

Problem Set 6(1) Distribution function for double occupancy statistics

The Gibbs sum for such a system is

$$\mathcal{Z} = \sum_{N=0,1,2} \sum_{s(N)} e^{(\mu N - E_{s(N)})/k_B T}$$

$$\text{with } E_{s(0)} = 0$$

$$E_{s(1)} = E$$

$$E_{s(2)} = 2E$$

$$= \sum_{s(0)}^{\overbrace{N=0}} e^{(\mu \cdot 0 - E_{s(0)})/k_B T} + \sum_{s(1)}^{\overbrace{N=1}} e^{(\mu \cdot 1 - E_{s(1)})/k_B T} + \sum_{s(2)}^{\overbrace{N=2}} e^{(\mu \cdot 2 - E_{s(2)})/k_B T}$$

In each remaining "sum" there is only one term (1 state)

$$= \mathbf{1} + e^{(\mu - E)/k_B T} + e^{2(\mu - E)/k_B T}$$

Thus

$$\mathcal{Z} = 1 + e^{(\mu - E)/k_B T} + e^{2(\mu - E)/k_B T}$$

$$\begin{aligned}
 \langle N \rangle &= \frac{1}{\mathcal{Z}} \sum_{N=0,1,2} \sum_{s(N)} N e^{(\mu N - E_{s(N)})/k_B T} \\
 &= \frac{e^{(\mu - E)/k_B T} + 2e^{2(\mu - E)/k_B T}}{1 + e^{(\mu - E)/k_B T} + e^{2(\mu - E)/k_B T}}
 \end{aligned}$$

② Gibbs sum for a two level system

$$\begin{aligned}
 \text{a). } \mathcal{Z} &= \sum_{N=0,1} \sum_{s(N)} e^{(\mu N - E_{s(N)})/k_B T} \\
 &= \underbrace{e^{(\mu \cdot 0 - 0)/k_B T}}_{N=0} + \underbrace{e^{(\mu \cdot 1 - 0)/k_B T} + e^{(\mu \cdot 1 - E)/k_B T}}_{N=1} \\
 &= 1 + e^{\mu/k_B T} + e^{(\mu - E)/k_B T}
 \end{aligned}$$

$$\begin{aligned}
 \text{b). } \langle N \rangle &= \frac{1}{\mathcal{Z}} \sum_{N=0,1} \sum_{s(N)} N e^{(\mu N - E_{s(N)})/k_B T} \\
 &= \frac{1}{\mathcal{Z}} \left[\underbrace{0 \cdot e^{(\mu \cdot 0 - 0)/k_B T}}_{N=0} + \underbrace{1 \cdot e^{(\mu \cdot 1 - 0)/k_B T} + 1 \cdot e^{(\mu \cdot 1 - E)/k_B T}}_{N=1} \right] \\
 &= \frac{1}{\mathcal{Z}} \left[e^{\mu/k_B T} + e^{(\mu - E)/k_B T} \right]
 \end{aligned}$$

c). The state is fixed — the one that has energy E (when occupied by one particle) \therefore no summation over s is involved

$$\langle N(E) \rangle = \frac{\sum_N N(E) e^{(\mu N(E) - E_{N(E)})/k_B T}}{\mathcal{Z}}$$

$$= \frac{1}{\mathcal{Z}} e^{(\mu - E)/k_B T}$$

$$d) U = \frac{1}{\mathcal{Z}} \sum_N \sum_{s(N)} E_s e^{(\mu N - E_s)/k_B T}$$

only one term survives — the one when you have one particle, at energy E
(other terms correspond to $E_s = 0$)

$$= \frac{1}{\mathcal{Z}} \left[\begin{array}{ccc} \text{at } (E=0) & + & \text{at } (E=0) & + & (E) \\ \text{"state 1"} & & \text{"state 2"} & & \text{"state 3"} \\ 0 \text{ particles, } \underline{E=0} & & 1 \text{ particle } \underline{E=0} & & 1 \text{ particle at energy } E \end{array} \right]$$

$$U = \frac{E \cdot e^{(\mu - E)/k_B T}}{1 + e^{\mu/k_B T} + e^{(\mu - E)/k_B T}} = E \langle N(E) \rangle$$

