① Ideal gas in 3D → Equation of state?

$$\mathcal{Z}_\ell = \sum_N e^{+\beta\mu N} \frac{1}{N!} \int \prod_i \frac{dq_i}{h} \int dp_i \, e^{-\beta H}$$

$$\int \prod_i \frac{dq_i}{h} = \left[\frac{V}{h^3}\right]^N \qquad \int_{-\infty}^{\infty} dp_i \, e^{-\beta p_i^2/2m} = \sqrt{\frac{2\pi m}{\beta}}$$

$$\int \prod_i dp_i \, e^{-\beta H} = \left(\sqrt{\frac{2\pi m}{\beta}}\right)^{3N}$$

$$\mathcal{Z}_\ell = \sum_N \underbrace{e^{\beta\mu N}}_{z^N} \left(\sqrt{\frac{2\pi m}{\beta}}\right)^{3N} \left(\frac{V}{h^3}\right)^N \frac{1}{N!} = \sum_N \frac{1}{N!}\left(z\left(\frac{2\pi m}{\beta}\right)^{3/2} \frac{V}{h^3}\right)^N$$

$$= e^{z\left(\frac{2\pi m}{\beta}\right)^{3/2} \frac{V}{h^3}}$$

$$\ln \mathcal{Z}_\ell = z\left(\frac{2\pi m}{\beta}\right)^{3/2} \frac{V}{h^3}$$

From class : $\ln \mathcal{Z} = \frac{PV}{k_B T}$ and $\langle N \rangle = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}_\ell}{\partial \mu}$

$$\langle N \rangle = \frac{1}{\beta} \boxed{\frac{\partial \ln \mathcal{Z}_\ell}{\partial z}} \cdot \underbrace{\boxed{\frac{\partial z}{\partial \mu}}}_{\to \beta \cdot z} = \frac{1}{\beta} \cdot \beta z \cdot \left(\frac{2\pi m}{\beta}\right)^{3/2} \frac{V}{h^3} = \ln \mathcal{Z}_\ell$$

So $\boxed{\langle N \rangle = \frac{PV}{k_B T}}$ — equation of state

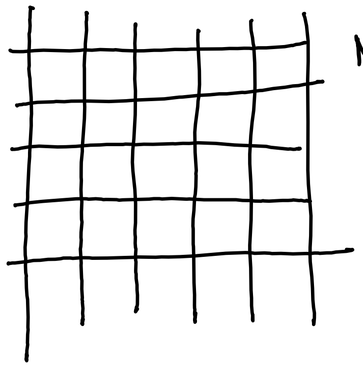
Chemical potential of an ideal gas:

$$z\left(2\pi m k_B T\right)^{3/2} \frac{\cancel{V}}{h^3} = \frac{P\cancel{V}}{k_B T} \qquad \lambda_T = \frac{\sqrt{2\pi m k_B T}}{h}$$

$$z = \frac{h^3}{k_B T} \cdot \frac{P}{\left(2\pi m k_B T\right)^{3/2}} = \frac{P}{k_B T \lambda_T^3}$$

$$e^{\beta\mu} = z \qquad \boxed{\mu = k_B T \log \frac{P}{k_B T \lambda_T^3}}$$

② Adsorption process.



N_0 adsorbing sites → $E_{ads} = +\epsilon$

In contact with a reservoir at temperature T and μ.

Find the coverage θ, i.e. fraction of occupied sites

Option 1 → compute $\mathcal{Z}_e$, obtain $\langle N \rangle$ → $\theta = \frac{\langle N \rangle}{N_0}$
(expected # of occupied sites.)

$$\mathcal{Z}_e = \sum_{N=0}^{N_0} e^{+\beta\mu n} \cdot \sum_{E,n} e^{-\beta E_n}$$

$$E_n = +n\epsilon \qquad \sum_{E} e^{-\beta E_n} = e^{-\beta\epsilon n} \cdot \sum_{s/n \text{ adsorbed sts}} = e^{-\beta\epsilon n}\binom{N_0}{n}$$

because fixed n = fixed E we just need to count the degeneration

$$\mathcal{Z}_e = \sum_{n=0}^{N_0} e^{\beta\mu n} e^{-\beta\epsilon n}\binom{N_0}{n} = \left(1 + e^{\beta(\mu-\epsilon)}\right)^{N_0}$$

$$= (z_1)^{N_0} \qquad \ln \mathcal{Z}_e = N_0 \ln z_1$$

$$\langle N \rangle = \frac{1}{\beta}\frac{\partial \ln \mathcal{Z}_e}{\partial \beta} = \frac{N_0}{\beta}\frac{1}{z_1} \cdot \beta e^{-\beta(\epsilon-\mu)} ; \boxed{\theta = \frac{\langle N \rangle}{N_0} = \frac{e^{-\beta(\epsilon-\mu)}}{1+e^{-\beta(\epsilon-\mu)}}}$$

Option 2.

