PHYS 418 Solutions Midterm Exam 2025

1) i) $\left(\frac{\partial T}{\partial N}\right)_{S,V}$ variables are $S, V, N \Rightarrow$ potential is $E(S,V,N)$. $T = \left(\frac{\partial E}{\partial S}\right)_{V,N}$

$$\Rightarrow \left(\frac{\partial T}{\partial N}\right)_{S,V} = \left(\frac{\partial^2 E}{\partial S \partial N}\right)_V = \frac{\partial}{\partial S}\left(\frac{\partial E}{\partial N}\right) = \boxed{\left(\frac{\partial \mu}{\partial S}\right)_{V,N}}$$

ii) $\left(\frac{\partial \mu}{\partial p}\right)_{T,N}$ variables are $T, p, N \Rightarrow$ potential is $G(T,p,N)$. $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,p}$

$$\Rightarrow \left(\frac{\partial \mu}{\partial p}\right)_{T,N} = \left(\frac{\partial^2 G}{\partial N \partial p}\right)_T = \frac{\partial}{\partial N}\left(\frac{\partial G}{\partial p}\right) = \boxed{\left(\frac{\partial V}{\partial N}\right)_{T,p}}$$

iii) $\left(\frac{\partial N}{\partial T}\right)_{V,\mu}$ variables are $T, V, \mu \Rightarrow$ potential is $\Phi(T,V,\mu)$. $N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V}$

$$\Rightarrow \left(\frac{\partial N}{\partial T}\right)_{V,\mu} = -\left(\frac{\partial^2 \Phi}{\partial \mu \partial T}\right) = -\frac{\partial}{\partial \mu}\left(\frac{\partial \Phi}{\partial T}\right) = \boxed{\left(\frac{\partial S}{\partial \mu}\right)_{T,V}}$$

iv) $\left(\frac{\partial T}{\partial p}\right)_{S,\mu}$ variables are S, p, μ. We did not define such a potential in class, but that does not mean we can't define it!

$$F(S,p,\mu) = E(S,V,N) + pV - \mu N$$

Legendre transform of E from V to $-p$ and from N to μ

$$\left(\frac{\partial F}{\partial S}\right)_{p,\mu} = T, \quad \left(\frac{\partial F}{\partial p}\right)_{S,\mu} = V, \quad \left(\frac{\partial F}{\partial \mu}\right)_{S,p} = -N$$

$$\Rightarrow \left(\frac{\partial T}{\partial p}\right)_{S,\mu} = \left(\frac{\partial^2 F}{\partial S\, \partial p}\right) = \frac{\partial}{\partial S}\left(\frac{\partial F}{\partial p}\right) = \boxed{\left(\frac{\partial V}{\partial S}\right)_{p,\mu}}$$

v) $\left(\frac{\partial p}{\partial T}\right)_{V,N}$ variables are $T, V, N \Rightarrow$ potential is $A(T,V,N)$. $-\left(\frac{\partial A}{\partial V}\right)_{T,N} = p$

$$\Rightarrow \left(\frac{\partial p}{\partial T}\right)_{V,N} = -\left(\frac{\partial^2 A}{\partial V\, \partial T}\right) = -\frac{\partial}{\partial V}\left(\frac{\partial A}{\partial T}\right) = \boxed{\left(\frac{\partial S}{\partial V}\right)_{T,N}}$$

2) a) $\boxed{Q_N = \frac{1}{N!} Q_1^N}$

$$Q_1 = \frac{1}{h^3} \int_V d^3r \int_{-\infty}^{\infty} d^3p \sum_{s_i=-1,0,1} e^{-\beta\left[\frac{p^2}{2m} - \mu h s_i\right]}$$

$$= \frac{V}{h^3} (2\pi m k_B T)^{3/2} \sum_{s_i} e^{+\beta \mu h s_i}$$

$$\boxed{Q_1 = \frac{V}{h^3} (2\pi m k_B T)^{3/2} \left[1 + e^{\beta \mu h} + e^{-\beta \mu h} \right]}$$

b) Helmholtz free energy $A = -k_B T \ln Q_N$

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

$$= -k_B T N \left[1 + \ln\left(\frac{Q_1}{N}\right) \right]$$

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

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

The only place V appears in Q_1 is in the prefactor V. So

$$\frac{\partial}{\partial V} \ln Q_1 = \frac{\partial}{\partial V} \ln V = \frac{1}{V}$$

$\boxed{p = k_B T N / V}$ just the ordinary ideal gas law!

