

## Grand Canonical partition function for non-interacting systems

$$\mathcal{Z} = \sum_{N=0}^{\infty} z^N Q_N(T, V)$$

$z = e^{\beta\mu}$  is the fugacity,  
 $Q_N(T, V)$  the canonical partition function

for non-interacting particles we saw

$$Q_N(T, V) = \frac{1}{N!} [Q_1(T, V)]^N \quad \text{indistinguishable particles (as in ideal gas)}$$

$$= [Q_1(T, V)]^N \quad \text{distinguishable particles (as in paramagnetic spins)}$$

⇒ Indistinguishable

$$\mathcal{Z} = \sum_{N=0}^{\infty} \frac{(z Q_1)^N}{N!} = e^{z Q_1}$$

Distinguishable

$$\mathcal{Z} = \sum_{N=0}^{\infty} (z Q_1)^N = \frac{1}{1 - z Q_1} \quad \leftarrow \text{must have } z Q_1 < 1 \text{ for series to converge}$$

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Indistinguishable:  $-pV = \Sigma = -k_B T \ln \mathcal{Z} = -k_B T z Q_1$

$$p = \frac{k_B T}{V} z Q_1$$

$$z = e^{\beta\mu}$$

also  $N = -\left(\frac{\partial \Sigma}{\partial \mu}\right)_{T, V} = k_B T \left(\frac{\partial z}{\partial \mu}\right) Q_1 = k_B T \cdot \beta z Q_1 = z Q_1$

⇒  $p = \frac{k_B T N}{V}$  ideal gas law no matter what  $Q_1!$

## Ideal gas

For a single gas of particles

$$Q_1 = \frac{\int d^3p \int d^3r}{h^3} e^{-\beta p^2/2m} = \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{V}{h^3}$$
$$= V f(T) \quad \text{with } f(T) = \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2}$$

will have this form <sup>with a different  $f(T)$ ,</sup> even for a more complicated gas in which the particles may have internal degrees of freedom.

$$\mathcal{Z} = e^{zQ_1} = e^{zVf(T)} \quad \ln \mathcal{Z} = zVf(T)$$

grand potential  $\Sigma = -k_B T \ln \mathcal{Z} = -k_B T z V f(T) = -pV$

$$p = k_B T z f(T) \quad z = e^{\beta \mu} \quad \beta = \frac{1}{k_B T}$$

$$N = - \left( \frac{\partial \Sigma}{\partial \mu} \right)_{T,V} = - \left( \frac{\partial \Sigma}{\partial z} \right)_{T,V} \left( \frac{\partial z}{\partial \mu} \right) = k_B T V f(T) \beta e^{\beta \mu}$$
$$= z V f(T)$$

Combine the above

$$\frac{p}{k_B T} = z f(T)$$

$$\frac{N}{V} = z f(T)$$

$$\Rightarrow pV = N k_B T$$

Ideal gas law!  
independent of what  
 $f(T)$  is!

$\Rightarrow$  Ideal gas law holds even for particles with internal degrees of freedom

Also

$$E = - \left( \frac{\partial \ln \Omega}{\partial \beta} \right)_{N, V} = k_B T^2 \left( \frac{\partial \ln \Omega}{\partial T} \right)_{N, V} \quad \text{use } \Omega = z^N V f(T)$$

$$= k_B T^2 z^N V \frac{df}{dT} = k_B T^2 N \frac{(df/dT)}{f} = k_B T^2 N \left( \frac{\partial \ln f}{\partial T} \right)$$

use  $N = z^N V$

$$C_V = \left( \frac{\partial E}{\partial T} \right)_{N, V} = 2 k_B T N \frac{\partial \ln f}{\partial T} + k_B T^2 N \frac{\partial^2 \ln f}{\partial T^2}$$

