Graduate stat. Mech

HW # 1 - Solution

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① $dE = dQ - PdV \Rightarrow dQ = dE + PdV$

for adiabatic process $dQ = 0 \quad \Rightarrow \quad 0 = dE + PdV$ --- (1)

equation of state contains only two independent variables.

let us pick up (P, V) i.e $E = E(P,V)$

$dE = \left(\frac{\partial E}{\partial P}\right)_V dP + \left(\frac{\partial E}{\partial V}\right)_P dV$, substitute in (1), we get

$$\left(\frac{\partial E}{\partial P}\right)_V dP + \left(\frac{\partial E}{\partial V}\right)_P dV + P\,dV = 0$$

$$\Big[\underbrace{\left(\frac{\partial E}{\partial V}\right)_P}_{?} + P\Big] dV + \underbrace{\left(\frac{\partial E}{\partial P}\right)_V}_{?} dP = 0 \quad ---- \quad (2)$$

Now $\left(\frac{\partial E}{\partial V}\right)_P = \left(\frac{\partial E}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P$ chain rule -- (3)

and using $dE = T ds - P dV$ 1^{st} and 2^{nd} laws

$$\left(\frac{\partial E}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P + \cancelto{0 \text{ adiabatic}}{ds} - P\left(\frac{\partial V}{\partial T}\right)_P - \cancelto{0 \; P = \text{constant}}{\left(\frac{\partial P}{\partial T}\right)_P} \left(\frac{\partial V}{\partial T}\right)_P$$

$$= C_P - P\left(\frac{\partial V}{\partial T}\right)_P$$

eq^n (3) becomes $\left(\frac{\partial E}{\partial V}\right)_P = C_P\left(\frac{\partial T}{\partial V}\right)_P - P\cancelto{=1}{\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P} = C_P\left(\frac{\partial T}{\partial V}\right)_P - P$ --- (4)

also from $\left(\frac{\partial E}{\partial P}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_P$ chain rule

$$= C_V \left(\frac{\partial T}{\partial P}\right)_P \quad --- (5)$$

substitute 4 and 5 in 2, we get

$$C_P \left(\frac{\partial T}{\partial V}\right)_P dV + C_V \left(\frac{\partial T}{\partial P}\right)_V dP = 0 \qquad Q.E.D$$

- for an ideal gas $PV = N k_B T \Rightarrow T = \frac{PV}{N k_B}$

$$\Rightarrow C_P \frac{dV}{V} + C_V \frac{dP}{P} = 0$$

integrate $C_P \ln V + C_V \ln P = \text{const}$

divide by C_V $\Rightarrow \frac{C_P}{C_V} \ln V + \ln P = \text{const}$

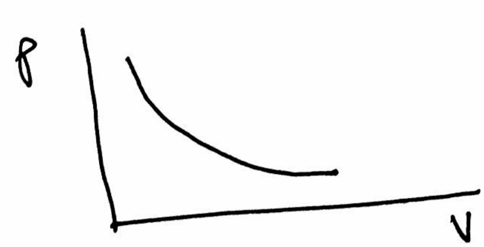
$\gamma = \frac{C_P}{C_V}$

$$\gamma \ln V + \ln P = \text{const}$$

$$\ln V^\gamma + \ln P = \text{const}$$

$$\ln PV^\gamma = \text{const}$$

$$\Rightarrow PV^\gamma = \text{constant} \qquad \underline{Q.E.D}$$



② a) $c_p = T\left(\frac{\partial S}{\partial T}\right)_p$; $\left(\frac{\partial c_p}{\partial p}\right)_T = T \frac{\partial}{\partial p}\left(\frac{\partial S}{\partial T}\right)_p$

$$= T \frac{\partial}{\partial T}\left(\frac{\partial S}{\partial p}\right)_T \quad \text{--- (1)}$$

but from

$$dG = -S\,dT + V\,dp + \mu\,dN \Rightarrow -\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p$$

