PHYS 418 Solutions Problem Set 6

1) The probability for the system to be in a state i in the grand canonical ensemble is

$$P_i = \frac{e^{-\beta(E_i - \mu N_i)}}{\mathcal{L}}$$

E_i = energy of state i
N_i = # particles in state i

To get the probability $P(N)$ that the system has exactly N particles, we sum P_i over all states i which have $N_i = N$.

$$P(N) = \sum_{\substack{i \text{ such} \\ \text{that } N_i = N}} P_i = \sum_{\substack{i \text{ such} \\ \text{that } N_i = N}} \frac{e^{-\beta(E_i - \mu N_i)}}{\mathcal{L}}$$

$$= \frac{e^{\beta\mu N}}{\mathcal{L}} \sum_{\substack{i \text{ such} \\ \text{that } N_i = N}} e^{-\beta E_i}$$

But $\displaystyle\sum_{\substack{i \text{ such} \\ \text{that } N_i = N}} e^{-\beta E_i}$ is just the canonical partition function Q_N

Using $z = e^{\beta\mu}$ we then have

$$\boxed{P(N) = \frac{z^N Q_N}{\mathcal{L}}}$$

The above result is true in general.

However, for non-interacting indistinguishable particles we have,

$$Q_N = \frac{[Q_1]^N}{N!}, \quad \mathcal{L} = \sum_N z^N Q_N = \sum_N \frac{(zQ_1)^N}{N!} = e^{zQ_1}$$

So $$P(N) = \frac{z^N Q_1^N}{N!\,\mathcal{L}} = \frac{(zQ_1)^N}{N!\, e^{zQ_1}}$$

$$\boxed{P(N) = \frac{(zQ_1)^N e^{-zQ_1}}{N!} = \frac{\lambda^N e^{-\lambda}}{N!}}$$

This is just a Poisson distribution with mean

$\boxed{\lambda = zQ_1}$ True for any Q_1! Particles can have internal degrees of freedom

From the well known properties of the Poisson distribution we then have

average $\langle N \rangle = \lambda = zQ_1$

variance $\langle N^2 \rangle - \langle N \rangle^2 = \lambda = zQ_1$

In case these properties of the Poisson distribution are not well known to you, we can derive them!

$$\langle N \rangle = \sum_N \frac{z^N Q_N\, N}{\mathcal{L}} = \frac{z}{\mathcal{L}} \frac{\partial}{\partial z}\left(\sum_N z^N Q_N\right)$$

$$= \frac{z}{\mathcal{L}} \frac{\partial}{\partial z}(\mathcal{L}) = \frac{z}{\mathcal{L}} \frac{\partial}{\partial z}\left(e^{zQ_1}\right) = \frac{zQ_1}{\mathcal{L}} e^{zQ}$$

$= zQ_1 = \lambda$ where we used $\mathcal{L} = e^{zQ_1}$

$$\langle N^2 \rangle = \sum_N \frac{z^N Q_N N^2}{\mathcal{L}} = \frac{z}{\mathcal{L}} \frac{\partial}{\partial z}\left(z \frac{\partial}{\partial z} \sum_N z^N Q_N \right)$$

$$= \frac{z}{\mathcal{L}} \frac{\partial}{\partial z}\left(z \frac{\partial}{\partial z}(\mathcal{L}) \right) = \frac{z}{\mathcal{L}} \frac{\partial}{\partial z}\left(z \frac{\partial}{\partial z} e^{zQ_1} \right)$$

$$= \frac{z}{\mathcal{L}} \frac{\partial}{\partial z}\left(zQ_1 e^{zQ_1} \right) = \frac{z}{\mathcal{L}}\left(Q_1 e^{zQ_1} + zQ_1^2 e^{zQ_1} \right)$$

$$= \frac{zQ_1}{\mathcal{L}} \mathcal{L} + \frac{z^2 Q^2}{\mathcal{L}} \mathcal{L} = zQ_1 + (zQ_1)^2$$

$$= \lambda + \lambda^2$$

So $\langle N^2 \rangle - \langle N \rangle^2 = \lambda + \lambda^2 - \lambda^2 = \lambda$

So $\langle N \rangle = \lambda$

and $\langle N^2 \rangle - \langle N \rangle^2 = \lambda$

2) a)

$$\langle E \rangle = \frac{\sum_i E_i e^{-\beta(E_i - \mu N_i)}}{\sum_i e^{-\beta(E_i - \mu N_i)}}$$

where E_i is energy of state i

N_i is total number of particles of state i

$$\rightarrow \left(\frac{\partial \langle E \rangle}{\partial \mu}\right)_{T,V} = \frac{\sum_i E_i \beta N_i e^{-\beta(E_i - \mu N_i)}}{\sum_i e^{-\beta(E_i - \mu N_i)}}$$

$$- \frac{\left[\sum_i E_i e^{-\beta(E_i - \mu N_i)}\right]\left[\sum_i \beta N_i e^{-\beta(E_i - \mu N_i)}\right]}{\left[\sum_i e^{-\beta(E_i - \mu N_i)}\right]^2}$$