Note, for harmonic degrees of freedom (ie  $\vec{p}$ , or harmonic internal degrees of freedom, such as internal vibrations of molecule)  $f \propto T^n$  for some power  $n$  (for single particle,  $n = 3/2$ )

$$\Rightarrow \frac{\partial \ln f}{\partial T} = \frac{\partial (n \ln T)}{\partial T} = \frac{n}{T} \Rightarrow E = k_B T^2 N \left( \frac{n}{T} \right) = n k_B T N$$

$$\frac{\partial^2 \ln f}{\partial T^2} = \frac{-n}{T^2}$$

and so

$$E = n k_B T N = n p V \Rightarrow \boxed{\frac{E}{V} = n p}$$

use ideal gas law

$$C_V = 2 n k_B N + k_B T^2 N \left( \frac{-n}{T^2} \right) = n k_B N$$

Helmholtz free energy

$$z = e^{\beta \mu}$$

$$A = \underbrace{\sum} + \underbrace{\mu}_{\mu} \underbrace{N}_{N} = -k_B T z V f(T) + k_B T (\ln z) z V f$$

$$= \underbrace{z V f}_{N} k_B T [\ln z - 1]$$

$$= N k_B T [\ln z - 1]$$

$$N = z V f$$

$$\Rightarrow z = \frac{N}{V f}$$

$$A(T, V, N) = N k_B T \left[ \ln \left( \frac{N}{V f(T)} \right) - 1 \right]$$

above agrees with direct result from canonical ensemble:

$$Q_N = \frac{V^N f^N}{N!} \Rightarrow A = -k_B T \ln Q_N = -k_B T \ln \left( \frac{V^N f^N}{N!} \right)$$

$$= -k_B T N \ln V f + k_B T (N \ln N - N)$$

$$= -N k_B T + N k_B T \ln (N/V f)$$

$$= N k_B T [\ln (N/V f) - 1]$$

entropy

$$S = - \left( \frac{\partial A}{\partial T} \right)_{V, N} = N k_B \left[ \ln \left( \frac{N}{V f(T)} \right) - 1 \right]$$

$$- N k_B T \frac{d(\ln f)}{dT}$$

## For distinguishable particles

- corresponds to situation where particles are localized - so we can distinguish them by their spatial location.

Now expect  $Q_1 = \phi(T)$  is not proportional to  $V$  as the particles are localized.

$$\mathcal{Z} = \frac{1}{1 - z Q_1} = \frac{1}{1 - z \phi(T)}$$

(if  $Q_1 \propto V$ , then series would not converge!)

$$\Sigma = -k_B T \ln \mathcal{Z}$$

$$N = - \frac{\partial \Sigma}{\partial \mu} \left( \frac{\partial \Sigma}{\partial z} \right)_{T, V} = -\beta e^{\beta \mu} (-k_B T) \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial z}$$

$$= z \cdot \frac{(1 - z \phi) (+ \phi)}{(1 - z \phi)^2} = \frac{z \phi}{1 - z \phi}$$

$$N = \frac{z \phi}{1 - z \phi}$$

$$\Rightarrow (1 - z \phi) N = z \phi$$

solve for  $z \phi$  in terms of  $N$

$$N = z \phi (1 + N)$$

$$z \phi = \frac{N}{1 + N} = \frac{1}{1 + 1/N} \approx 1 - \frac{1}{N} \text{ for } N \gg 1$$

$$E = - \left( \frac{\partial}{\partial \beta} \ln \mathcal{Z} \right)_{z, V} = k_B T^2 \left( \frac{\partial}{\partial T} \ln \mathcal{Z} \right)_{z, V}$$

$$= k_B T^2 (1 - z \phi) \frac{+ z d\phi/dT}{(1 - z \phi)^2}$$

$$E = \frac{k_B T^2 z (d\phi/dT)}{1 - z \phi} = k_B T^2 N \frac{(d\phi/dT)}{\phi} = k_B T^2 N \left( \frac{d \ln \phi}{dT} \right)$$

$$A = \overbrace{\Sigma} + \mu N = -k_B T \ln \left( \frac{1}{1-z\phi} \right) + \overbrace{k_B T (\ln z) N} \\ = k_B T \left[ \ln(1-z\phi) + N \ln z \right]$$

use  $1-z\phi \simeq 1/N$  and  $z \simeq 1/\phi$   
to get

$$A = -k_B T N \ln \phi(T) + o(\ln N)$$

## Chemical equilibrium

Suppose  $n_1 A_1 + n_2 A_2 \leftrightarrow n_3 A_3$

chemical reaction among species  $A_1, A_2, A_3$

What determines equilib concentrations of  $A_1, A_2, A_3$ ?

