Graduate stat. Mech

HW # 2 - solution

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① Pathria 1.8:

we have N quasiparticles, where each quasiparticle has one quantum number n_r with corresponding energy $\varepsilon(n_r) = n_r h\nu$, $n_r = 0, 1, 2, \ldots$. The total energy E

$$E = \sum_{r=1}^{N} \varepsilon(n_r) = \sum_{r=1}^{N} n_r h\nu \Rightarrow \frac{E}{h\nu} = \sum_{r=1}^{N} n_r \equiv R \quad \text{--- (1)}$$

where R is the total # of quanta available to the entire system. the condition $\sum n_r = R$ means that the sum of all occupation numbers have to be equal to R. so each possible distribution of the R quanta is described by a set of integers values $\{n_r\}$, which uniquely describes a microstate of the system. the R quanta must be distributed among the N quasiparticles with the condition $\sum n_r = R$ is always satisfied. let us consider each quasiparticle as a box and each quanta as a ball. The balls and the boxes are indistinguishable. Now the # of ways of putting R quanta in N boxes can be calculated using equation (3.8.25 Pathria)

$$\Omega = \frac{(R+N-1)!}{R!\,(N-1)!}$$

which is the total # of microstates available to the system (microcanonical ensemble)

$$\ln\Omega = \ln(R+N-1)! - \ln R! - \ln(N-1)!$$

The assymptotic limit corresponds to $R \gg 1$ and $N \gg 1$ and using stirling approximation $\ln n! \approx n \ln n - n$, we have

$$\ln \Omega = (R+N-1)\ln(R+N-1) - (R+N-1) - (R\ln R - R) - (N-1\ln(N-1) - (N-1))$$

$$\underset{R+N\gg 1}{=} (R+N)\ln(R+N) - (R+N) - R\ln R + R - N\ln N$$

$$= R\ln\left(\frac{R+N}{R}\right) + N\ln\left(\frac{R+N}{N}\right) \quad ; \text{ using } R = \frac{E}{h\nu}$$

$$\boxed{\underset{R+N\gg 1}{\ln \Omega} = \frac{E}{h\nu}\ln\left(\frac{E+Nh\nu}{E}\right) + N\ln\left(\frac{E+Nh\nu}{Nh\nu}\right) \quad \text{--- (2)}}$$

Now need to find $T\left(\frac{E}{N}, h\nu\right)$. This can be done using the formula $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_N$ ---------- (3)

but $S = k_B \ln \Omega = \frac{k_B E}{h\nu}\ln\left(\frac{E+Nh\nu}{E}\right) + k_B N\ln\left(\frac{E+Nh\nu}{Nh\nu}\right)$

$$= \frac{k_B N}{Nh\nu}E\ln\left(\frac{E+Nh\nu}{E}\right) + k_B N\ln\left(\frac{E+Nh\nu}{Nh\nu}\right)$$

let $Nh\nu = a$; $k_B N = b$; $E = x$

$$\Rightarrow S = \frac{b}{a}x\ln\left(\frac{x+a}{x}\right) + b\ln\left(\frac{x+a}{a}\right)$$

Now $\frac{\partial S}{\partial E} = \frac{\partial S}{\partial x} = \frac{b}{a}\ln\left(\frac{x+a}{a}\right)$ using online derivative calculator

$$= \frac{k_B N}{Nh\nu}\ln\left(\frac{E+Nh\nu}{E}\right) = \frac{k_B}{h\nu}\ln\left(1+\frac{Nh\nu}{E}\right)$$

$$= \frac{k_B}{h\nu}\ln\left(1+\frac{h\nu}{(E/N)}\right)$$

from (3)

$$\Rightarrow T = \frac{h\nu}{k_B\ln\left(1+\frac{h\nu}{(E/N)}\right)}$$

$$\therefore \quad T = \frac{h\nu}{k_B \ln\left(1 + \frac{h\nu}{E/N}\right)}$$

now when $\frac{E}{N h\nu} >> 1$ or $\frac{N h\nu}{E} << 1$, we have

$\ln\left(1 + \frac{N h\nu}{E}\right) \approx \frac{N h\nu}{E}$, when I used $\ln(1+x) \approx x$ if $x << 1$

$$\Rightarrow T = \frac{h\nu}{k_B \frac{N h\nu}{E}} = \frac{E}{N k_B}$$

② pathria 1.11

4 moles of N_2 and 1 mole of O_2 are mixed at $P = 1\,atm$ and T

what is ΔS?

from eqⁿ 1.41 in our lecture notes and using $E = \frac{3}{2} N k_B T$ for an ideal gas, we find

$$S = N k_B \ln \frac{V}{N\lambda^3} + \frac{5}{2} N k_B \; ; \quad \text{with } \lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

let N_2 be gas $\underline{\underline{1}}$ and O_2 be gas $\underline{\underline{2}}$

$$S_i = N_1 k_B \ln \frac{V_1}{N_1 \lambda_1^3} + \frac{5}{2} N_1 k_B + N_2 k_B \ln \frac{V_2}{N_2 \lambda_2^3} + \frac{5}{2} N_2 k_B$$

$$S_f = N_1 k_B \ln \frac{V_f}{N_1 \lambda_1^3} + \frac{5}{2} N_1 k_B + N_2 k_B \ln \frac{V_f}{N_2 \lambda_2^3} + \frac{5}{2} N_2 k_B$$

$$\Delta S = S_f - S_i = N_1 k_B \ln \frac{V_f}{V_1} + N_2 k_B \ln \frac{V_f}{V_2}$$