Noting that the probability to be in state i is

$$p_i = \frac{e^{-\beta(E_i - \mu N_i)}}{\sum_i e^{-\beta(E_i - \mu N_i)}}$$

the above is just

$$\left(\frac{\partial \langle E \rangle}{\partial \mu}\right)_{T,V} = \beta \left\{ \sum_i E_i N_i p_i - \left[\sum_i E_i p_i\right]\left[\sum_i N_i p_i\right] \right\}$$

$$= \beta \left\{ \langle EN \rangle - \langle E \rangle \langle N \rangle \right\}$$

So $$\frac{1}{T}\left(\frac{\partial \langle E \rangle}{\partial \mu}\right)_{T,V} = \frac{1}{k_B T^2} \left\{ \langle EN \rangle - \langle E \rangle \langle N \rangle \right\}$$

b) $$\langle N \rangle = \frac{\sum_i N_i \, e^{-\beta(E_i - \mu N_i)}}{\sum_i e^{-\beta(E_i - \mu N_i)}}$$

$$= \frac{\sum_i N_i \, z^{N_i} e^{-\beta E_i}}{\sum_i z^{N_i} e^{-\beta E_i}}$$

where $z = e^{\beta\mu}$. We write it in terms of z since in the next step we will take derivative at <u>constant z</u>.

$$\left(\frac{\partial \langle N \rangle}{\partial T}\right)_{z,V} = \frac{\sum_i N_i \left(\frac{E_i}{k_B T^2}\right) z^{N_i} e^{-\beta E_i}}{\sum_i z^{N_i} e^{-\beta E_i}}$$

$$- \frac{\left[\sum_i N_i z^{N_i} e^{-\beta E_i}\right]\left[\sum_i \left(\frac{E_i}{k_B T^2}\right) z^{N_i} e^{-\beta E_i}\right]}{\left[\sum_i z^{N_i} e^{-\beta E_i}\right]^2}$$

using $p_i = \dfrac{z^{N_i} e^{-\beta E_i}}{\sum_i z^{N_i} e^{-\beta E_i}}$ prob to be in state i

we have

$$\left(\frac{\partial \langle N \rangle}{\partial T}\right)_{z,V} = \frac{1}{k_B T^2}\left\{ \langle EN \rangle - \langle N \rangle \langle E \rangle \right\}$$

$$= \frac{1}{T}\left(\frac{\partial \langle E \rangle}{\partial \mu}\right)_{T,V}$$

3)

a) Since the particles of the different species do not interact with each other we can write

$$\mathcal{H} = \mathcal{H}^{(1)} + \mathcal{H}^{(2)} + \cdots + \mathcal{H}^{(m)}$$

where $\mathcal{H}^{(i)}$ is Hamiltonian for molecules of species (i) only. If we denote $\{\alpha^{(i)}\}$ as the states of the gas of molecules of species (i) alone, then

$$Q = \sum_{\{\alpha^{(1)}\}} \sum_{\{\alpha^{(2)}\}} \cdots \sum_{\{\alpha^{(m)}\}} e^{-\beta\mathcal{H}}$$

$$= \sum_{\{\alpha^{(1)}\}} e^{-\beta\mathcal{H}^{(1)}} \sum_{\{\alpha^{(2)}\}} e^{-\beta\mathcal{H}^{(2)}} \cdots \sum_{\{\alpha^{(m)}\}} e^{-\beta\mathcal{H}^{(m)}}$$

$$Q = Q^{(1)} Q^{(2)} \cdots Q^{(m)}$$

where $Q^{(i)} = \sum_{\{\alpha^{(i)}\}} e^{-\beta\mathcal{H}^{(i)}}$ is partition function of the gas of molecules of species (i) alone.