Consider total entropy as function of  $N_1, N_2, N_3$   
numbers of  $A_1, A_2, A_3$

$S(N_1, N_2, N_3)$   $N_i$  adjust to maximize  $S$

$$dS = 0 = \sum_i \frac{\partial S}{\partial N_i} dN_i = \sum_i \left( -\frac{\mu_i}{T} \right) dN_i \quad (\text{all species in equilibrium at common } T)$$

Now if  $N_3$  decreases by  $-dN$

Then  $N_1$  and  $N_2$  increase by  $\frac{n_1}{n_3} dN$  and  $\frac{n_2}{n_3} dN$  respectively.

$$\text{or if } dN_3 = -n_3 dN$$

$$dN_1 = n_1 dN$$

$$dN_2 = n_2 dN$$

$$\text{So } -\frac{\mu_1}{T} dN_1 - \frac{\mu_2}{T} dN_2 - \frac{\mu_3}{T} dN_3 = 0$$

$$\Rightarrow \mu_1 n_1 + \mu_2 n_2 - \mu_3 n_3 = 0$$

$$\boxed{\mu_1 n_1 + \mu_2 n_2 = \mu_3 n_3}$$

goal will be to  
choose  $N_i$  such that  
the  $\mu_i(T, V, N_i)$   
satisfy this condition

Let "A" be a gas atom, "B" be an adsorbed atom  
 $A \leftrightarrow B \rightarrow \mu_A = \mu_B$

Example



Consider an ideal gas at temperature  $T$  and pressure  $p$  that is in equilibrium with a surface containing  $N_0$  adsorption sites. Each adsorption site can hold at most one particle of the gas. The binding energy of a particle to the adsorption site is  $-\epsilon$ . What is the fraction of occupied adsorption sites as a function of  $T$  and  $p$ ?

Solution: Regard the ideal gas and the gas of adsorbed particles as two separate systems. Since these two systems are in equilibrium with each other, and can exchange particles between each other, they must be at the same temperature and equal chemical potential.

To solve the problem we

- ① Find the number  $N$  of occupied adsorption sites assuming the gas of adsorbed particles is at temperature  $T$  and chemical potential  $\mu$
- ② Find the chemical potential  $\mu(T, p)$  of the ideal gas at temperature  $T$ , pressure  $p$ .
- ③ Insert  $\mu$  from ② into result from ① since the chemical potentials of the two systems must be equal. From this we can get  $(N/N_0)$  as function of  $T$  and  $p$ .



step ① We can do this using either the canonical or grand canonical ensembles

canonical ensemble - compute  $Q_N$

let  $\{\alpha\}$  be the set of states of adsorbed particles that have exactly  $N$  sites occupied and the rest empty.

$$Q_N = \sum_{\alpha} e^{-\beta E_{\alpha}}$$

In general case,  $E_{\alpha}$  will depend on the state  $\alpha$ . But here  $E_{\alpha} = -\epsilon N$  is the same for all states - it does not matter which of the sites are occupied since they all have the same binding energy  $-\epsilon$ .

