\epsilon \cdot g(\epsilon) \frac{1}{\exp[\beta(\epsilon - \epsilon_0 - \mu)] - 1} \end{aligned}$$

We thus need  $\bar{\epsilon}$  2D density of states.  $\bar{\epsilon}$  number of states in a shell of radius  $p$  is:  $N(k) = \frac{\pi k^2}{(2\pi/L)^2}$

$$\Rightarrow N(k) = \frac{\pi k^2}{4\pi} \Rightarrow N(\epsilon) = \frac{Am}{2\pi\hbar^2} \epsilon$$

Thus,  $\bar{\epsilon}$  density of states is simply  $g(\epsilon) = \frac{dN(\epsilon)}{d\epsilon} = \frac{Am}{2\pi\hbar^2}$

$$\Rightarrow N = \frac{Am}{2\pi\hbar^2} \int d\epsilon \frac{1}{\exp[\beta(\epsilon - \epsilon_0 - \mu)] - 1}$$

$\bar{\epsilon}$  surface density is simply:  $\frac{N}{A} = \frac{m}{2\pi\hbar^2} \int \frac{d\epsilon}{\exp[-\beta(\epsilon_0 + \mu)] \exp(\beta\epsilon) - 1}$  (let  $e^{-\beta(\epsilon_0 + \mu)} = \alpha$ )

$$= \frac{m}{2\pi\hbar^2} \int \frac{d\epsilon}{\alpha \exp(\beta\epsilon) - 1} \quad (\text{let } \beta\epsilon = x, d\epsilon = \frac{1}{\beta} dx)$$

$$= \frac{m}{2\pi\hbar^2 \beta} \int_0^{\infty} \frac{dx}{\alpha e^x - 1}$$

$$= \frac{-m}{2\pi\hbar^2 \beta} \int_0^{\infty} \frac{dx}{1 + \eta e^x} \quad (\text{w/ } \eta = -\alpha)$$

$$\Rightarrow \frac{N}{A} = \frac{m}{2\pi\hbar^2\beta} \log\left(\frac{1}{1-\alpha}\right)$$

Finally, we just use  $\bar{\epsilon}$  express<sup>n</sup> for  $\alpha$  &  $\mu$  from  $\bar{\epsilon}$  3D gas:

$$\begin{aligned} \frac{N}{A} &= \frac{m}{2\pi\hbar^2\beta} \log\left(\frac{1}{1-\exp[-\beta(\epsilon_0 + \mu)]}\right) \\ &= \frac{mk_B T}{2\pi\hbar^2} \log\left[\frac{1}{1-\exp[-\epsilon_0/k_B T - \log(\rho\lambda^3/k_B T)]}\right] \\ &= \frac{mk_B T}{2\pi\hbar^2} \log\left[\frac{1}{1-(k_B T/\rho\lambda^3)\exp(-\epsilon_0/k_B T)}\right] \end{aligned}$$