Now since the molecules of species (i) do not interact among themselves, we have

$$Q^{(i)} = \frac{[Q_1^{(i)}]^{N_i}}{N_i!} \longleftarrow \text{molecules of species } (i) \text{ are indistinguishable}$$

where $Q_1^{(i)}$ is the single molecule partition function for molecules of species (i)

b) The total Helmholtz free energy for the mixture is

$$A(T,V,N_1,\dots,N_m) = -k_BT\ln Q = -k_BT\ln Q^{(1)}Q^{(2)}\cdots Q^{(m)}$$
$$= -k_BT\left[\ln Q^{(1)} + \ln Q^{(2)} + \cdots + \ln Q^{(m)}\right]$$
$$= A^{(1)}(T,V,N_1) + A^{(2)}(T,V,N_2) + \cdots + A^{(m)}(T,V,N_m)$$

Total free energy is sum of free energies of each species separately. The pressure is then

$$p = \left(\frac{\partial A}{\partial V}\right)_{T,N} = \sum_{i=1}^{m}\left(\frac{\partial A^{(i)}}{\partial V}\right)_{T,N} = \sum_{i=1}^{m} \underset{\uparrow}{p^{(i)}}$$

pressure of species (i) if it were alone

total pressure is sum of the partial pressures

Similarly the total entropy is

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,N} = -\sum_{i=1}^{m}\left(\frac{\partial A^{(i)}}{\partial T}\right)_{V,N} = \sum_{i=1}^{m} \underset{\uparrow}{S^{(i)}}$$

entropy of species (i) alone

Total entropy is sum of entropies of each species separately.

c) Chemical potential of species (i)

$$\mu_i = \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_j \atop j\neq i} = \sum_{j=1}^{m} \left(\frac{\partial A^{(j)}}{\partial N_i}\right)_{T,V,N_j \atop j\neq i}$$

$$= \left(\frac{\partial A^{(i)}}{\partial N_i}\right)_{T,V}$$ since only $A^{(i)}$ depends on N_i

$$A^{(i)} = -k_B T \ln Q^{(i)} = -k_B T \ln\left(\frac{[Q_1^{(i)}]^{N_i}}{N_i!}\right)$$

$$= -k_B T \left\{ N_i \ln Q_1^{(i)} \underset{\uparrow}{- N_i \ln N_i} + N_i \right\}$$

using Sterling's formula

$$\mu_i = \left(\frac{\partial A^{(i)}}{\partial N_i}\right)_{T,V} = -k_B T \left\{ \ln Q_1^{(i)} - \ln N_i - 1 + 1 \right\}$$

$$\boxed{\mu_i = -k_B T \ln\left(\frac{Q_1^{(i)}}{N_i}\right)}$$ ← write this way to see that μ_i is intensive

d)

Now $$Q_1^{(i)} = \int \frac{d^3q \int d^3p}{h^3} \sum_{\{x\}} e^{-\beta H_1^{(i)}(\vec{p}, \{x\})}$$

where $\vec{q}$ is the center of mass position of the molecule, $\vec{p}$ is its total momentum, and $\{x\}$ are whatever internal degrees of freedom the molecule might have.

The important point is that $H_1^{(i)}$, the single molecule Hamiltonian for species (i), does not depend on $\vec{q}$, since the molecule is free. Hence we can do the $\int d^3q$ integral and get a factor V

$$Q_1^{(i)} = V \int \frac{d^3p}{h^3} \sum_{\{x\}} e^{-\beta H_1^{(i)}(\vec{p},\{x\})}$$

$$\boxed{Q_1^{(i)} = V\, q_1^{(i)}(T)} \quad \text{where } q_1^{(i)} = \int \frac{d^3p}{h^3} \sum_{\{x\}} e^{-\beta H_1^{(i)}(\vec{p},\{x\})}$$

The $\sum_{\{x\}}$ and $\int d^3p$ depend on thermodynamic parameters only through β, hence $q_1^{(i)}$ is a function only of T.

e) Chemical equilibrium $\Rightarrow$

$$\sum_{i=1}^{j} \mu_i a_i = \sum_{k=j+1}^{m} \mu_k a_k$$

Now $\mu_i = -k_BT \ln\left(\frac{Q_1^{(i)}}{N_i}\right) = -k_BT \ln\left(\frac{V}{N_i} q_1^{(i)}\right)$

$$= -k_BT \ln\left(q_1^{(i)}/n_i\right)$$

where $n_i = N_i/V$ is the density of species (i)

$$\sum_{i=1}^{j} \mu_i a_i = -k_BT \sum_{i=1}^{j} a_i \ln\left(q_1^{(i)}/n_i\right)$$

$$= k_BT \sum_{i=1}^{j} \ln\left(\left[n_i/q_1^{(i)}\right]^{a_i}\right)$$

$$= k_BT \ln\left[\prod_{i=1}^{j}\left(\frac{n_i}{q_1^{(i)}}\right)^{a_i}\right]$$