$$Q_N = e^{+\beta \epsilon N} \sum_{\alpha}$$

The sum is now over all states with exactly  $N$  occupied sites. The number of ways to choose which  $N$  of the  $N_0$  sites are occupied is

$$\frac{N_0!}{N! (N_0 - N)!}$$

so the canonical partition function

is

$$Q_N = \frac{N_0!}{N! (N_0 - N)!} e^{\beta \epsilon N}$$

Now find the Helmholtz free energy

$$\begin{aligned} A(T, N) &= -k_B T \ln \Omega_N \\ &= -\epsilon N - k_B T \left\{ \ln N_0! - \ln N! - \ln (N_0 - N)! \right\} \\ &= -\epsilon N - k_B T \left\{ N_0 \ln N_0 - N_0 \right. \\ &\quad \left. - N \ln N + N \right. \\ &\quad \left. - (N_0 - N) \ln (N_0 - N) + (N_0 - N) \right\} \\ &= -\epsilon N - k_B T \left\{ N_0 \ln N_0 - N \ln N - (N_0 - N) \ln (N_0 - N) \right\} \end{aligned}$$

$$\begin{aligned} \mu &= \left( \frac{\partial A}{\partial N} \right)_T = -\epsilon + k_B T \left\{ \ln N + N \left( \frac{1}{N} \right) \right. \\ &\quad \left. - \ln (N_0 - N) - \frac{(N_0 - N)}{(N_0 - N)} \right\} \end{aligned}$$

$$\mu = -\epsilon + k_B T \ln \left( \frac{N}{N_0 - N} \right)$$

$$\frac{N}{N_0 - N} = e^{\beta(\epsilon + \mu)}$$

solve above for  $N \Rightarrow N = \frac{N_0 e^{\beta(\epsilon + \mu)}}{1 + e^{\beta(\epsilon + \mu)}} = \frac{N_0}{1 + e^{-\beta(\epsilon + \mu)}}$

Fraction occupied is

$$\frac{N}{N_0} = \frac{1}{1 + e^{-\beta(\epsilon + \mu)}}$$

Now we do the same calculation, but in the grand canonical ensemble

Let  $\{\alpha\}$  be the set of states of adsorbed particles, where the number of adsorbed particles is free to be anything from zero to  $N_0$ . The grand partition function is:

$$\mathcal{Z} = \sum_{\alpha} e^{-\beta(E_{\alpha} - \mu N_{\alpha})}$$

$E_{\alpha}$  is total energy of state  $\alpha$

$N_{\alpha}$  is the number of occupied ~~site~~ sites in state  $\alpha$

For adsorption site  $i$  define a variable  $s_i$  such that

$$s_i = \begin{cases} 1 & \text{if site } i \text{ is occupied} \\ 0 & \text{if site } i \text{ is empty} \end{cases}$$

a particular state  $\alpha$  can then be specified by giving the values 1 or 0 of each of the  $N_0$  variables  $s_i$ . In terms of these variables we have for the energy and number of adsorbed particles:

$$\alpha = \{s_i\} \Rightarrow E_{\alpha} = -\epsilon \sum_i s_i$$

$$N_{\alpha} = \sum_i s_i$$

The partition function can then be written as

$$\mathcal{Z} = \sum_{\{s_i\}} e^{-\beta[-\epsilon \sum_i s_i - \mu \sum_i s_i]} = \sum_{\{s_i\}} e^{\beta(\epsilon + \mu) \sum_i s_i}$$

We can factor the exponential since the degrees of freedom  $s_i$  are non-interacting with each other

$$\begin{aligned} \mathcal{Z} &= \sum_{\{s_i\}} \prod_{i=1}^{N_0} e^{\beta(\epsilon + \mu)s_i} = \prod_{i=1}^{N_0} \left[ \sum_{s_i=0,1} e^{\beta(\epsilon + \mu)s_i} \right] \\ &= \prod_{i=1}^{N_0} [1 + e^{\beta(\epsilon + \mu)}] = [1 + e^{\beta(\epsilon + \mu)}]^{N_0} \end{aligned}$$

Now we compute the grand potential

$$\Sigma(T, \mu) = -k_B T \ln \mathcal{Z}$$

$$= -k_B T N_0 \ln [1 + e^{\beta(\epsilon + \mu)}]$$

The average number of adsorbed particles is then

$$N = - \left( \frac{\partial \Sigma}{\partial \mu} \right)_T = \frac{k_B T N_0 \beta e^{\beta(\epsilon + \mu)}}{(1 + e^{\beta(\epsilon + \mu)})}$$

$$N = \frac{N_0}{1 + e^{-\beta(\epsilon + \mu)}}$$

This is the same result as we found using the canonical ensemble, as it must be!