Maxwell's relation

$\Rightarrow$ eq^n (1) becomes

$$\left(\frac{\partial c_p}{\partial p}\right)_T = T\frac{\partial}{\partial T}\left(-\frac{\partial V}{\partial T}\right)_p = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p \qquad \text{Q.E.D}$$

b) $$\left(\frac{\partial T}{\partial p}\right)_S = \frac{\partial(T,S)}{\partial(p,S)} = \frac{\partial(T,S)}{\partial(T,p)}\,\frac{\partial(T,p)}{\partial(p,S)} = -\underbrace{\left(\frac{\partial S}{\partial p}\right)_T}_{?}\,\underbrace{\left(\frac{\partial T}{\partial S}\right)_p}_{?} \quad \text{--- (2)}$$

from part a) we found $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$

and using $\left(\frac{\partial T}{\partial S}\right)_p\left(\frac{\partial S}{\partial p}\right)_T\left(\frac{\partial p}{\partial T}\right)_S = -1 \Rightarrow \left(\frac{\partial T}{\partial S}\right)_p = -\frac{1}{\underbrace{\left(\frac{\partial S}{\partial p}\right)_T\cdot\left(\frac{\partial p}{\partial T}\right)_S}} \quad \text{--- (3)}$

now $$\left(\frac{\partial S}{\partial p}\right)_T\left(\frac{\partial p}{\partial T}\right)_S = \frac{\cancel{\partial(T,S)}}{\partial(T,p)}\,\frac{\partial(S,p)}{\cancel{\partial(S,T)}} = \left(\frac{\partial S}{\partial T}\right)_p = \frac{c_p}{T}$$

$$\Rightarrow \text{from (3)} \quad \left(\frac{\partial T}{\partial S}\right)_p = -\frac{1}{\left(\frac{\partial S}{\partial T}\right)_p} = -\frac{T}{c_p}$$

eq^n (2) becomes

$$\left(\frac{\partial T}{\partial p}\right)_S = -\left(\frac{\partial V}{\partial T}\right)_p\left(-\frac{T}{c_p}\right) = \frac{T}{c_p}\left(\frac{\partial V}{\partial T}\right)_p \qquad \text{Q.E.D}$$

③ pathria 1.2

given $S = S_1 + S_2$; $\Omega = \Omega_1 \Omega_2$; $S_1 = f(\Omega_1)$

show that $f(\Omega) = k \ln \Omega$ $\quad S_2 = f(\Omega_2)$

$S = f(\Omega) = f(\Omega_1 \Omega_2)$

starting from

$S = S_1 + S_2$

$S = f(\Omega) = f(\Omega_1 \Omega_2) = f(\Omega_1) + f(\Omega_2)$

Now $\dfrac{dS}{d\Omega_1} = \Omega_2 f'(\Omega_1 \Omega_2) = f'(\Omega_1) + \cancel{\dfrac{d f(\Omega_2)}{d\Omega_1}} \to 0$

and $\dfrac{dS}{d\Omega_2} = \Omega_1 f'(\Omega_1 \Omega_2) = \cancel{\dfrac{d f(\Omega_1)}{d\Omega_2}} \to 0 + f'(\Omega_2)$

$\Rightarrow f'(\Omega_1 \Omega_2) = \dfrac{f'(\Omega_1)}{\Omega_2} = \dfrac{f'(\Omega_2)}{\Omega_1}$

$\Rightarrow \Omega_1 f'(\Omega_1) = \Omega_2 f'(\Omega_2)$

L.H.S and R.H.S are functions of two different variables, so the only way they are equal is that both sides equal the same constant (say k)

$\Rightarrow \Omega_1 f'(\Omega_1) = k \Rightarrow f'(\Omega_1) = \dfrac{k}{\Omega_1}$

integrate $f(\Omega_1) = k \ln \Omega_1$ $\quad$ Q.E.D

similarly $f(\Omega_2) = k \ln \Omega_2$

④ a) ideal gas $PV = Nk_BT$ only two independent variables

i.e $E = E(T,V)$, $S = S(T,V)$, let us go with T and V

$dE = TdS - PdV$ with $dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$

$$dE = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV - PdV \quad \text{---} \quad (1)$$

let us check the dependence of E on V

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P \quad \text{---} \quad (2)$$

but $\left(\frac{\partial S}{\partial V}\right)_T = \frac{\partial(T,S)}{\partial(T,V)} = \frac{\partial(P,V)}{\partial(T,V)} = \left(\frac{\partial P}{\partial T}\right)_V$

