Problem 1. Charge Neutrality

Consider a lattice of protons consisting of a total of N sites. The protons (located at the sites) share the available electrons which can hop from site to site. The total system is neutral so that the number of electrons is equal to the number of protons (or lattice sites). Electrons can hop from site to site, so each site does not need to be neutral. Suppose that each atom can exist in four states which are listed and illustrated schematically below.

state	$N_{\text{electrons}}$	Energy
ground state	1	$-\frac{1}{2}\Delta$
positive ion	0	$-\frac{1}{2}\delta$
negative ion	2	$\frac{1}{2}\delta$
excited hydrogen	1	$\frac{1}{2}\Delta$

H	H+	H−	H⋆
H−	H−	H+	H+
H	H⋆	H⋆	H⋆
H−	H	H+	H

(a) Compute the grand potential $\Phi_G = -kT \log \mathcal{Z}_G$ of a single site by evaluating the grand partition function, $\mathcal{Z}_G$. After some algebra you should find

$$Z_G = 2e^{\beta\mu}\cosh(\beta\Delta/2) + 2e^{\beta\mu}\cosh(\beta(\delta/2 - \mu)) \tag{1}$$

(b) Determine the mean number of electrons per site as a function of the electron chemical potential and temperature.

(c) Show that the electron chemical potential is $\delta/2$ and that probability of having neutral hydrogen is

$$\frac{e^{\beta(\Delta+\delta)/2}}{4e^{\beta\delta/2}\cosh^2(\beta\Delta/4)} \tag{2}$$

and that grand partition function at this chemical potential.

$$\mathcal{Z}_G = 4e^{\beta\delta/2}\cosh^2(\beta\Delta/4) \tag{3}$$

Hint: The indentity $(\cosh(x)+1)/2 = \cosh^2(x/2)$, is the hyperbolic analog of the cosine identity $(\cos(\theta)+1)/2 = \cos^2\theta$.

(d) Determine the the entropy per site. You should find

$$\frac{S}{k_B} = \log\left[4\cosh^2(\tfrac{\beta\Delta}{4})\right] - \frac{\beta\Delta}{2}\tanh(\tfrac{\beta\Delta}{4}) \tag{4}$$

Make a sketch of this function as function of $\beta\Delta$. What is the limit of this function as $\beta\Delta \to 0$? Give a physical interpretation of this limit.

Neutrality

a) $$\mathcal{Z} = \sum_s e^{-\beta(\varepsilon_s - \mu N_s)}$$

$$= e^{-\beta(-\Delta/2 - \mu)} + e^{-\beta(\Delta/2 - \mu)}$$

$$+ e^{+\beta\delta/2} + e^{-\beta(\delta/2 - 2\mu)}$$

$$= e^{\beta\mu}\left(e^{\beta\Delta/2} + e^{-\beta\Delta/2}\right) + e^{\beta\delta/2} + e^{2\beta\mu} e^{-\beta\delta/2}$$

$$\boxed{\begin{aligned}\mathcal{Z} &= 2e^{\beta\mu}\cosh(\beta\Delta/2) + e^{\beta\delta/2} + e^{2\beta\mu}e^{-\beta\delta/2} \\ \mathcal{Z} &= 2e^{\beta\mu}\left(\mathrm{ch}(\beta\Delta/2) + \mathrm{ch}(\beta(\delta/2 - \mu))\right)\end{aligned}}$$

b)

$$\bar{N} = \Big[1 \cdot e^{-\beta(-\Delta/2 - \mu)} + 1 \cdot e^{-\beta(\Delta/2 - \mu)}$$

$$+ 2e^{2\beta\mu} e^{-\beta\delta/2}\Big]/\mathcal{Z}$$

So

this can be simplified see last page

$$\boxed{\bar{N} = \frac{2e^{\beta\mu}\cosh(\beta\Delta/2) + 2e^{2\beta\mu}e^{-\beta\delta/2}}{\mathcal{Z}}}$$

c) Skipped -- included below if really interested.