Now using $N_1 = n_1 N_A = 4 N_A$ and $N_2 = n_2 N_A = 1 N_A$; and $N = N_1 + N_2 = 5 N_A$

$$\Delta S = 4 N_A k_B \ln \frac{V_f}{V_1} + N_A k_B \ln \frac{V_f}{V_2} = 4R \ln \frac{V_f}{V_1} + R \ln \frac{V_f}{V_2}$$

$$\frac{\Delta S}{n} = \frac{\Delta S}{5} = \frac{4}{5} R \ln \frac{V_f}{V_1} + \frac{R}{5} \ln \frac{V_f}{V_1} \; ; \text{ but}$$

$$= \frac{4}{5} R \ln \frac{n}{n_1} + \frac{R}{5} \ln \frac{n}{n_2}$$

$$= R \left[\frac{4}{5} \ln \frac{5}{4} + \frac{1}{5} \ln \frac{5}{1} \right]$$

$$\approx 0.5 R = 4.2 \; J/mol.K$$

where $R = 8.314 \; J/mol.K$

$P_1 V_1 = N_1 k_B T$

$P_2 V_2 = N_2 k_B T$

$P V_f = (N_1 + N_2) k_B T$

$$V_f = \frac{k_B T}{P}(N_1 + N_2) = \frac{k_B T}{P} N \; ; \; P_1 = P_2 = P = 1\,atm$$

$$\Rightarrow \frac{V_f}{V_1} = \frac{N}{N_1} = \frac{n}{n_1}$$

$$V_f / V_2 = \frac{N}{N_2} = \frac{n}{n_2}$$

③ Pathria 1.16

Ω = grand canonical potential or shortly grand potential

$$\Omega = E - TS - \mu N \equiv -PV$$

$$d\Omega = dE - TdS - SdT - \mu dN - Nd\mu = -PdV - VdP$$

$$= \cancel{TdS} - \cancel{PdV} + \cancel{\mu dN} - \cancel{TdS} - SdT - \cancel{\mu dN} - Nd\mu = \cancel{-PdV} - VdP$$

$$\Rightarrow \quad -SdT - Nd\mu = -VdP$$

i) at constant $\mu \Rightarrow d\mu = 0 \Rightarrow S = V\left(\frac{\partial P}{\partial T}\right)_\mu$

ii) at constant $T \Rightarrow dT = 0 \Rightarrow N = V\left(\frac{\partial P}{\partial \mu}\right)_T$

Now need to find P of an ideal gas as a function of μ and T i.e $P(\mu, T)$

from equation 1.42 in our lecture notes, we have

$S(E,N,V) = Nk_B \ln\left[\frac{V}{N}\left(\frac{4\pi m E}{3Nh^2}\right)^{3/2}\right]$. This equation can be inverted to get $E(S,N,V)$

$$E(S,N,V) = \frac{3h^2 N^{5/3}}{4\pi V^{2/3} m} e^{\left(\frac{2S}{3Nk_B} - \frac{5}{3}\right)}$$ [see Pathria eq (1.4.22.a)

Now from first law $dE = TdS - PdV + \mu dN$

$$\Rightarrow \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}$$

$$= \frac{3h^2 N^{5/3}}{4\pi m V^{2/3}}\left(\frac{-2S}{3k_B N^2}\right) e^{\left(\frac{2S}{3Nk_B} - \frac{5}{3}\right)} + \frac{3h^2 N^{2/3}}{4\pi m V^{2/3}} e^{\left(\frac{2S}{3Nk_B} - \frac{5}{3}\right)}$$

$$= \underbrace{\frac{3h^2 N^{5/3}}{4\pi m V^{2/3}} e^{\left(\frac{2S}{3Nk_B} - \frac{5}{3}\right)}}_{E}\left(\frac{5}{3N} - \frac{2S}{3N^2 k_B}\right) = E\left(\frac{5}{3N} - \frac{2S}{3N^2 k_B}\right)$$

$$\mu = E\left(\frac{5}{3N} - \frac{2S}{3N^2 k_B}\right)$$

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

$$= E\left(\cancel{\frac{5}{3N}} - \frac{2}{3N} \ln \frac{V}{N}\left(\frac{4\pi m E}{3N h^2}\right)^{3/2} - \cancel{\frac{5}{3N}}\right)$$

$$= -\frac{2E}{3N} \ln \frac{V}{N}\left(\frac{4\pi m E}{3N h^2}\right)^{3/2} ; \quad \text{but } E = \frac{3}{2} N k_B T$$

$$= k_B T \ln \frac{N}{V}\left(\frac{h^2}{2\pi m k_B T}\right)^{3/2} = k_B T \ln \frac{N}{V}\lambda^3 \; ; \; \lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