Gibbs sum: Since the state of each adsorbing site is independent from the others, we can just compute the partition function for one site:

$$z_1 = \text{empty} + \text{occupied} = e^{\beta\mu 0}e^{-\beta\epsilon 0} + e^{\beta\mu 1}e^{-\beta\epsilon 1}$$

$$= 1 + e^{-\beta(\epsilon-\mu)}$$ — (This is the Gibbs sum)

The probability that one site is occupied is then:

$$p_1 = \frac{1}{z_1} \cdot e^{-\beta(\epsilon-\mu)}$$ → the expected # of occupied sites is then $\langle N \rangle = p_1 \cdot N_0$
so that $\theta = \frac{\langle N \rangle}{N_0} = p_1$

Option 3 Since all sites are independent we note that $\mathcal{Z}_e = z_1 \cdot z_2 \cdot z_3 \cdots z_{N_0}$

So that if $z_1 = 1 + e^{-\beta(\epsilon-\mu)} = z_k \quad \forall k = 1, N_0$

$$\mathcal{Z}_e = z_1^{N_0}$$ (which is the same as the first result)

from here $\langle N \rangle = N_0 \cdot \frac{e^{-\beta(\epsilon-\mu)}}{z_1}$ $\boxed{\theta = \frac{e^{-\beta(\epsilon-\mu)}}{z_1}}$.

Problem 3. Find the chemical potential μ as a function of θ.

$$\theta = \frac{e^{-\beta\epsilon_0} z}{1 + e^{-\beta\epsilon_0} z} = \frac{N_{ads}}{N_0}$$

$$e^{-\beta\epsilon_0} z N_0 = (1 + e^{-\beta\epsilon_0} z) N_{ads}$$

$$z (N_0 - N_{ads}) e^{-\beta\epsilon_0} = N_{ads} \qquad z = \frac{N_{ads}\, e^{\beta\epsilon_0}}{N_0 - N_{ads}}$$

$$\mu = k_B T \log \frac{N_{ads}}{(N_0 - N_{ads}) \cdot [e^{-\beta\epsilon_0}]} \qquad a(T) = e^{-\beta\epsilon_0}$$

Problem 4

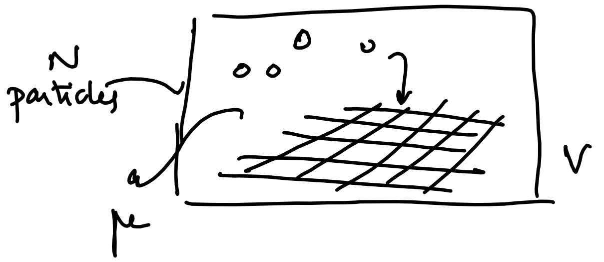
$$\mu_{\text{adsorbed gas}} = - k_B T \log \left[e^{-\beta\epsilon_0} \left(\frac{N_0}{N_{ads}} - 1 \right) \right]$$

$$\boxed{\mu_{\substack{\text{ideal}\\\text{gas}}} = k_B T \log \frac{h^3 P}{k_B T \lambda_T^3}}$$

$$\mu_{\substack{\text{ideal}\\\text{gas}}} = \mu_{ads} \Rightarrow \frac{h^3 P}{k_B T \lambda_T^3} = \frac{N_{ads}}{N_0 - N_{ads}} \cdot e^{\beta\epsilon_0}$$

$$\frac{N_{ads}}{N_0 - N_{ads}} = \frac{h^3 P}{k_B T \lambda_T^3} e^{-\beta\epsilon_0}$$

Problem 5



Ideal gas

$$PV = \langle N_{gas} \rangle k_B T$$

with $\mu_{gas} = k_B T \ln \frac{P}{k_B T \lambda_T^3}$ $\qquad \lambda_T = \frac{\sqrt{2\pi m k_B T}}{h}$

adsorbed gas particles:

$\rightarrow$ Independent sites: each site

$$Z_{site} = 1 + e^{\beta\epsilon_0 + \beta\mu} + e^{2(\beta\epsilon_0 + \beta\mu)}$$

$$\langle N_{ads} \rangle_{per\ site} = \frac{1 \cdot e^{\beta\epsilon_0} \cdot e^{\beta\mu} + 2 \cdot e^{(\beta\epsilon_0 + \beta\mu)2}}{Z_{site}}$$

$$\langle N_{ads} \rangle = N_0 \langle N_{ads} \rangle_{per\ site}$$

$$N = \langle N_{gas} \rangle + \langle N_{ads} \rangle$$

$$\frac{PV}{k_B T} = \langle N_{gas} \rangle = N - \langle N_{ads} \rangle$$

$$\frac{PV}{k_B T N} = 1 - \frac{\langle N_{ads} \rangle}{N}$$

Since $\mu_{gas} = \mu_{ads}$

$$e^{\beta\mu} = \frac{P}{\lambda_T^3 k_B T} \qquad \langle N_{ads} \rangle = \frac{P \cdot f + (Pf)^2 \cdot 2}{1 + Pf + (Pf)^2}$$

$$f = e^{\beta\epsilon_0} / \lambda_T^3 k_B T$$

$$\boxed{\frac{PV}{N k_B T} = 1 - \frac{N_0}{N} \cdot \frac{Pf + (Pf)^2 \cdot 2}{1 + Pf + (Pf)^2}}$$