d) We require $\bar{N} = 1$, or wiriting $\bar{N} = \text{numerator}/\text{den}$

$$2e^{\beta\mu}\cosh(\beta\Delta/2) + 2e^{2\beta\mu}e^{-\beta\delta/2} = 2e^{\beta\mu}\cosh(\beta\Delta/2) + e^{\beta\delta/2}$$

$$+ e^{2\beta\mu}e^{-\beta\delta/2}$$

So we have

$$2 e^{2\beta\mu} e^{-\beta\delta/2} = e^{\beta\delta/2} + e^{2\beta\mu} e^{-\beta\delta/2}$$

$$e^{2\beta\mu} e^{-\beta\delta/2} = e^{\beta\delta/2}$$

So $\mu = \delta/2$

e) Lets Find The entropy at the neutrality point

First note that for $\frac{\delta}{2} = \mu$ we have

$$\mathcal{Z} = 2e^{\beta\delta/2}\cosh(\beta\Delta/2) + 2e^{\beta\delta/2}$$

$$= 2e^{\beta\delta/2}\left(\mathrm{ch}(\beta\Delta/2) + 1\right) = 4e^{\beta\delta/2}\,\mathrm{ch}^2(\beta\Delta/4)$$

Now

$$\Phi_G = -k_B T \ln \mathcal{Z} \quad \text{and} \quad S = -\left(\frac{\partial \Phi_G}{\partial T}\right)_\mu$$

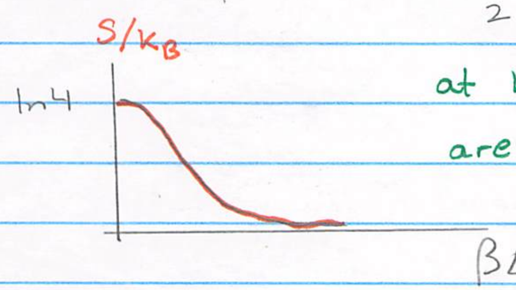
$$\frac{S}{k_B} = \ln \mathcal{Z} + T\frac{\partial}{\partial T}\ln \mathcal{Z}$$

$$= \ln \mathcal{Z} - \beta\frac{\partial}{\partial \beta}\ln \mathcal{Z}$$

$$= \ln(4\,\mathrm{ch}^2(\beta\Delta/4)) + \frac{\beta\delta}{2} - \beta\frac{\partial}{\partial\beta}\left(\frac{\beta\delta}{2} + \ln(4\,\mathrm{ch}^2(\beta\Delta/4))\right)$$

$$\boxed{\frac{S}{k_B} = \ln(4\,\mathrm{ch}^2(\beta\Delta/4)) - \frac{\beta\Delta}{2}\tanh\left(\frac{\beta\Delta}{4}\right)}$$

Sketch



at high T, $\beta\Delta \simeq 0$, and all four states are equally likely and thus the entropy is $\ln 4$. At low T only one state is possible and $\ln(1) = 0 = S$

Problem 2. Yields of three species

Consider three ideal gasses in equilibrium. They participate in the following chemical reaction

$$A + B \leftrightarrow C\,. \tag{5}$$

It is energetically favorable to form atom C, so that the energy of one molecule of C is

$$\epsilon_C = \frac{p^2}{2m_C} - \Delta\,, \tag{6}$$

where $\Delta > 0$ is the binding energy of C. The molecule C has only one internal state. The other two atoms have energies $\epsilon_A = p^2/2m_A$ and $\epsilon_B = p^2/2m_B$ and form simple ideal gasses

(a) If the partition function $Z_{\rm tot}$ of a gas of N indistinguishable particles is given by $Z_{\rm tot} = Z_1^N/N!$, where Z_1 is the single–particle partition function, show that the chemical potential is given by

$$\mu = -kT \log\left(\frac{Z_1}{N}\right) \tag{7}$$

(b) Assume that at one moment there are N_A, N_B, and N_C particles of type A, B, and C, respectively. Determine the partition function of each species, and find the corresponding chemical potentials.

(c) Show that

$$n_A = \frac{e^{\mu_A/kT}}{\lambda_A^3} \tag{8}$$

$$n_B = \frac{e^{\mu_B/kT}}{\lambda_B^3} \tag{9}$$

$$n_C = \frac{e^{\mu_C/kT}e^{\beta\Delta}}{\lambda_C^3} \tag{10}$$

Here $n_A = N_A/V$ is the density of species A, and λ_A is the thermal wavelength of A, with an analogous notation for B and C.