\hookrightarrow from (c)

e)

$$Z = \sum_N \sum_{s(N)} e^{(\mu N - E_{s(N)})/k_B T}$$

$$= \underbrace{\sum_{s(0)} e^{(\mu \cdot 0 - E_{s(0)})/k_B T}}_{N=0} + \underbrace{\sum_{s(1)} e^{(\mu \cdot 1 - E_{s(1)})/k_B T}}_{N=1}$$

$$+ \underbrace{\sum_{s(2)} e^{(\mu \cdot 2 - E_{s(2)})/k_B T}}_{N=2}$$

$$= \underbrace{e^{(\mu \cdot 0 - 0)/k_B T}}_{N=0} + \underbrace{e^{(\mu \cdot 1 - 0)/k_B T} + e^{(\mu \cdot 1 - E)/k_B T}}_{N=1}$$

$$+ \underbrace{e^{(\mu \cdot 2 + E)/k_B T}}_{N=2 \text{ (one in orbital at 0 and one in orbital at E)}}$$

$$= 1 + e^{\mu/k_B T} + e^{(\mu - E)/k_B T} + e^{(2\mu - E)/k_B T}$$

~~$e^{(\mu - E)/k_B T} + e^{(2\mu - E)/k_B T}$~~

$$e^{(\mu - E)/k_B T} (1 + e^{\mu/k_B T})$$

(5)

$$= \underbrace{\left(1 + e^{\mu/k_B T}\right)}_{Z_0} \underbrace{\left(1 + e^{(\mu-E)/k_B T}\right)}_{Z_E}$$

E —

0 —

3. Alternative expressions for the chemical potential

Since $S = S(U, V, N)$, taking the full differential gives

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN$$

With $dV = 0$ (const Volume)

we are left with

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN$$

(6)

Choosing $(\delta S)_T$, $(\delta U)_T$, and $(\delta N)_T$ independently such that $dT=0$ (T const.) we get

$$(\delta S)_T = \left(\frac{\partial S}{\partial U}\right)_{N,V} (\delta U)_T + \left(\frac{\partial S}{\partial N}\right)_{U,V} (\delta N)_T$$

Dividing by $(\delta N)_T$:

$$\left(\frac{\delta S}{\delta N}\right)_{T,V} = \underbrace{\left(\frac{\partial S}{\partial U}\right)_{N,V} \left(\frac{\delta U}{\delta N}\right)_{T,V}}_{\equiv \frac{1}{T}} + \left(\frac{\partial S}{\partial N}\right)_{U,V}$$

Thus

$$\left(\frac{\partial S}{\partial N}\right)_{T,V} = \frac{1}{T} \left(\frac{\partial U}{\partial N}\right)_{T,V} + \left(\frac{\partial S}{\partial N}\right)_{U,V} \quad (*)$$

From $F = U - TS$, by taking its derivative $\left(\frac{\partial F}{\partial N}\right)_{T,V}$ we get for μ

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial (U - TS)}{\partial N}\right)_{T,V} = \underbrace{\left(\frac{\partial U}{\partial N}\right)_{T,V}}_{\text{Eq. (*)}} - T \left(\frac{\partial S}{\partial N}\right)_{T,V}$$

Eq. (*) can be rewritten as:

$$\underbrace{\left(\frac{dU}{dN}\right)_{T,V} - T \left(\frac{\partial S}{\partial N}\right)_{T,V}}_{\text{Eq. (*)}} = -T \left(\frac{\partial S}{\partial N}\right)_{U,V}$$

Therefore

$$\mu = -T \left(\frac{\partial S}{\partial N} \right)_{U,V} \quad \text{as required to show}$$

(b) From page 5.

