PHYS 418 Solutions Midterm Exam 2026

1)

i) $\left(\frac{\partial V}{\partial T}\right)_{p,N}$ variables are T, p, N

$\Rightarrow$ potential is $G(T,p,N)$ Gibbs

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

ii) $\left(\frac{\partial T}{\partial V}\right)_{S,N}$ variables are S, V, N

$\Rightarrow$ potential is $E(S,V,N)$ energy

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

iii) $\left(\frac{\partial p}{\partial \mu}\right)_{T,V}$ variables are T, V, μ

$\Rightarrow$ potential is $\Phi(T, V, \mu)$ grand potential

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

iv) $\left(\frac{\partial \mu}{\partial p}\right)_{S,N}$ variables are S, p, N

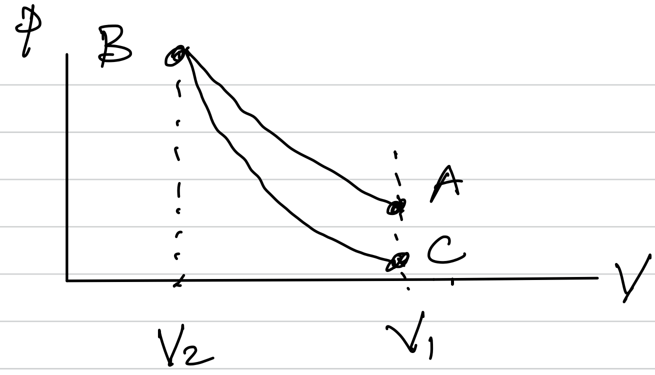
$\Rightarrow$ potential is $H(S,p,N)$ Enthalpy

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

v) $\left(\frac{\partial \mu}{\partial T}\right)_{V,N}$ variables are T, V, N

$\Rightarrow$ potential is $A(T,V,N)$ Helmholtz

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

b) 

particles N stays constant

$T_A = T_1$, $V_A = V_1$

$T_B = T_1$ since $A \to B$ is isothermal , $V_B = V_2$

$V_c = V_1$, what is $T_c = T_2$?

$$S(E,V,N) = \frac{5}{2} N k_B + N k_B \ln\left[\frac{V}{h^3 N}\left(\frac{4\pi m E}{3N}\right)^{3/2}\right]$$

since $B \to C$ is adiabatic, the entropy does not change

$$\Rightarrow S_c - S_B = \Delta S = N k_B \ln\left[\left(\frac{E_C}{E_B}\right)^{3/2}\left(\frac{V_C}{V_B}\right)\right] = 0$$

since N is constant

$$\Rightarrow \left(\frac{E_C}{E_B}\right)^{3/2}\left(\frac{V_C}{V_B}\right) = 1$$

For ideal gas, $E = \frac{3}{2} N k_B T$

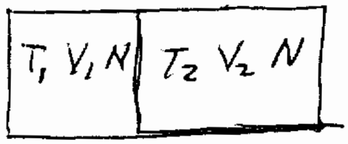
$$\Rightarrow \left(\frac{T_C}{T_B}\right)^{3/2}\left(\frac{V_C}{V_B}\right) = 1$$

$V_c = V_1$, $V_B = V_2$

$T_B = T_1$, $T_C = T_2$

$$\Rightarrow \left(\frac{T_2}{T_1}\right)^{3/2}\left(\frac{V_1}{V_2}\right) = 1 \Rightarrow \boxed{T_2 = T_1\left(\frac{V_2}{V_1}\right)^{2/3}}$$

2)



ideal gas, so $pV = Nk_BT$

$$E = \frac{3}{2}Nk_BT$$

a) When the wall is removed, a constraint on the system is lifted, so the entropy of the system must increase

$$\Delta S = S_f - S_i > 0$$

b) When the wall is removed, and the gases fill the entire box, energy is conserved.

$$E = E_1 + E_2 \quad \text{is constant}$$

The initial energy of the gases on each side is

$$E_1 = \frac{3}{2}Nk_BT_1 \quad , \quad E_2 = \frac{3}{2}Nk_BT_2$$

The final energy of the gas must be related to the final temperature by

$$E_1 + E_2 = E = \frac{3}{2}(2N)k_BT_f$$

(2N on right side since total gas has 2N particles)

$$\Rightarrow \frac{3}{2}Nk_BT_1 + \frac{3}{2}Nk_BT_2 = \frac{3}{2}2Nk_BT_f$$

$$\Rightarrow T_1 + T_2 = 2T_f \Rightarrow \boxed{T_f = \frac{T_1 + T_2}{2}}$$

final temperature is the average of the initial temperatures

c) The final pressure p_f is obtained by the ideal gas law. Again the total gas has 2N particles

$$p_f = \frac{(2N)k_B T_f}{V} = \frac{2N k_B}{(V_1 + V_2)}\left(\frac{T_1 + T_2}{2}\right)$$