(d) Show that in equilibrium the densities of A, B and C satisfy

$$\frac{n_A n_B}{n_C} = \frac{(2\pi m_{\rm red} kT)^{3/2}}{h^3} e^{-\beta\Delta} \tag{11}$$

where $m_{\rm red} = m_A m_B/(m_A + m_B)$ is the reduced mass. Note $m_C = m_A + m_B$.

Problem: Yields

- a) So

$$Z_{tot} = \frac{Z_1^N}{N!} \simeq \left(\frac{e Z_1}{N}\right)^N$$

Then

$$F = -kT \ln Z_{tot} = -kTN \ln\left(\frac{eZ_1}{N}\right) = -kTN\left[\ln\frac{Z_1}{N} + 1\right]$$

So

$$\mu = \left(\frac{\partial F}{\partial N}\right)_T = -kT\left[\ln\left(\frac{Z_1}{N}\right) + 1\right] + kTN \frac{\partial}{\partial N}(\ln N + const)$$

$$\boxed{\mu = -kT \ln Z_1/N}$$

Now

b) • $Z_1 = Z_1^{trans} \, Z_{int}$

- $Z_1^A = V n_Q^A \cdot 1$ with $n_Q^A = \frac{(2\pi m^A k_B T)^{3/2}}{h^3}$
- $Z_1^B = V n_Q^B \cdot 1$
- $Z_1^C = V n_Q^C \cdot \sum_s e^{-\beta \varepsilon_s}$

$$Z_1^C = V n_Q^C \, e^{\beta \Delta}$$

Then

$$e^{\mu_A/kT} = \frac{N}{Z_1}$$

Now this yields:

$$\boxed{e^{\mu_A/kT} = \frac{N}{V n_Q^A} = \frac{n^A}{n_Q^A}}$$

Similarly

$$\boxed{\begin{aligned} e^{\mu_B/kT} &= \frac{n}{n_Q^B} \\ e^{\mu_c/kT} &= \frac{n}{n_Q^c} e^{-\beta\Delta} \end{aligned}}$$

Finally sine

$e^{+(\mu_A+\mu_B-\mu_c)/kT} = 1$ we have:

$$\left(\frac{n^A}{n_Q^A}\right)\left(\frac{n^B}{n_Q^B}\right)\left(\frac{n_Q^c \, e^{\beta\Delta}}{n_c}\right) = 1$$

Or

$$\frac{n^A n^B}{n_c} = \left(\frac{n_Q^A n_Q^B}{n_Q^c}\right) e^{-\beta\Delta}$$

So

$$n_C \propto n^A n^B e^{\beta \Delta}$$

if the Binding energy is strong we get lots of particle C. But the yield of C is limitted by the availability of A and B.

We note $\quad n_Q = C_0 m^{3/2} \quad$ or $\quad n_Q = (2\pi m kT)^{3/2}/h^3$

$$\frac{n_Q^A n_Q^B}{n_Q^C} = C_0 \left(\frac{m_A m_B}{m_A + m_B}\right)^{3/2} \qquad \hookrightarrow C_0 = (2\pi kT)^{3/2}/h^3$$

$$= C_0 m_{red}^{3/2} \qquad \text{with} \quad m_{red} = \frac{m_A m_B}{m_A + m_B}$$

So finally we have

$$\boxed{\frac{n_A n_B}{n_C} = \frac{(2\pi m_{red} kT)^{3/2}}{h^3} e^{-\beta \Delta}}$$

Problem 3. The Saha Equation

The Saha equation describes the relative abundance of neutral hydrogen to ionized hydrogen at a given temperature. The reaction here is

$$p + e \leftrightarrow H \tag{12}$$

The bound states of the hydrogen atom have internal energies

$$\epsilon_n = -\frac{R}{n^2} \qquad n = 1, 2, 3, \ldots. \tag{13}$$

where $R = -13.6\,\text{eV}$ as well as translational kinetic energy

$$\epsilon(\boldsymbol{p}, n) = \frac{p^2}{2m} + \epsilon_n \tag{14}$$

Following Saha approximate the internal partition function of hydrodygen by just including the lowest energy state (the n=1 state) with energy $-R$. This amounts to treating the hydrogen atom as a single bound state with binding energy $\Delta = R = 13.6\,\text{eV}$ and then evaluate the partition function of hydrogen with the same approximation in a previous problem. You can also approximate the reduced mass of the electron and proton as $m_{\text{red}} = m_e m_p/(m_e + m_p) \simeq m_e\,(1 + \mathcal{O}(m_e/m_p))$.