$$dS = \left(\frac{\partial S}{\partial U} \right)_{V,N} dU + \left(\frac{\partial S}{\partial N} \right)_{U,V} dN$$

choosing $(\delta U)_S$ and $(\delta N)_S$ [at const. S]

so that $dS = 0$

(since we want to show that

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{S,V} \quad \leftarrow \text{constant } S$$

we get

$$0 = \left(\frac{\partial S}{\partial U} \right)_{V,N} (\delta U)_S + \left(\frac{\partial S}{\partial N} \right)_{U,V} (\delta N)_S$$

$$\text{or} \quad \underbrace{\left(\frac{\partial S}{\partial U} \right)_{V,N}}_{\frac{1}{T}} \left(\frac{\partial U}{\partial N} \right)_{S,V} + \left(\frac{\partial S}{\partial N} \right)_{U,V} = 0$$

or

$$\frac{1}{T} \left(\frac{\partial U}{\partial N} \right)_{S,V} + \left(\frac{\partial S}{\partial N} \right)_{U,V} = 0$$

or

$$\left(\frac{\partial U}{\partial N} \right)_{S,V} = -T \left(\frac{\partial S}{\partial N} \right)_{U,V}$$

this is μ from (a) \therefore the left hand side is also μ

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{S,V}$$

4. Average number of particles and particle number fluctuations in a single-orbital system

$$(a). \quad \tilde{Z}_0 = \sum_{N_0} e^{(\mu N_0 - E_0 N_0)/k_B T}$$

Take the derivative of $\ln \tilde{Z}_0$ with respect to μ :

$$\begin{aligned} \frac{\partial \ln \tilde{Z}_0}{\partial \mu} &= \frac{1}{\tilde{Z}_0} \underbrace{\sum_{N_0} N_0 e^{N_0(\mu - E_0)/k_B T}}_{\text{definition of } \langle N_0 \rangle} \cdot \frac{1}{k_B T} \\ &= \frac{1}{k_B T} \langle N_0 \rangle \end{aligned}$$

$$\therefore \langle N_G \rangle = k_B T \frac{\partial \ln Z_G}{\partial \mu}$$

(b) $\langle (N_G)^2 \rangle - ?$

$$\frac{\partial Z_G}{\partial \mu} = \frac{1}{k_B T} \sum_{N_G} N_G e^{N_G(\mu - E_G)/k_B T}$$

Take the derivative again

$$\frac{\partial^2 Z_G}{\partial \mu^2} = \left(\frac{1}{k_B T} \right)^2 \sum_{N_G} N_G^2 e^{N_G(\mu - E_G)/k_B T}$$

multiply and divide by Z_G

$$= \frac{Z_G}{(k_B T)^2} \cdot \underbrace{\frac{1}{Z_G} \sum_{N_G} (N_G)^2 e^{N_G(\mu - E_G)/k_B T}}_{\text{definition of } \langle (N_G)^2 \rangle}$$

$$= \frac{Z_G}{(k_B T)^2} \langle (N_G)^2 \rangle$$

$$\therefore \left(\langle N_G^2 \rangle = \frac{(k_B T)^2}{Z_G} \frac{\partial^2 Z_G}{\partial \mu^2} \right)$$

$$(c) \quad \langle (\Delta N_G)^2 \rangle = \langle [N_G - \langle N_G \rangle]^2 \rangle$$

$$\begin{aligned} &= \langle (N_G)^2 \rangle - 2 \langle N_G \rangle \langle N_G \rangle + \langle N_G \rangle^2 \\ &\quad \text{here } \langle N_G \rangle \text{ is already an average, with a single numerical value} \end{aligned}$$

$$= \langle (N_G)^2 \rangle - 2 \langle N_G \rangle \langle N_G \rangle + \langle N_G \rangle^2$$

$$= \langle (N_G)^2 \rangle - \langle N_G \rangle^2$$

$$\therefore \langle (\Delta N_G)^2 \rangle = \langle N_G^2 \rangle - \langle N_G \rangle^2$$

Then, from (a) and (b) :

$$\langle (\Delta N_G)^2 \rangle = (k_B T)^2 \left[\frac{1}{Z_G} \frac{\partial^2 Z_G}{\partial \mu^2} - \frac{1}{Z_G^2} \left(\frac{\partial Z_G}{\partial \mu} \right)^2 \right]$$

(11)