$$\text{so } \sum_{i=1}^{j} \mu_i a_i = \sum_{k=j+1}^{m} \mu_k a_k$$

$$\Rightarrow \ln\left[\prod_{i=1}^{j}\left(\frac{n_i}{q_1^{(i)}}\right)^{a_i}\right] = \ln\left[\prod_{k=j+1}^{m}\left(\frac{n_k}{q_1^{(k)}}\right)^{a_k}\right]$$

$$\Rightarrow \frac{\prod_{i=1}^{j} n_i^{a_i}}{\prod_{k=j+1}^{m} n_k^{a_k}} = \frac{\prod_{i=1}^{j} \left(q_1^{(i)}\right)^{a_i}}{\prod_{k=j+1}^{m} \left(q_1^{(k)}\right)^{a_k}} = K(T)$$

$$\boxed{\begin{array}{l} \text{or } \dfrac{n_1^{a_1} n_2^{a_2} \cdots n_j^{a_j}}{n_{j+1}^{a_{j+1}} \cdots n_m^{a_m}} = K(T) \\ \text{where } K(T) = \dfrac{\left(q_1^{(1)}\right)^{a_1}\left(q_1^{(2)}\right)^{a_2} \cdots \left(q_1^{(j)}\right)^{a_j}}{\left(q_1^{(j+1)}\right)^{a_{j+1}} \cdots \left(q_1^{(m)}\right)^{a_m}} \end{array}}$$

and each $q_1^{(i)}$ is a function of only T

$\Rightarrow$ K is only a function of T (ie K is indep of V and N_i)

f) $A + B \rightarrow C$ $\qquad$ A, B, C have no internal degrees of freedom

$$\mathcal{H}_1^{(A)} = \frac{p^2}{2m_A}, \quad \mathcal{H}_1^{(B)} = \frac{p^2}{2m_B}, \quad \mathcal{H}_1^{(C)} = \frac{p^2}{2m_C} - \underset{\substack{\uparrow \\ \text{binding energy of} \\ C \text{ wrt } A, B}}{E_0}$$

$$q_1^{(A)} = \int \frac{d^3p}{h^3} e^{-\beta \mathcal{H}_1^{(A)}} = \frac{(2\pi m_A k_B T)^{3/2}}{h^3}$$

$$g_1^{(B)} = \int \frac{d^3p}{h^3} e^{-\beta H_1^{(B)}} = \frac{(2\pi m_B k_B T)^{3/2}}{h^3}$$

$$g_1^{(C)} = \int \frac{d^3p}{h^3} e^{-\beta H_1^{(C)}} = e^{+E_0/k_B T} \frac{(2\pi m_C k_B T)^{3/2}}{h^3}$$

Here $a_A = a_B = a_C = 1$ so

$$K(T) = \frac{g_1^{(A)} g_1^{(B)}}{g_1^{(C)}} = \frac{(2\pi m_B k_B T)^{3/2} (2\pi m_A k_B T)^{3/2}}{h^3 (2\pi m_C k_B T)^{3/2} e^{+E_0/k_B T}}$$

$$\boxed{K(T) = \frac{e^{-E_0/k_B T}}{h^3} \left(\frac{2\pi m_A m_B k_B T}{m_C} \right)^{3/2}}$$

Note: K(T) depends explicitly on h, which is Planck's constant! So quantum mechanics plays a role in equilibrium densities!

g) If initially $n_A = n_B = n_0$ and $n_C = 0$, then at any time t it must be true that

$n_A + n_C = \text{const}$ — this is the total # of A (whether alone, or in C)

$n_B + n_C = \text{const}$ — this is the total # of B (whether alone, or in C)

from the initial conditions we know that both the above constants are n_0

$$\Rightarrow \quad n_A + n_C = n_0 \Rightarrow n_A = n_0 - n_C$$

$$n_B + n_C = n_0 \Rightarrow n_B = n_0 - n_C$$

mass acton

$$\frac{m_A m_B}{m_C} = K(T)$$

$$\Rightarrow \quad \frac{(m_0 - m_C)(m_0 - m_C)}{m_C} = K(T)$$

$$m_C^2 - 2 m_0 m_C - K m_C + m_0^2 = 0$$

$$m_C^2 - 2\left(m_0 + \frac{K}{2}\right) m_C + m_0^2 = 0$$

$$m_C = \left(m_0 + \frac{K}{2}\right) \pm \sqrt{\left(m_0 + \frac{K}{2}\right)^2 - m_0^2}$$

$$\boxed{m_C = \left(m_0 + \frac{K}{2}\right) - \sqrt{m_0 K + \frac{K^2}{4}}}$$

(−) sign since m_C cannot be bigger than initial concentration m_0

$$m_A = m_B = m_0 - m_C$$

$$= -\frac{K}{2} + \sqrt{m_0 K + \frac{K^2}{4}}$$