(a) Explain why charge neutrality implies that $\mathrm{n}_e = n_p$ and conservation of nucleons implies $n_H + n_p = n$, where n is the total number density of hydrogen (neutral and ionized). Writing $\mathrm{y} = n_p/n$ as the degree of ionization, show that

$$\frac{y^2}{1-y} = \frac{e^{-\beta R}}{n\lambda_{\text{th}}^3} \tag{15}$$

where λ_{th} is the thermal wavelength for the electrons. Solve for y in terms of $x(T) = e^{-\beta R}/n{\lambda_{\text{th}}}^3$ and graph the degree of of ionization as a function of temperature in kelvin for a density of $10^{20}\,\text{m}^{-3}$. You should find that the temperature where the system becomes fully ionizied is approximately $10000\,^\circ\text{K}$.

(b) Equation 15 shows that the degree of ionization goes up when the density n goes down. Why is that? Answer the following closely related question: The temperature where the hydrogen becomes fully ionized is approximately $10000\,^\circ\text{K}$. But, the Boltzmann factor at this temperature is very small

$$e^{-R/k_BT} = e^{-13.6\,\text{eV}/k_B(10^4\,^\circ\text{K})} \simeq e^{-16.} \sim 10^{-7}\,, \tag{16}$$

Qualitatively explain why the ionized fraction at this temperature is of order unity in spite of this penalizing factor.

b)

- We charge neutrality implies

$$\star \quad n_e = n_p$$

- And we must have

$$\star\star \quad n_p + n_H = n \quad \text{constant}$$

- Since the total number of protons (free + bound) is constant, we have from $\star$

$$\frac{n_e n_p}{n_H} = \frac{1}{\lambda_{th}^3} e^{-\beta R} \quad \text{where} \quad \lambda_{th} = \left(\frac{2\pi m_e k_B T}{h^3}\right)^{3/2}$$

$$\frac{n_p^2}{n_H} = \frac{1}{\lambda_{th}^3} e^{-\beta R}$$

- So the ionization fraction $y = n_p/n$ satifies

$$n \frac{y^2}{n_H/n} = \frac{1}{\lambda_{th}^3} e^{-\beta R} \quad \text{note}$$

Now note $n_H/n = 1-y$ from $\star\star$
So

$$\boxed{\frac{y^2}{1-y} = \frac{1}{n\lambda_{th}^3} e^{-\beta R}}$$

- So Lets substitute #'s

$m_e c^2 = 0.511 \text{ MeV} = 0.5 \times 10^6 \text{ eV}$

$hc = 1240 \text{ eV nm}$

$n = 10^{-7} \text{ nm}^3$

$$\lambda_{th} = \frac{h}{(2\pi m_e k_B T)^{1/2}} = 2.40 \text{ nm}$$

$1/n\lambda_{th}^3 = 7.25 \times 10^5$

$\log(1/n\lambda_{th}^3) = 13.4951$ $\qquad \beta = \frac{1}{kT} \qquad kT = 0.0833 \text{ eV}$

$$\beta R = \frac{13.6 \text{eV}}{\frac{0.025 \text{eV}}{300°\text{K}} \; 1000\text{K}} = 163.2$$

So

$$x \equiv \frac{1}{n\lambda_{th}^3} e^{-\beta R} = e^{13.5 - 163.2} = e^{-150}$$

- This is very small which means, that y will be small.