c) $\langle E \rangle = -\left(\frac{\partial}{\partial\beta} \ln Q_N\right)_{V,N}$

$$= -\frac{\partial}{\partial\beta} N\left[1 + \ln\left(\frac{Q_1}{N}\right)\right] = -N\frac{\partial}{\partial\beta}\ln Q_1$$

write $Q_1 = Q_1^0 q$ where

$Q_1^0 \equiv \frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}$ is what we would have for an ideal gas of point particles

$q \equiv \left[1 + e^{\beta\mu h} + e^{-\beta\mu h}\right]$ is extra factor from spin

$$\langle E \rangle = -N\frac{\partial}{\partial\beta}\left(\ln Q_1^0 + \ln q\right)$$

$$= -N\frac{\partial}{\partial\beta}\left(\frac{-3}{2}\ln\beta\right) - N\frac{\partial}{\partial\beta}\ln q$$

$$= \frac{3}{2}N\frac{1}{\beta} - \frac{N}{q}\frac{\partial}{\partial\beta}q$$

$$= \underbrace{\frac{3}{2}Nk_BT}_{\text{contribution from kinetic energy}} - \underbrace{\frac{N}{q}\left(\mu h e^{\beta\mu h} - \mu h e^{-\beta\mu h}\right)}_{\text{contribution from spin}}$$

$$\boxed{\langle E \rangle = \frac{3}{2}Nk_BT - N\mu h\frac{\left(e^{\beta\mu h} - e^{-\beta\mu h}\right)}{\left(1 + e^{\beta\mu h} + e^{-\beta\mu h}\right)}}$$

d) We can also write

$$\langle E \rangle = N \left\langle \frac{p^2}{2m} \right\rangle - N\mu h \langle s_i \rangle$$

comparing to the previous part we conclude

$$\langle M \rangle = \mu \sum_i \langle s_i \rangle = \mu N \langle s_i \rangle$$

$$\boxed{\langle M \rangle = \mu N \frac{\left(e^{\beta\mu h} - e^{-\beta\mu h}\right)}{\left(1 + e^{\beta\mu h} + e^{-\beta\mu h}\right)}}$$

we could also have computed this directly from

$$\langle s_i \rangle = \frac{\sum_{s_i=-1,0,1} e^{\beta\mu h s_i}\, s_i}{\sum_{s_i=-1,0,1} e^{\beta\mu h s_i}}$$

3) Label particles A by $i = 1, \dots, N_A$

Label particles B by $j = 1, \dots, N_B$

a) If all particles were <u>distinguishable</u>, the partition function would be

$$Q = \prod_i \prod_j \frac{\int d^3 r_i \int d^3 p_i}{h^{3N_A}} \frac{\int d^3 r_j \int d^3 p_j}{h^{3N_B}} \, e^{-\beta H}$$

Now $$H = \sum_i \frac{p_i^2}{2m_A} + \sum_j \frac{p_j^2}{2m_B} = H_A + H_B$$

So $e^{-\beta H} = e^{-\beta H_A} e^{-\beta H_B}$ and Q factors

$$Q = Q_A Q_B \quad \text{where}$$

$$Q_A = \frac{1}{h^{3N_A}} \prod_i \int d^3 r_i \int d^3 p_i \, e^{-\beta \sum_i \frac{p_i^2}{2m_A}}$$

$$= \frac{1}{h^{3N_A}} \prod_i \left(\int d^3 r_i \int d^3 p_i \, e^{-\beta \frac{p_i^2}{2m_A}} \right)$$

$$= \frac{1}{h^{3N_A}} \left(\int d^3 r \int d^3 p \, e^{-\frac{\beta p^2}{2m_A}} \right)^{N_A}$$

$$= \frac{V^{N_A}}{h^{3N_A}} \left(2\pi m_A k_B T \right)^{\frac{3}{2} N_B}$$

and similarly $$Q_B = \frac{V^{N_B}}{h^{3N_B}} \left(2\pi m_B k_B T \right)^{\frac{3}{2} N_B}$$

But the particles A are <u>indistinguishable</u> from each other, and the particles B are <u>indistinguishable</u> from each other, so when we did the above integrals we overcounted states. To correct we follow Gibbs and divide Q_A by $\frac{1}{N_A!}$ and Q_B by $\frac{1}{N_B!}$

so we set

$$Q = \frac{V^{N_A}}{h^{3N_A} N_A!} (2\pi m_A k_B T)^{\frac{3}{2} N_A} \frac{V^{N_B}}{h^{3N_B} N_B!} (2\pi m_B k_B T)^{\frac{3}{2} N_B}$$