(d) Take derivative of $\langle N_G \rangle$ from (a) with respect to μ

$$\frac{\partial \langle N_G \rangle}{\partial \mu} = \frac{\partial}{\partial \mu} \left[k_B T \cdot \frac{\partial \ln Z_G}{\partial \mu} \right] =$$

$$= \frac{\partial}{\partial \mu} \left[k_B T \cdot \frac{1}{Z_G} \frac{\partial Z_G}{\partial \mu} \right] =$$

$$= k_B T \cdot \left[\frac{\partial}{\partial \mu} \left(\frac{1}{Z_G} \right) \cdot \frac{\partial Z_G}{\partial \mu} + \frac{1}{Z_G} \frac{\partial^2 Z_G}{\partial \mu^2} \right]$$

$$= k_B T \left[\frac{1}{Z_G} \frac{\partial^2 Z_G}{\partial \mu^2} - \frac{1}{Z_G^2} \frac{\partial Z_G}{\partial \mu} \cdot \frac{\partial Z_G}{\partial \mu} \right]$$

$$= k_B T \left[\frac{1}{Z_G} \frac{\partial^2 Z_G}{\partial \mu^2} - \frac{1}{Z_G^2} \left(\frac{\partial Z_G}{\partial \mu} \right)^2 \right]$$

multiply by $(k_B T)$, both sides:

$$k_B T \frac{\partial \langle N_G \rangle}{\partial \mu} = \underbrace{(k_B T)^2 \left[\frac{1}{Z_G} \frac{\partial^2 Z_G}{\partial \mu^2} - \frac{1}{Z_G^2} \left(\frac{\partial Z_G}{\partial \mu} \right)^2 \right]}_{\langle (\Delta N_G)^2 \rangle \text{ from (c)}}$$

Therefore

$$\langle (\Delta N_G)^2 \rangle = k_B T \frac{\partial \langle N_G \rangle}{\partial \mu}$$

(e)

$$\langle N_G \rangle \equiv \begin{cases} f_F(E) = \frac{1}{e^{(E-\mu)/k_B T} + 1} \\ f_B(E) = \frac{1}{e^{(E-\mu)/k_B T} - 1} \\ f_C(E) = e^{-(E-\mu)/k_B T} \end{cases}$$

Differentiate each of these with respect to μ :

$$\begin{aligned} \frac{\partial f_F(E)}{\partial \mu} &= \frac{\partial}{\partial \mu} \left(\frac{1}{e^{(E-\mu)/k_B T} + 1} \right) = \\ &= \frac{\frac{1}{k_B T} \left[e^{(E-\mu)/k_B T} (+1 - 1) \right]}{\left(e^{(E-\mu)/k_B T} + 1 \right)^2} = \\ &= \frac{1}{k_B T} \left[\frac{e^{(E-\mu)/k_B T} + 1}{\left(e^{(E-\mu)/k_B T} + 1 \right)^2} - \frac{1}{\left(e^{(E-\mu)/k_B T} + 1 \right)^2} \right] \end{aligned}$$

add and subtract 1

$$= \frac{1}{k_B T} \left[\underbrace{\frac{1}{e^{(E-\mu)/k_B T} + 1}}_{f_F(E)} - \underbrace{\frac{1}{(e^{(E-\mu)/k_B T} + 1)^2}}_{(f_F(E))^2} \right]$$

$$= \frac{1}{k_B T} [f_E - f_E^2]$$

\therefore

$$\langle (\Delta N_\sigma)^2 \rangle = \underset{\substack{\text{from} \\ (d)}}{k_B T \frac{\partial f_F}{\partial \mu}} = f_E - f_E^2$$

$$= f_E (1 - f_E) \equiv \langle N_\sigma \rangle (1 - \langle N_\sigma \rangle)$$

- fermions

For $f_B(E)$ - similarly:

$$\langle (\Delta N_\sigma)^2 \rangle = k_B T \frac{\partial f_B}{\partial \mu} = k_B T \cdot \frac{\partial}{\partial \mu} \left[\frac{1}{e^{(E-\mu)/k_B T} - 1} \right]$$

$$= k_B T \cdot \frac{\frac{1}{k_B T} \left[e^{\frac{E-\mu}{k_B T}} - 1 + 1 \right]}{(e^{(E-\mu)/k_B T} - 1)^2} =$$

$$= \frac{1}{e^{(E-\mu)/k_B T} - 1} + \frac{1}{(e^{(E-\mu)/k_B T} - 1)^2}$$

$$= f_B + f_B^2 = \langle N_G \rangle + \langle N_G \rangle^2$$

$$\therefore \boxed{\langle (\Delta N_G)^2 \rangle = \langle N_G \rangle (1 + \langle N_G \rangle)}$$