$$\text{so } \left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \quad \text{---} \quad (3)$$

for an ideal gas $PV = Nk_BT \Rightarrow P = \frac{Nk_BT}{V}$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{Nk}{V} = \frac{P}{T}$$

$$\Rightarrow \left(\frac{\partial E}{\partial V}\right)_T = T\frac{P}{T} - P$$

$$= P - P = 0$$

so E does not depend on V

i.e $E = E(T)$ only Q.E.D

b) if $E = E(T)$, then $\left(\frac{\partial E}{\partial V}\right)_T = 0$

i.e $\boxed{T\left(\frac{\partial p}{\partial T}\right)_V - p = 0}$ or $p = T\left(\frac{\partial p}{\partial T}\right)_V$

$= T \underbrace{f(V)}_{\text{any function of } V}$

for ideal gas $f(V) = \frac{N k_B}{V}$

c) van der waals eqⁿ of state is

$$\left[p - a\left(\frac{N}{V}\right)^2\right](V - Nb) = N k_B T$$

$\Rightarrow$ solve for p

$$p = \frac{N k_B T}{(V - Nb)} + a\left(\frac{N}{V}\right)^2$$

now $C_V = \left(\frac{\partial E}{\partial T}\right)_V$

$$\Rightarrow \left(\frac{\partial C_V}{\partial V}\right)_T = \frac{\partial}{\partial V}\left(\frac{\partial E}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{\partial E}{\partial V}\right)$$

$$= \frac{\partial}{\partial T}\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]$$

$$= \cancel{\left(\frac{\partial p}{\partial T}\right)_V} + T\left(\frac{\partial^2 p}{\partial T^2}\right)_V - \cancel{\left(\frac{\partial p}{\partial T}\right)_V}$$

$$= T\left(\frac{\partial^2 p}{\partial T^2}\right)_V$$; as $\left(\frac{\partial p}{\partial T}\right)_V = \frac{N k}{V}$

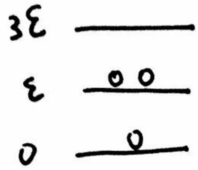
$\left(\frac{\partial^2 p}{\partial T^2}\right)_V = 0$

$$= 0$$

so $C_V = C_V(T)$

⑤ $N = 3$ distinguishable particles

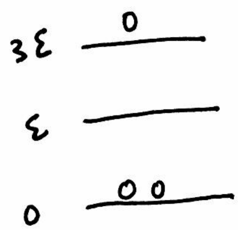
a) $E = 2\varepsilon$



$2 \times (1\varepsilon) + 1 \times (0\varepsilon)$

$$\Omega = \frac{3!}{2!\,1!} = \frac{3 \times 2}{2 \times 1 \times 1} = 3 \Rightarrow S = k_B \ln 3$$

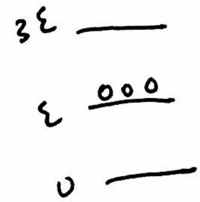
b) $E = 3\varepsilon$



$1 \times (3\varepsilon) + 2 \times (0\varepsilon)$

$$\Omega_1 = \frac{3!}{2!\,1!} = 3$$

or



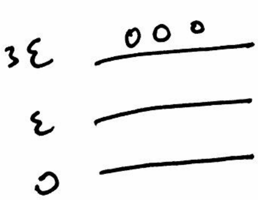
$3 \times (1\varepsilon) + 0 \times (3\varepsilon) + 0 \times (3\varepsilon)$

$$\Omega_2 = \frac{3!}{3!\,0!} = 1$$

$$\Omega_{tot} = \Omega_1 + \Omega_2 = 3 + 1 = 4 \Rightarrow$$

$$S = k_B \ln 4$$

c) $E = 9\varepsilon$



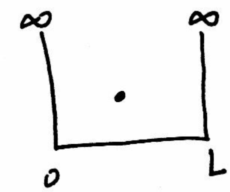
$3 \times (3\varepsilon) + 0 \times (1\varepsilon) + 0 \times (0\varepsilon)$

$$\Omega = \frac{3!}{3!\,0!} = 1 \Rightarrow S = k_B \ln 1 = 0$$

$S = 0$ as expected as there is only one unique configuration

⑥ particle in a 1D box

$$\frac{d^2\phi(x)}{dx^2} + k^2\phi(x) = 0 \quad ; \quad k^2 = \frac{2mE}{\hbar^2} \quad \text{and } \phi(0) = \phi(L) = 0$$