Q is just the product of the partition functions for only particles A and only particles B

Helmholtz free energy is then

$$A(T, V, N_A, N_B) = -k_B T \ln Q$$

$$= -k_B T \Big\{ N_A \ln\Big[\frac{V}{h^3}(2\pi m_A k_B T)^{3/2}\Big] - N_A \ln N_A + N_A$$

$$+ N_B \ln\Big[\frac{V}{h^3}(2\pi m_B k_B T)^{3/2}\Big] - N_B \ln N_B + N_B \Big\}$$

where we used $\ln N! \approx N \ln N - N$

$$\boxed{A(T, V, N_A, N_B) = -k_B T \Big\{ N_A + N_B + N_A \ln\Big[\frac{V}{h^3 N_A}(2\pi m_A k_B T)^{3/2}\Big] + N_B \ln\Big[\frac{V}{h^3 N_B}(2\pi m_B k_B T)^{3/2}\Big] \Big\}}$$

b) $$p = -\left(\frac{\partial A}{\partial V}\right)_{T, N_A, N_B} = k_B T \left\{ \frac{N_A}{V} + \frac{N_B}{V} \right\}$$

$$\boxed{p = \frac{N_A k_B T}{V} + \frac{N_B k_B T}{V}}$$

p is the sum of the "partial pressures" from gas A and from gas B. If we write $N = N_A + N_B$ then

$p = \frac{N k_B T}{V}$ and the ideal gas law holds!

c) $$\mu_A = \left(\frac{\partial A}{\partial N_A}\right)_{T, V, N_B} = -k_B T \left\{ 1 + \ln\left[\frac{V}{h^3 N_A}(2\pi m_A k_B T)^{3/2}\right] - 1 \right\}$$

comes from $N_A \frac{d}{dN_A}\left(\ln \frac{1}{N_A}\right)$

$$\boxed{\mu_A = -k_B T \ln\left[\frac{V}{h^3 N_A}(2\pi m_A k_B T)^{3/2}\right]}$$

Similarly

$$\boxed{\mu_B = -k_B T \ln\left[\frac{V}{h^3 N_B}(2\pi m_B k_B T)^{3/2}\right]}$$

Chemical potentials μ_A and μ_B are the same as if there was only gas A and only gas B.

When the wall is thermally conducting but immovable and impermeable, then each side is separately in equilibrium. We can therefore use the ideal gas law

For only $N_A^{(0)}$ particles A and no particles B on side 1 we set

$$\boxed{P_1 = \frac{N_A^{(0)} k_B T}{V_1}}$$

Similarly for only $N_B^{(0)}$ particles B and no particles A on side 2 we set

$$\boxed{P_2 = \frac{N_B^{(0)} k_B T}{V_2}}$$

In general, $P_1 \neq P_2$

d)

Now the wall becomes permeable and particles flow through the wall and come into a new equilibrium with N_{A1} and N_{B1} particles A and B on side 1 and N_{A2} and N_{B2} particles A and B on side 2.

We still must have $N_{A1} + N_{A2} = N_A^{(0)}$

$$N_{B1} + N_{B2} = N_B^{(0)}$$

Remember, for an ideal gas, $E = \frac{3}{2} N k_B T$

So initially, before the wall became permeable, the energy was

$$E^{(0)} = E_1^{(0)} + E_2^{(0)} = \frac{3}{2} N_A^{(0)} k_B T + \frac{3}{2} N_B^{(0)} k_B T$$

$$= \frac{3}{2} k_B T \left(N_A^{(0)} + N_B^{(0)} \right)$$

Then after the wall became permeable the energy becomes

$$E = E_1 + E_2 = \left(\frac{3}{2} N_{A1} k_B T' + \frac{3}{2} N_{B1} k_B T' \right)$$

$$+ \left(\frac{3}{2} N_{A2} k_B T' + \frac{3}{2} N_{B2} k_B T' \right)$$

where T' is the new temperature

$$E = \frac{3}{2} k_B T' \left(N_{A1} + N_{B1} + N_{A2} + N_{B2} \right)$$

$$= \frac{3}{2} k_B T' \left(N_A^{(0)} + N_B^{(0)} \right) \quad \text{since } N_{A1} + N_{A2} = N_A^{(0)}$$

$$\text{and } N_{B1} + N_{B2} = N_B^{(0)}$$

Now since the exterior walls of the box are thermally insulating we must have $E = E^{(0)}$