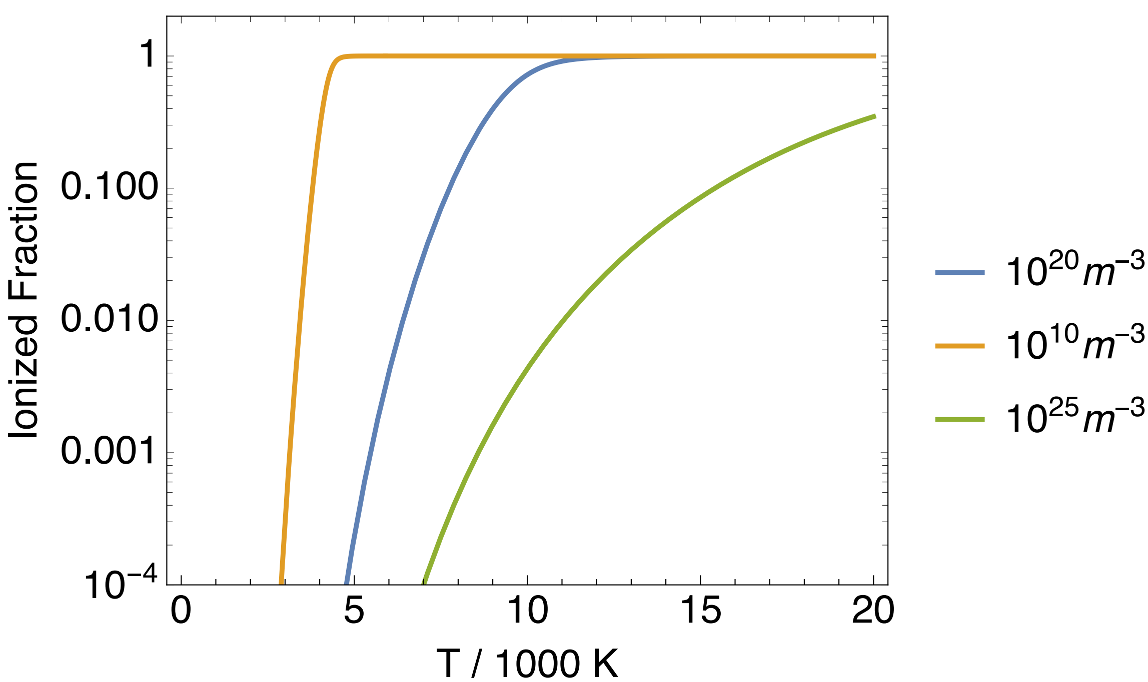
$$\frac{y^2}{1-y} \equiv x$$

$$y \simeq \sqrt{x} \simeq e^{-75} \simeq \boxed{10^{-32.5}}$$

Once can just solve the Saha equation. It is a quadratic equation for y

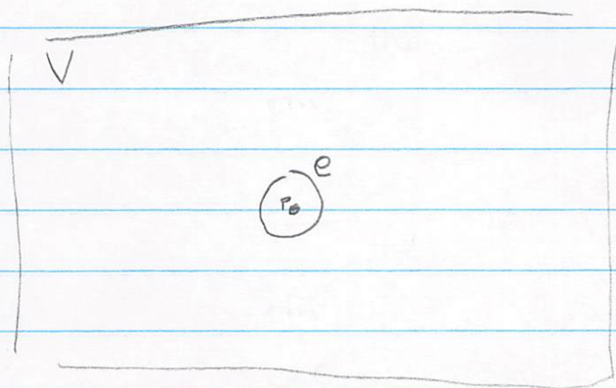
$$y^2 = x(\beta, n)(1 - y)$$

Where $x(\beta, n) = e^{-\ln(n\lambda_{\mathrm{th}}^3) - \beta R}$. I did this and made a graph of the ionization fraction versus temperature. Notice that at low density, the system very rapidly transitions from bound to unbound.



Ionized Fraction
1
0.100
0.010
0.001
10^{-4}
0
5
10
15
20
T / 1000 K
$10^{20} m^{-3}$
$10^{10} m^{-3}$
$10^{25} m^{-3}$

c) To understand the phenomena consider one hydrogen atom in a big box



$$\frac{N}{V} = \frac{1}{V}$$

There is a small amount of phase space of order 1 where the electron is bound, and a large phase-space of order $V p_e^3 / h^3$, where the electron is unbound.