$\phi(x) = A\cos kx + B\sin kx$

but $\phi(0) = 0 \Rightarrow A = 0$

$\Rightarrow \phi(x) = B\sin kx$

and $\phi(L) = 0 \Rightarrow \sin kL = 0$, $kL = n\pi \Rightarrow k_n = \frac{n\pi}{L}$

$n = 1, 2, 3, \ldots$

$$\Rightarrow \varepsilon_n = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2\pi^2 n^2}{2mL^2}$$

B can be found from normalization $\int_0^L |\phi(x)|^2 dx = 1$

$$B^2\int_0^L \sin^2\left(\frac{n\pi x}{L}\right)dx = 1 \Rightarrow B^2\frac{L}{n\pi}\int_0^{n\pi}\sin^2 y\, dy = 1$$

$$B^2\frac{L}{n\pi}\,\frac{n\pi}{2} = 1 \Rightarrow B = \sqrt{\frac{2}{L}}$$

$$\Rightarrow \boxed{\phi_n(x) = \sqrt{\frac{2}{L}}\sin(k_n x)}$$

for 3-non interacting particles, $E = 38\,\varepsilon_0 = 38\,\frac{\hbar^2\pi^2}{2mL^2}$

$$E = \sum_{i=1}^{3} E_i = \sum_{i=1}^{3}\varepsilon_0 n_i^2 = \varepsilon_0 n_1^2 + \varepsilon_0 n_2^2 + \varepsilon_0 n_3^2$$

$$= \cancel{\varepsilon_0}(n_1^2 + n_2^2 + n_3^2) \equiv 38\cancel{\varepsilon_0}$$

$$\Rightarrow \boxed{n_1^2 + n_2^2 + n_3^2 = 38}$$

two possibilities $(5,3,2)$ or $(6,1,1)$

a) 3 distinguishable particles

- $(5,3,2) \Rightarrow 3!$ microstates $= 3\times 2\times 1 = 6$ microstates

5	3	3	2	2	5
3	5	2	3	5	2
2	2	5	5	3	3
(2,3,5)	(2,5,3)	(5,2,3)	(5,3,2)	(3,5,2)	(3,2,5)

- $(6,1,1) \Rightarrow \frac{3!}{2!\,1!} = 3$ microstates $(6,1,1), (1,6,1), (1,1,6)$

let us label our 3 particles by 1,2,3 $\Rightarrow$ such that the state $n=1$ is doubly occupied.

$n=6$	3	2	1
$n=1$	1,2	1,3	3,2

$\Rightarrow$ total # of microstates $= 6+3 = 9 = \Omega$

$\Rightarrow S = k_B \ln 9$

b) 3 indistinguishable bosons

the 6 microstates of the $(5,3,2)$ are counted now as one microstate as they are identical. similarly the 3 microstates of the $(6,1,1)$ are counted one microstate for the same reason

$\Rightarrow \Omega_{tot} = 1+1 = 2 \quad \Rightarrow S = k_B \ln 2$

c) 3 indistinguishable spin 1/2 fermions

Assuming that each energy level has $(2s+1)$ degeneracy, for spin 1/2, we have two particles at most for each energy level (one $\uparrow$ and one $\downarrow$)

- $(5,3,2)$, we have $2^3 = 8$ microstates

5	$\uparrow$	$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$
3	$\uparrow$	$\uparrow$	$\downarrow$	$\downarrow$	$\uparrow$	$\uparrow$	$\downarrow$	$\downarrow$
2	$\uparrow$	$\uparrow$	$\uparrow$	$\downarrow$	$\downarrow$	$\downarrow$	$\uparrow$	$\downarrow$

- $(6,1,1)$, here the state with $n_2 = n_3 = 1$ is doubly occupied, so we have only <u>two microstates</u>

6	$\uparrow$	$\downarrow$
1	$\uparrow\downarrow$	$\uparrow\downarrow$

$$\Rightarrow \Omega_{tot} = 8 + 2 = 10$$

$$\Rightarrow \underline{S = k_B \ln 10}$$