↪ bosons

classical (Boltzmann) distribution:

$$\langle (\Delta N_G)^2 \rangle = k_B T \frac{\partial f_c(E)}{\partial \mu} = k_B T \frac{\partial}{\partial \mu} e^{-(E-\mu)/k_B T}$$

$$= k_B T \cdot \frac{1}{k_B T} e^{-(E-\mu)/k_B T} = f_c(E)$$

$$= \langle N_G \rangle$$

5. Carbon monoxide poisoning.

- (a) In the absence of CO molecules, the Gibbs sum for this single-site system has just two terms

$$\tilde{Z}_{(a)} = 1 + e^{-(E_0 - \mu_0)/k_B T}$$

where μ_0 is the chemical potential for the O_2 molecules at concentration λ^{n_0} corresponding to the partial pressure of 0.2 atm and $T = 310\text{ K}$ (corresponding to body temperature of $\sim 37^\circ\text{C}$).

The probability of the site being occupied is

$$\begin{aligned} P_{(a)}(\text{occupied by } O_2, \text{ no CO}) &= \frac{\text{Gibbs factor}}{\text{Gibbs sum}} = \\ &= \frac{e^{-(E_0 - \mu_0)/k_B T}}{1 + e^{-(E_0 - \mu_0)/k_B T}} \end{aligned}$$

The first term in $\tilde{Z}_{(a)}$ corresponds to ~~the state~~ an unoccupied state, with $N_0 = 0$ and energy 0; the second term corresponds to the state occupied by one ($N_0 = 1$) O_2 molecule, with $E_0 = -0.62\text{ eV}$.

(b) If there is also some carbon monoxide present, which can be absorbed into the same site instead of O_2 , then the Gibbs sum has three terms:

$$\mathcal{Z}_{(b)} = 1 + e^{-(E_0 - \mu_0)/k_B T} + e^{-(E_c - \mu_c)/k_B T}$$

where μ_c is the chemical potential for the CO molecules at concentration that is 100 smaller than n_0 ; $n_c = 0.01 n_0$.

In this situation, the probability of the site being occupied by the same O_2 molecules is

$$P(\text{occupied by } O_2, \text{ (b) in the presence of CO}) = \frac{e^{-(E_0 - \mu_0)/k_B T}}{1 + e^{-(E_0 - \mu_0)/k_B T} + e^{-(E_c - \mu_c)/k_B T}}$$

To calculate $P_{(a)}$ and $P_{(b)}$, we need to know μ_0 at n_0 , and μ_c at $n_c = 0.01 n_0$.

The concentration n_0 corresponding to the partial pressure of 0.2 atm can be found from the equation of state for the classical ideal gas

$$pV = Nk_B T \Rightarrow \underbrace{\frac{N}{V}}_{\text{concentration } n} = \frac{p}{k_B T}$$

$n = \frac{p}{k_B T}$ - is the concentration of an ideal monoatomic gas in the classical regime at temperature T and pressure p .

For $p = 1 \text{ atm} = 10^5 \text{ N/m}^2$ and $T = 310 \text{ K}$, this would give $n = \frac{10^5 \text{ N/m}^2}{k_B \cdot 310 \text{ K}} = \dots \approx 2.34 \times 10^{25} \text{ m}^{-3}$

For the partial pressure of oxygen molecules in the atmosphere 0.2 atm , the corresponding concentration is:

$$n_O = \frac{0.2 \times 1 \text{ atm}}{k_B T} = \frac{0.2 \times 10^5 \text{ N/m}^2}{1.38 \cdot 10^{-23} \text{ J/K} \cdot 310 \text{ K}} \approx 4.7 \times 10^{24} \text{ m}^{-3}$$

100 times lower concentration for CO molecules gives

$$n_C = 4.7 \times 10^{22} \text{ m}^{-3}$$

To determine the chemical potentials μ_O and μ_C for O_2 and CO molecules from the classical ideal gas formula

$$\mu_O = k_B T \ln \left(\frac{n_O}{n_{Q,O}} \right), \quad \mu_C = k_B T \ln \left(\frac{n_C}{n_{Q,C}} \right)$$

[see Lecture 11]

we need to calculate the respective quantum concentrations $n_{Q,O}$ and $n_{Q,C}$.