$$\boxed{p_f = \frac{N k_B (T_1 + T_2)}{(V_1 + V_2)}}$$

to express in terms of the initial pressures p_1 and p_2

$$p_1 = \frac{N k_B T_1}{V_1} \qquad p_2 = \frac{N k_B T_2}{V_2}$$

$$\Rightarrow V_1 = \frac{N k_B T_1}{p_1} \qquad V_2 = \frac{N k_B T_2}{p_2}$$

$$p_f = \frac{N k_B (T_1 + T_2)}{N k_B \frac{T_1}{p_1} + N k_B \frac{T_2}{p_2}} = \frac{T_1 + T_2}{\frac{T_1}{p_1} + \frac{T_2}{p_2}}$$

$$\boxed{p_f = \frac{p_1 p_2 (T_1 + T_2)}{p_2 T_1 + p_1 T_2}}$$

If we had $T_1 = T_2$ then

$$p_f = \frac{2 p_1 p_2}{p_1 + p_2}$$

To compare to average initial pressure

$\bar{p} = \frac{p_1 + p_2}{2}$ write $p_1 = \bar{p} + \delta p$, $p_2 = \bar{p} - \delta p$

Then $p_f = \frac{2(\bar{p}+\delta p)(\bar{p}-\delta p)}{\bar{p}+\delta p + \bar{p} - \delta p}$

$$= \frac{2(\bar{p}^2 - \delta p^2)}{2\bar{p}}$$

$$= \bar{p} - \frac{\delta p^2}{\bar{p}} < \bar{p}$$

so $\boxed{p_f < \bar{p}}$

d)

From problem 1 we are given the entropy of the ideal gas

$$S(E,V,N) = \frac{5}{2} N k_B + N k_B \ln\left[\frac{V}{h^3 N}\left(\frac{4\pi m E}{3N}\right)^{3/2}\right]$$

Since our problem is in terms of temperature T and not total energy E, we use the result for an ideal gas $E = \frac{3}{2} N k_B T$ and substitute into the above to get:

$$S = k_B N\left[\frac{5}{2} + \ln\left(\frac{V}{N h^3}(2\pi m k_B T)^{3/2}\right)\right]$$

The initial entropy is then:

$$S_i = S(T_1, V_1, N) + S(T_2, V_2, N)$$

$$= k_B N\left[5 + \ln\left(\frac{V_1 V_2}{N^2 h^6}(2\pi m k_B)^3 (T_1 T_2)^{3/2}\right)\right]$$

The final entropy is:

$$S_f = S(T_f, V, 2N)$$ as $2N$ particles in total gas, $V = V_1 + V_2$

$$= k_B 2N\left[\frac{5}{2} + \ln\left(\frac{(V_1+V_2)}{2N h^3}(2\pi m k_B T_f)^{3/2}\right)\right]$$

$$= k_B N\left[5 + 2\ln\left(\frac{(V_1+V_2)}{2N h^3}(2\pi m k_B T_f)^{3/2}\right)\right]$$

$$= k_B N\left[5 + \ln\left(\left(\frac{V_1+V_2}{2}\right)^2 \frac{1}{N^2 h^6}(2\pi m k_B)^3 T_f^{\,3}\right)\right]$$

So $\Delta S = S_f - S_i$

$$= k_B N \ln\left(\left(\frac{V_1+V_2}{2}\right)^2 \frac{1}{N^2 h^6} (2\pi m k_B)^3 \left(\frac{T_1+T_2}{2}\right)^3 \right)$$

$$- k_B N \ln\left(\frac{V_1 V_2}{N^2 h^6} (2\pi m k_B)^3 (T_1 T_2)^{3/2} \right)$$

$$\boxed{\Delta S = k_B N \ln\left[\frac{\left(\frac{V_1+V_2}{2}\right)^2 \left(\frac{T_1+T_2}{2}\right)^3}{V_1 V_2 \ (T_1 T_2)^{3/2}} \right]}$$

If $T_1 = T_2$ then $\frac{T_1+T_2}{2} = T_1$, $T_1 T_2 = T_1^2$

If $V_1 = V_2$ then $\frac{V_1+V_2}{2} = V_1$, $V_1 V_2 = V_1^2$

and

$$\Delta S = k_B N \ln\left(\frac{V_1^2}{V_1^2} \frac{T_1^3}{T_1^3} \right) = k_B N \ln(1) = 0$$

$$\boxed{\Delta S = 0}$$

3) The single particle Hamiltonian is

$$\mathcal{H}^{(1)} = \frac{p^2}{2m} + U(x) = \frac{p^2}{2m} + \alpha|x|$$

a) $Q_N = \frac{Q_1^N}{N!}$ where Q_1 is the single particle partition function

$$Q_1 = \frac{1}{h}\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp \; e^{-\beta\left[\frac{p^2}{2m} + \alpha|x|\right]}$$

$$= \frac{1}{h}\int_{-\infty}^{\infty} dp \; e^{-\frac{\beta p^2}{2m}} \; 2\int_0^{\infty} dx \; e^{-\beta\alpha x}$$

where we used $\int_{-\infty}^{\infty} dx \; e^{-\beta\alpha|x|} = 2\int_0^{\infty} dx \; e^{-\beta\alpha x}$

