

PHYS 418 Solutions Problem Set 6

1)

we know $\sum_i P_i E_i = \langle E \rangle$

and we know $\sum_i P_i N_i = \langle N \rangle$

we want to maximize $S = -k_B \sum_i P_i \ln P_i$

subject to the above constraints, as well

as $\sum_i P_i = 1$

So we want to use Lagrange multipliers and maximize

$$\tilde{S} \equiv S + \lambda k_B \sum_j P_j - \beta k_B \sum_j P_j E_j + \alpha k_B \sum_j P_j N_j$$

$$0 = \frac{\partial \tilde{S}}{\partial P_i} = \frac{\partial}{\partial P_i} \left\{ -k_B \sum_j \left[P_j \ln P_j - \lambda P_j + \beta P_j E_j - \alpha P_j N_j \right] \right\}$$

$$\Rightarrow 0 = 1 + \ln P_i - \lambda + \beta E_i - \alpha N_i$$

$$\Rightarrow \ln P_i = \lambda - \beta E_i + \alpha N_i - 1$$

$$P_i = e^{\lambda-1} e^{-\beta E_i + \alpha N_i}$$

If we define $\alpha = \beta\mu$ then we have

$$P_i = e^{\lambda-1} e^{-\beta(E_i - \mu N_i)}$$

$$\sum_i P_i = e^{\lambda-1} \sum_i e^{-\beta(E_i - \mu N_i)} = 1$$

$$\Rightarrow e^{\lambda-1} = \frac{1}{\sum_i e^{-\beta(E_i - \mu N_i)}}$$

$$S_b \quad P_i = \frac{e^{-\beta(E_i - \mu N_i)}}{\sum_j e^{-\beta(E_j - \mu N_j)}}$$

This is just the probability distribution of the grand canonical ensemble, if we interpret $\beta = \frac{1}{k_B T}$ and μ is the chemical potential.

β and μ are determined by the conditions

$$\sum_i P_i E_i = \langle E \rangle \quad \text{and} \quad \sum_i P_i N_i = \langle N \rangle$$

$$\frac{\sum_i e^{-\beta(E_i - \mu N_i)} E_i}{\sum_j e^{-\beta(E_j - \mu N_j)}} = \langle E \rangle \quad \text{and} \quad \frac{\sum_i e^{-\beta(E_i - \mu N_i)} N_i}{\sum_j e^{-\beta(E_j - \mu N_j)}} = \langle N \rangle$$

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

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

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

The above result is true in general.

However, for non-interacting indistinguishable particles we have,

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

$$\text{So } P(N) = \frac{z^N Q_N}{N! \mathcal{Z}} = \frac{(zQ_1)^N}{N! e^{zQ_1}}$$

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

This is just a Poisson distribution with mean

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

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

$$\text{average } \langle N \rangle = \lambda = zQ_1$$

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

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

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

$$= \frac{z}{\mathcal{Z}} \frac{\partial}{\partial z} (\mathcal{Z}) = \frac{z}{\mathcal{Z}} \frac{\partial}{\partial z} (e^{zQ_1}) = \frac{zQ_1}{\mathcal{Z}} e^{zQ_1}$$

$$= zQ_1 = \lambda \quad \text{where we used } \mathcal{Z} = e^{zQ_1}$$

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

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

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

$$= \frac{zQ_1}{\mathcal{Z}} \mathcal{Z} + \frac{z^2 Q_1^2}{\mathcal{Z}} \mathcal{Z} = zQ_1 + (zQ_1)^2$$

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

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

$$\text{So } \langle N \rangle = \lambda$$

$$\text{and } \langle N^2 \rangle - \langle N \rangle^2 = \lambda$$

3)

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

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

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

$$\begin{aligned}
 b) \quad \langle N \rangle &= \frac{\sum_i N_i e^{-\beta(E_i - \mu N_i)}}{\sum_i e^{-\beta(E_i - \mu N_i)}} \\
 &= \frac{\sum_i N_i z^{N_i} e^{-\beta E_i}}{\sum_i z^{N_i} e^{-\beta E_i}}
 \end{aligned}$$

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

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

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

we have

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

4)

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

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

where $H^{(i)}$ 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

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

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

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

where $Q^{(i)} = \sum_{\{\alpha^{(i)}\}} e^{-\beta H^{(i)}}$ 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

$$Q^{(i)} = \frac{[Q_1^{(i)}]^{N_i}}{N_i!} \leftarrow \begin{array}{l} \text{molecules of species (i)} \\ \text{are indistinguishable} \end{array}$$

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

b) The total Helmholtz free energy for the mixture is

$$\begin{aligned} A(T, V, N_1, \dots, N_m) &= -k_B T \ln Q = -k_B T \ln Q^{(1)} Q^{(2)} \dots Q^{(m)} \\ &= -k_B T [\ln Q^{(1)} + \ln Q^{(2)} + \dots + \ln Q^{(m)}] \\ &= A^{(1)}(T, V, N_1) + A^{(2)}(T, V, N_2) \\ &\quad + \dots + A^{(m)}(T, V, N_m) \end{aligned}$$