The quantum concentration (from Lecture 11) is given by

$$n_Q = \left(\frac{m k_B T}{2 \pi \hbar^2} \right)^{3/2}$$

where we substitute with

$$m_{O_2} \approx (2 \times 16) \times 1.67 \times 10^{-27} \text{ kg} = 5.3 \times 10^{-26} \text{ kg} \quad \text{for } O_2,$$

and

$$m_{CO} \approx (12 + 16) \times 1.67 \times 10^{-27} \text{ kg} \approx 4.7 \times 10^{-26} \text{ kg}, \quad \text{for } CO.$$

At $T = 310 \text{ K}$, we obtain:

$$n_{Q,O} \approx 1.85 \times 10^{32} \text{ m}^{-3} \quad - \text{ for } O_2$$

$$n_{Q,C} \approx 1.55 \times 10^{32} \text{ m}^{-3} \quad - \text{ for } CO.$$

Therefore

$$\begin{aligned} \mu_O &= k_B T \ln \left(\frac{n_O}{n_{Q,O}} \right) = 1.38 \times 10^{-23} \text{ J/K} \cdot 310 \text{ K} \ln \left(\frac{4.7 \times 10^{24}}{1.85 \times 10^{32}} \right) \\ &\approx -7.48 \times 10^{-20} \text{ J} \quad (\underline{\underline{= -0.47 \text{ eV}}}) \end{aligned}$$

$$\begin{aligned} \mu_C &= k_B T \ln \left(\frac{n_C}{n_{Q,C}} \right) = 1.38 \times 10^{-23} \text{ J/K} \cdot 310 \text{ K} \ln \left(\frac{4.7 \times 10^{22}}{1.55 \times 10^{32}} \right) \\ &\approx -9.45 \times 10^{-20} \text{ J} \quad (\underline{\underline{= -0.59 \text{ eV}}}) \end{aligned}$$

$$[1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}]$$

With these values of μ_o and μ_c
 (together with $E_o = -0.57 \text{ eV} = -0.57 \times 1.6 \times 10^{-19} \text{ J}$
 and $E_c = -0.72 \text{ eV} = -0.72 \times 1.6 \times 10^{-19} \text{ J}$),
 the Gibbs factors for the O_2 and CO
 molecules are

$$e^{-(E_o - \mu_o)/k_B T} = e^{0.1 \text{ eV}/k_B T} = e^{0.1 \times 1.6 \times 10^{-19} / k_B T} \dots = 42$$

$$e^{-(E_c - \mu_c)/k_B T} = e^{0.13 \text{ eV}/k_B T} = 129$$

Therefore $Z_{(a)} = 1 + 42 = 43$

$$Z_{(b)} = 1 + 42 + 129 = 172$$

Therefore

$$P_{(a)} = \frac{42}{43} \approx 0.98 \quad (98\%)$$

$$P_{(b)} = \frac{42}{172} \approx 0.23 \quad (23\%)$$

↳ this is too low to
sustain life!

If, on the other hand, E_c was

$E_c = E_0 = -0.57 \text{ eV}$, we would obtain

for the CO Gibbs factor

$$e^{-(E_c - \mu_c)/k_B T} = e^{0.02 \text{ eV}/k_B T} = e^{0.02 \cdot 1.6 \times 10^{-19} \text{ J}/k_B T} \\ \approx 2$$

Therefore $Z_{(b)} = 1 + 42 + 2 = 45$

and we would get

$$P_{(b)} = \frac{42}{45} \approx 0.93 \text{ (93\%)},$$

which is still rather high.

Thus, the reason for significantly low

$P_{(b)}$ in the previous case was the stronger binding of the CO molecules

(the binding energy $|E_c| = 0.72 \text{ eV}$ was larger than $|E_0| = 0.57 \text{ eV}$)