The entropy associated with the unbound states is of order $S/k \sim k \ln \Omega \sim k \ln (V/\lambda_{th}^3)$

So, this grows with the accessible volume when the density is low. Indeed the formula is roughly

$$y^2 \propto e^{(TS_{unbnd} - u)/kT}$$

any y becomes appreciable for $\frac{S}{k_B} \sim \frac{u}{k_B T}$.

So in short the unbound states are penalized energetically, but there are a lot of them, i.e. they are favored entropically.

Problem 4. Absorption and Oscillations

Consider an ideal mono-atomic gas at temperature T and pressure P in contact with a surface. The atoms of the gas can be absorbed on specific sites on the surface, which are sparsely enough distributed over the surface that they do not interact. There are N_0 such sites and each one one can absorb zero, one, or two atoms. If a site is empty, we can take that energy as zero. If the site is singly occupied the energy is ϵ_1. If it is doubly occupied, the two absorbed atoms interact in a vibrational mode of frequency ω_0, so that the corresponding energy levels are $\epsilon_2 + n'\hbar\omega_0$. Here ϵ_2 is the energy for absorbing a pair and $n' = 0, 1, \ldots$ is the vibrational quantum number, parametrizing the additional energy associated with the vibrations.

(a) The temperature and chemical potential that the absorption site experiences is determined by the properties of the surrounding gas. The chemical potential of this gas is determined by its temperature and pressure, in much the same way that the temperature is determined by the energy per particle of the gas $kT = 2/3(E/N)$.

Recall that the single particle partition function of the gas (mono-atomic or even poly-atomic) is

$$Z_1 = \sum_s \int \frac{d^3r d^3p}{h^2} e^{-\beta p^2/2m} e^{-\beta\epsilon_s} \tag{17}$$

Let's strip off the overall dependence on volume and define:

$$Z_1 \equiv V\zeta_1(T) \tag{18}$$

Show that the so-called *fugacity* $z \equiv e^{\beta\mu}$ of the gas is proportional to the pressure, with proportionality constant determined by $\zeta_1(T)$:

$$z \equiv \frac{P}{kT\zeta_1(T)} \tag{19}$$

Show that for a mono-atomic gas

$$z = \frac{P}{kTn_Q(T)} \tag{20}$$

(b) Compute the grand partition function for an absorption site.

(c) Compute the grand potential Φ_G for an absorption site.

(d) Compute the mean number of atoms absorbed by a site by finding the probabilities for each state and then using these probabilities to find the average number of atoms absorbed by a site.

(e) Compute the mean number of atoms absorbed by a site by differentiating (c).

(f) What is the probability that a site will absorb two atoms? And what is the probability that the site will absorb two atoms and that the pair will vibrate with three vibrational quanta?

Answers:

(b) See (c).

(c)

$$\Phi_G = -kT \ln[1 + z\, e^{-\beta\epsilon_1} + z^2\, e^{-\beta\epsilon_2} Z_{HO}(\beta)] \tag{21}$$

where z is the fugacity of the surrounding gas, and $Z_{HO}(\beta) = 1/(1 - e^{-\beta\hbar\omega_0})$ is the partition function of the Harmonic Oscillator (HO).

(d)

$$\bar{n} = \frac{ze^{-\beta\epsilon_1} + 2z^2 e^{-\beta\epsilon_2} Z_{HO}}{1 + ze^{-\beta\epsilon_1} + z^2 e^{-\beta\epsilon_2} Z_{HO}} \tag{22}$$

(e) Same as (d).

(f)

$$\mathscr{P}_2 = \frac{z^2 e^{-\beta\epsilon_2} Z_{HO}}{1 + ze^{-\beta\epsilon_1} + z^2 e^{-\beta\epsilon_2} Z_{HO}}\,, \qquad \mathscr{P}_{2,3} = \mathscr{P}_2 \cdot \left(\frac{e^{-3\beta\hbar\omega_0}}{Z_{HO}}\right)\,. \tag{23}$$

Solution

(a) We have

$$Z_N = \frac{V^N}{N!}\zeta_1^N = (eV\zeta_1/N)^N \tag{24}$$

and

$$F = -NkT\ln(eV\zeta_1/N) \tag{25}$$

We note

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT\ln(eV\zeta_1/N) + kT = -kT\ln(V\zeta_1/N) \tag{26}$$