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

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

↑ pressure of species (i)
if it were alone

total pressure is sum of the partial pressures

Similarly the total entropy is

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

↑ entropy of
species (i) alone

Total entropy is sum of entropies of each species separately.

c) Chemical potential of species (i)

$$\begin{aligned}\mu_i &= \left(\frac{\partial A}{\partial N_i} \right)_{T, V, N_j, j \neq i} = \sum_{j=1}^m \left(\frac{\partial A^{(j)}}{\partial N_i} \right)_{T, V, N_j, j \neq i} \\ &= \left(\frac{\partial A^{(i)}}{\partial N_i} \right)_{T, V} \text{ since only } A^{(i)} \text{ depends on } N_i\end{aligned}$$

$$\begin{aligned}A^{(i)} &= -k_B T \ln Q^{(i)} = -k_B T \ln \left(\frac{[Q_1^{(i)}]^{N_i}}{N_i!} \right) \\ &= -k_B T \left\{ N_i \ln Q_1^{(i)} - N_i \ln N_i + N_i \right\} \\ &\quad \uparrow \\ &\quad \text{using Stirling's formula}\end{aligned}$$

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

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

d)

$$\text{Now } Q_1^{(i)} = \int \frac{d^3 \vec{g}}{h^3} \int d^3 \vec{p} \sum_{\xi \times \xi} e^{-\beta H_1(\vec{p}, \xi \times \xi)} \quad (i)$$

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

The important point is that $H_i^{(i)}$, 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

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

$$Q_i^{(i)} = V g_i^{(i)}(T) \quad \text{where} \quad g_i^{(i)} = \int \frac{d^3p}{h^3} \sum_{\{x\}} e^{-\beta H_i^{(i)}(\vec{p}, \{x\})}$$

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

c) Chemical equilibrium $\Rightarrow$

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

$$\begin{aligned} \text{Now } \mu_i &= -k_B T \ln \left(\frac{Q_i^{(i)}}{N_i} \right) = -k_B T \ln \left(\frac{V}{N_i} g_i^{(i)} \right) \\ &= -k_B T \ln (g_i^{(i)} / m_i) \end{aligned}$$

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

$$\begin{aligned} \sum_{i=1}^J \mu_i a_i &= -k_B T \sum_{i=1}^J a_i \ln (g_i^{(i)} / m_i) \\ &= k_B T \sum_{i=1}^J \ln ([m_i / g_i^{(i)}]^{a_i}) \\ &= k_B T \ln \left[\prod_{i=1}^J \left(\frac{m_i}{g_i^{(i)}} \right)^{a_i} \right] \end{aligned}$$

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

$$\Rightarrow \ln \left[\prod_{i=1}^j \left(\frac{m_i}{g_i^{(i)}} \right)^{a_i} \right] = \ln \left[\prod_{k=j+1}^m \left(\frac{m_k}{g_k^{(k)}} \right)^{a_k} \right]$$

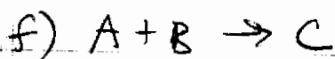
$$\Rightarrow \frac{\prod_{i=1}^j m_i^{a_i}}{\prod_{k=j+1}^m m_k^{a_k}} = \frac{\prod_{i=1}^j (g_i^{(i)})^{a_i}}{\prod_{k=j+1}^m (g_k^{(k)})^{a_k}} = K(T)$$

$$\text{or } \frac{m_1^{a_1} m_2^{a_2} \dots m_j^{a_j}}{m_{j+1}^{a_{j+1}} \dots m_m^{a_m}} = K(T)$$

$$\text{where } K(T) = \frac{(g_1^{(1)})^{a_1} (g_1^{(2)})^{a_2} \dots (g_1^{(j)})^{a_j}}{(g_1^{(j+1)})^{a_{j+1}} \dots (g_1^{(m)})^{a_m}}$$

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

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



A, B, C have no internal degrees of freedom

$$H_i^{(A)} = \frac{p^2}{2m_A}, \quad H_i^{(B)} = \frac{p^2}{2m_B}, \quad H_i^{(C)} = \frac{p^2}{2m_C} - E_0$$

$$g_i^{(A)} = \int \frac{d^3 p}{h^3} e^{-\beta H_i^{(A)}} = \left(\frac{2\pi m_A k_B T}{h^2} \right)^{3/2}$$

$\uparrow$
binding energy of C w.r.t A, B

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

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

Here $a_A = a_B = a_C = 1$ so

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

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

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

g) If initially $m_A = m_B = m_0$ and $m_C = 0$, then at any time t it must be true that

$$m_A + m_C = \text{const} \quad - \text{this is the total \# of A (whether alone, or in C)}$$

$$m_B + m_C = \text{const} \quad - \text{this is the total \# of B (whether alone, or in C)}$$

from the initial conditions we know that both the above constants are m_0

$$\Rightarrow m_A + m_C = m_0 \Rightarrow m_A = m_0 - m_C$$

$$m_B + m_C = m_0 \Rightarrow m_B = m_0 - m_C$$

mass action

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

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

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

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

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

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

(-) sign since m_c cannot be bigger than initial concentration m_0

$$m_A = m_B = m_0 - m_c$$

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