Step ② Now we compute the chemical potential  $\mu$  of the ideal gas at temperature  $T$  and pressure  $P$ .

We will use the grand canonical ensemble. Since particles in the gas are non-interacting we have

$$\mathcal{Z} = e^{\beta Q_1} \quad \text{where } z = e^{\beta \mu} \text{ and } Q_1 \text{ is the one particle partition function}$$

$$\begin{aligned} Q_1 &= \int d^3p \int d^3r \frac{e^{-\beta p^2/2m}}{h^3} = \frac{V}{h^3} \sqrt{\frac{2\pi m}{\beta}}^3 \\ &= V \sqrt{\frac{2\pi m k_B T}{h^2}}^3 = \frac{V}{\lambda^3} \end{aligned}$$

where  $\lambda \equiv \sqrt{\frac{h^2}{2\pi m k_B T}}$  is called the "thermal wavelength"

$$-pV = \Sigma = -k_B T \ln \mathcal{Z} = -k_B T \ln Q_1$$

$$p = \frac{k_B T}{V} \ln Q_1 = \frac{k_B T}{V} \ln \frac{V}{\lambda^3}$$

$$p = \frac{k_B T}{\lambda^3} z$$

$$z = e^{\beta \mu} = \frac{\lambda^3 p}{k_B T}$$

This then gives the factor  $e^{\beta \mu}$  that we need for inserting into our expression for  $\frac{N}{N_0}$

or we could get  $\mu(T, p)$  using the canonical ensemble

$$Q_N = \frac{1}{N!} Q_1^N$$

using Stirling approx

$$A = -k_B T \ln Q_N = -k_B T \left[ N \ln Q_1 - N \ln N + N \right]$$

$$\begin{aligned} \mu &= \left( \frac{\partial A}{\partial N} \right)_{T, V} = -k_B T \left[ \ln Q_1 - \ln N - \frac{N}{N} + 1 \right] \\ &= -k_B T \ln \left( \frac{Q_1}{N} \right) \end{aligned}$$

$$\mu = -k_B T \ln \left( \frac{V}{N \lambda^3} \right) \quad \text{gives } \mu(T, V, N)$$

to write  $\mu$  in terms of  $p$  and  $T$  we then need

$$p = - \left( \frac{\partial A}{\partial V} \right)_{T, N} = k_B T \frac{N}{Q_1} \left( \frac{\partial Q_1}{\partial V} \right)_T$$

$$= k_B T \left( \frac{N/Q_1}{V} \right) \left( \frac{\partial Q_1}{\partial V} \right) = k_B T \frac{N}{V} \quad \text{ideal gas law!}$$

so we can write  $\frac{V}{N \lambda^3} = \frac{k_B T}{p \lambda^3}$  and so

$$\mu(T, p) = -k_B T \ln \left( \frac{k_B T}{p \lambda^3} \right)$$

or

$$Z = e^{\beta \mu} = \frac{p \lambda^3}{k_B T}$$

same as found by grand canonical ensemble

step ③ substitute  $\mu$  from step ②  
into result from step ①

$$\frac{N}{N_0} = \frac{1}{1 + e^{-\beta\mu} e^{-\beta\epsilon}}$$

$$= \frac{1}{1 + \frac{k_B T}{p \lambda^3} e^{-\beta\epsilon}}$$

$$\frac{N}{N_0} = \left[ 1 + \frac{k_B T}{p} \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} e^{-\epsilon/k_B T} \right]^{-1}$$

Note: as  $T \rightarrow 0$ ,  $\frac{N}{N_0} \rightarrow 1$  as expected

as  $T \rightarrow \infty$ ,  $\frac{N}{N_0} \rightarrow 0$  as expected