So

$$z = e^{\beta\mu} = \frac{N\zeta_1}{V} = \frac{P}{kT\zeta_1} \tag{27}$$

Now in the mono-atomic case

$$\zeta_1(T) = n_Q(T) = \int \frac{d^3p}{h}e^{-\beta p^2/2m} \tag{28}$$

So for a mono-atomic gas

$$z = e^{\beta\mu} = \frac{N\zeta_1}{V} = \frac{P}{kTn_Q(T)} \tag{29}$$

(b) The states are listed below

- ground state $E = 0$, $N = 0$
- first state $E = \epsilon_1$, $N = 1$
- second and higher states $E = \epsilon_2 + n_{\rm vib}\hbar\omega_0$, $N = 2$, with $n_{\rm vib} = 0, 1, 2, \ldots$.

So

$$Z_G = 1 + e^{-\beta(\epsilon_1-\mu)} + \sum_{n_{\rm vib}} e^{-\beta(\epsilon_2+n_{\rm vib}\hbar\omega_0-2\mu)} \tag{30}$$

$$Z_G = 1 + e^{-\beta(\epsilon_1-\mu)} + e^{-\beta(\epsilon_2-2\mu)}Z_{HO}(\beta) \tag{31}$$

$$= 1 + ze^{-\beta\epsilon_1} + z^2e^{-\beta\epsilon_2}Z_{HO} \tag{32}$$

with $Z_{HO} = 1/(1-e^{-\beta\hbar\omega_0})$.

(c) So

$$\Phi_G = -kT\ln\left(1 + ze^{-\beta\epsilon_1} + z^2e^{-\beta\epsilon_2}Z_{HO}\right) \tag{33}$$

(d) The probability of being in a state is

$$P_s = e^{-\beta(\epsilon_s-\mu N_s)}\mathcal{Z}_G \tag{34}$$

The probability of being in a state with $N = 1$ is given by the probability of being in just one state:

$$P_{N=1} = e^{-\beta(\epsilon_1-\mu)}\mathcal{Z}_G = ze^{-\beta\epsilon_1}\mathcal{Z}_G \tag{35}$$

The probability of being in *any* state with $N = 2$ is found by summing up the harmonic oscillator states:

$$P_{N=2} = \sum_{n_{\rm vib}} P_s|_{N=2} = \frac{1}{Z_G}\sum_{n_{\rm vib}} e^{-\beta(\epsilon_2 + n_{\rm vib}\hbar\omega_0 - 2\mu)} = \frac{e^{-\beta(\epsilon_2-2\mu)}Z_{HO}(\beta)}{\mathcal{Z}_G} = z^2\frac{e^{-\beta\epsilon_2}Z_{HO}(\beta)}{\mathcal{Z}_G} \tag{36}$$

So the mean N is

$$\langle N \rangle = P_{N=1}\cdot 1 + P_{N=2}\cdot 2 \tag{37}$$

$$= \frac{ze^{-\beta\epsilon_1} + 2z^2 e^{-\beta\epsilon_2}}{\mathcal{Z}_G} \tag{38}$$

(e) Alternatively we may differentiate the partition function

$$\langle N \rangle = -\left(\frac{\partial \Phi_G}{\partial \mu}\right)_T \tag{39}$$

Using

$$\partial_\mu z = \partial_\mu e^{\beta\mu} = \beta z \tag{40}$$

we find after differentiation of Eq. (33)

$$\langle N \rangle = \frac{kT}{\mathcal{Z}_G} \times (z\beta e^{-\beta\epsilon_1} + 2z^2\beta e^{-\beta\epsilon_2}) \tag{41}$$

$$= \frac{ze^{-\beta\epsilon_1} + 2z^2 e^{-\eta\epsilon_2}}{\mathcal{Z}_G} \tag{42}$$

in agreement with part (d)

(f) We already worked this out in Eq. (36). If we ask to be in one specific state with $N_S = 2$ and $\epsilon_S = \epsilon_2 + 3\hbar\omega_0$

$$P_s = \frac{e^{-\beta(\epsilon_S - \mu N_S)}}{Z_G} = z^2 e^{-\beta\epsilon_2}\frac{e^{-3\hbar\omega_0}}{\mathcal{Z}_G} \tag{43}$$