$\Rightarrow T = T'$ and $\boxed{\text{the temperature does } \underline{\text{NOT}} \text{ change}}$

e) The new equilibrium will be determined by the condition that the chemical potentials of the two species of gas are the same on side 1 as on side 2

$$\boxed{\begin{aligned} \mu_A(T, V_1, N_{A1}, N_{B1}) &= \mu_A(T, V_2, N_{A2}, N_{B2}) \\ \mu_B(T, V_2, N_{A2}, N_{B2}) &= \mu_B(T, V_2, N_{A2}, N_{B2}) \end{aligned}}$$

The above is easy to solve for since μ_A does not depend on N_B and μ_B does not depend on N_A.

$$\mu_A(T, V_1, N_{A1}, N_{B1}) = \mu_A(T, V_2, N_{A2}, N_{B2})$$

from part d):

$$\Rightarrow -k_B T \ln \left[\frac{V_1}{h^3 N_{A1}} (2\pi m_A k_B T)^{3/2} \right] = -k_B T \ln \left[\frac{V_2}{h^3 N_{A2}} (2\pi m_A k_B T)^{3/2} \right]$$

$$\Rightarrow \frac{V_1}{N_{A1}} = \frac{V_2}{N_{A2}} \Rightarrow \frac{N_{A1}}{V_1} = \frac{N_{A2}}{V_2} = \frac{N_A^{(0)} - N_{A1}}{V_2}$$

$$\Rightarrow N_{A1} \left(\frac{1}{V_1} + \frac{1}{V_2} \right) = \frac{N_A^{(0)}}{V_2} \Rightarrow N_{A1} \left(\frac{V_2 + V_1}{V_1 V_2} \right) = \frac{N_A^{(0)}}{V_2}$$

$$\Rightarrow \quad N_{A1} = N_A^{(0)} \frac{V_1}{V_1+V_2} = N_A^{(0)} \frac{V_1}{V}$$

$$N_{A2} = N_A^{(0)} - N_{A1} = N_A^{(0)}\left(1-\frac{V_1}{V}\right) = N_A^{(0)}\frac{V_2}{V}$$

So
$$\boxed{\begin{array}{ll} N_{A1} = \left(\frac{V_1}{V}\right) N_A^{(0)} & N_{A2} = \left(\frac{V_2}{V}\right) N_A^{(0)} \\ N_{B1} = \left(\frac{V_1}{V}\right) N_B^{(0)} & N_{B2} = \left(\frac{V_2}{V}\right) N_B^{(0)} \end{array}}$$
similarly

So the fraction of particles in a given side is just equal to the fraction of the total volume that side contains.

This is exactly what one would expect without any detailed calculation. The particles just spread out evenly over all the possible volume, so that there is a constant density of particles

density of A is $\frac{N_A^{(0)}}{V}$, density of B is $\frac{N_B^{(0)}}{V}$

so number of A in side 1 is just $V_1 \frac{N_A^{(0)}}{V}$ etc.

f) Now the pressure on side 1 is by part (c) just

$$P_1 = \frac{(N_{A1}+N_{B1})k_BT}{V_1} = \frac{\left[\left(\frac{V_1}{V}\right)N_A^{(0)} + \left(\frac{V_1}{V}\right)N_B^{(0)}\right]k_BT}{V_1}$$

$$\boxed{P_1 = \frac{(N_A^{(0)} + N_B^{(0)})k_BT}{V}}$$

and the pressure on side 2 is

$$p_2 = \frac{(N_{A2} + N_{B2}) k_B T}{V_2} = \frac{\left[\left(\frac{V_2}{V}\right) N_A^{(0)} + \left(\frac{V_2}{V}\right) N_B^{(0)}\right] k_B T}{V_2}$$

$$\boxed{p_2 = \frac{(N_A^{(0)} + N_B^{(0)}) k_B T}{V}} \quad \text{so} \quad \boxed{p_1 = p_2}$$

So the pressure on the two sides of the internal wall have become equal even though the wall remained fixed in position the whole time!

When the wall was impermeable, the pressure on side 1 was

p_1 = N_A^(0) k_BT/V_1

and the pressure on side 2 was

p_2 = N_B^(0) k_BT/V_2

and so in that case p_1 ≠ p_2.

Hence, the pressures changed when the wall became permeable.