$$Q_1 = \frac{1}{h}\sqrt{2\pi m/\beta} \; \frac{2}{\beta\alpha} = \frac{1}{h}\frac{2}{\alpha}\sqrt{2\pi m}\,(k_B T)^{3/2}$$

$$\boxed{Q_N = \frac{1}{N!}\left[\frac{1}{h}\frac{2}{\alpha}\sqrt{2\pi m}\,(k_B T)^{3/2}\right]^N}$$

b) $S = -\left(\frac{\partial A}{\partial T}\right)_N$ where $A = -k_B T \ln Q_N$ is Helmholtz free energy

$$= k_B T \left(\frac{\partial \ln Q_N}{\partial T}\right)_N + k_B \ln Q_N$$

$\ln Q_N = N \ln Q_1 - N \ln N + N$ using Sterling's formula for $\ln N! = N \ln N - N$

$$\frac{\partial \ln Q_N}{\partial T} = \frac{N}{Q_1} \frac{\partial Q_1}{\partial T}$$

$$\frac{\partial Q_1}{\partial T} = \frac{3}{2} \frac{Q_1}{T}$$

$$S = k_B T \frac{N}{Q_1} \frac{3}{2} \frac{Q_1}{T} + k_B N \left[\ln \frac{Q_1}{N} + 1 \right]$$

$$= \frac{3}{2} N k_B + k_B N \left[\ln \frac{Q_1}{N} + 1 \right]$$

$$S = N k_B \left[\frac{5}{2} + \ln \left(\frac{2}{\hbar \alpha N} \sqrt{2\pi m} \, (k_B T)^{3/2} \right) \right]$$

c) $C = T\left(\frac{\partial S}{\partial T}\right)_N = T N k_B \frac{3}{2} \frac{1}{T} = \frac{3}{2} N k_B$

d) Integrating the density function $\rho(\{x_i, p_i\})$ over all other particles than the one of interest, and integrating over the momentum of that particle of interest, we get that the probability density for a particle to be at position x is

$$P(x) = \frac{e^{-\beta U(x)}}{\int_{-\infty}^{\infty} dx\, e^{-\beta U(x)}} = \frac{e^{-\beta\alpha|x|}}{\int_{-\infty}^{\infty} dx\, e^{-\beta\alpha|x|}}$$

$$= \frac{e^{-\beta\alpha|x|}}{2\int_0^{\infty} dx\, e^{-\beta\alpha x}} = \frac{e^{-\beta\alpha|x|}}{\left(\frac{2}{\beta\alpha}\right)}$$

$$\boxed{P(x) = \frac{\beta\alpha\, e^{-\beta\alpha|x|}}{2}}$$

$$x_{rms}^2 = \langle x^2 \rangle = \int_{-\infty}^{\infty} dx\, P(x)\, x^2$$

$$= 2\int_0^{\infty} dx\, \frac{\beta\alpha}{2}\, e^{-\beta\alpha x}\, x^2$$

Let $y = \beta\alpha x$ so $dy = dx\, \beta\alpha$

$$x_{rms}^2 = \frac{1}{(\beta\alpha)^2} \int_0^\infty dy\, e^{-y}\, y^2$$

We can do the integral by integrating by parts twice

$$\int_0^\infty dy\, e^{-y} y^2 = \underbrace{-e^{-y} y^2 \Big|_0^\infty}_{=0} + 2\int_0^\infty dy\, e^{-y} y$$

$$= \underbrace{-2e^{-y} y \Big|_0^\infty}_{=0} + 2\int_0^\infty dy\, e^{-y} = -2e^{-y}\Big|_0^\infty = 2$$

So

$$x_{rms}^2 = 2\left(\frac{k_B T}{\alpha}\right)^2 \quad > \quad \boxed{x_{rms} = \sqrt{2}\,\frac{k_B T}{\alpha}}$$

e) Prob that $|x| > x_{rms}$ is equal to prob$(x > x_{rms})$ + prob$(x < -x_{rms})$ = 2 prob$(x > x_{rms})$

$$= 2\int_{x_{rms}}^\infty dx\, P(x) = 2\int_{x_{rms}}^\infty dx\, \frac{\beta\alpha}{2} e^{-\beta\alpha|x|}$$

let $y = \beta\alpha x$, $dy = dx\,\beta\alpha$

$$= 2\int_{y_{rms}}^\infty \frac{dy}{2}\, e^{-y} \qquad \text{where } y_{rms} = \beta\alpha x_{rms}$$

$$= \int_{y_{rms}}^\infty dy\, e^{-y} = -e^{-y}\Big|_{y_{rms}}^\infty = e^{-y_{rms}}$$

$$\simeq e^{-\beta\alpha x_{rms}} \simeq e^{-\frac{\alpha}{k_B T}\frac{k_B T\sqrt{2}}{\alpha}} \simeq e^{-\sqrt{2}}$$

$$\boxed{\text{Prob}(|x| > x_{rms}) \simeq e^{-\sqrt{2}} = 0.243}$$

Note: this does not depend on the temperature T!