now using $PV = N k_B T \Rightarrow \frac{N}{V} = \frac{P}{k_B T}$

$$\Rightarrow \mu = k_B T \ln\left(\frac{P}{k_B T}\lambda^3\right) \Rightarrow \boxed{P = \frac{k_B T}{\lambda^3} e^{\mu/k_B T}}$$

using this result one can verify that

$$V\left(\frac{\partial P}{\partial \mu}\right)_T = V \frac{k_B T}{\lambda^3} \frac{1}{k_B T} e^{\mu/k_B T} = \frac{V}{\lambda^3} e^{\mu/k_B T} = V \frac{P}{k_B T} = N$$

similarly
$$\left(\frac{\partial P}{\partial T}\right)_\mu = \frac{1}{\lambda^3}\left[k_B e^{\mu/k_B T} + k_B T\left(\frac{1}{k_B T}\right) e^{\mu/k_B T} + k_B T e^{\mu/k_B T}\left(-\frac{3\lambda^2}{\lambda^6}\frac{d\lambda}{dT}\right)\right]$$

$$\therefore \left(\frac{\partial P}{\partial T}\right)_\mu = \frac{e^{\mu/k_B T}}{\lambda^3}\left[k - \frac{\mu}{T} + \frac{3}{2}k\right] = \frac{P}{k_B T}\left[\frac{5}{2}k - \frac{\mu}{T}\right]$$

Now

$$V\left(\frac{\partial P}{\partial \mu}\right)_T = \underbrace{\frac{PV}{k_B T}}_{N}\left[\frac{5}{2}k - \frac{\mu}{T}\right] = \frac{5}{2}Nk_B - \frac{\mu N}{T}$$

$$= \frac{5}{2}Nk_B - k_B N \ln\left(\frac{P}{k_B T}\lambda^3\right)$$

$$= \frac{5}{2}Nk_B - k_B N \ln\left(\frac{N}{V}\lambda^3\right)$$

$$= \frac{5}{2}Nk_B + \underbrace{k_B N \ln\left(\frac{V}{N\lambda^3}\right)}_{S - \frac{5}{2}Nk_B}$$

$$= \cancel{\frac{5}{2}Nk_B} + S \cancel{- \frac{5}{2}Nk_B} = S$$

Remark: the entropy of an ideal gas can be expressed as

$$S = Nk_B \ln\frac{V}{N\lambda^3} + \frac{5}{2}Nk_B$$

4 + 5

a) 1 D: $\quad E_p = \frac{p^2}{2m} \quad ; \; p^2 = 2mE_p \; ; \; 2p\,dp = 2m\,dE_p$

$$dp = \frac{m}{p} dE_p = \frac{m}{\sqrt{2mE_p}} dE_p$$

$$w(E) = \int dq\, dp\, \delta(E - H) =$$

$$= \frac{Lm}{(2m)^{1/2}} \int_0^\infty E_p^{-1/2} dE_p \, \delta(E - E_p) = L\left(\frac{m}{2E}\right)^{1/2}$$

Now $w(E) = \frac{d\,\Sigma(E)}{dE} \Rightarrow \Sigma(E) = \int_0^E w(E)\, dE = 2L\left(\frac{m}{2}\right)^{1/2} \int_0^E E^{-1/2} dE$

$$= 2L\left(\frac{m}{2}\right)^{1/2} E^{1/2}$$

$$= 2L(2mE)^{1/2}$$

$$\Gamma(E) = w(E)\,\delta E = L\left(\frac{m}{2E}\right)^{1/2} \delta E \times \frac{2E}{2E}$$

$$= \frac{L}{2}(2mE)^{1/2} \frac{\delta E}{E}$$

$$\Omega = \frac{\Gamma(E)}{h} = \frac{L}{2h}(2mE)^{1/2} \frac{\delta E}{E}$$

$$S = k_B \ln \Omega = k_B \ln\left[\frac{L}{2h}(2mE)^{1/2} \frac{\delta E}{E}\right]$$

$$= k_B \left[\ln \frac{L}{2h}(2mE)^{1/2} + \cancel{\ln \frac{\delta E}{E}}\right]$$

small as $\delta E \ll E$

$$\approx k_B \ln \frac{L}{2h}(2mE)^{1/2}$$

b) 2D $\qquad E_p = \frac{p^2}{2m}$

$$\omega(E) = \int d^2q\, d^2p\; \delta(E - E_p) \quad ; \quad d^2p = p\,dp\,d\theta$$ in polar coordinates

$$0 < p < \infty$$
$$0 < \theta < 2\pi$$

$$= 2\pi A \int_0^\infty p\,dp\; \delta(E - E_p)$$

$$= 2\pi A m \int_0^\infty dE_p\; \delta(E - E_p) = 2\pi m A = \text{constant}$$

$$\Sigma(E) = \int_0^E \omega(E)\,dE = 2\pi m A E$$

$$\Gamma(E) = \omega(E)\,\delta E = 2\pi m A\,\delta E \times \frac{E}{E} = 2\pi m A E \frac{\delta E}{E}$$

$$\Omega = \frac{\Gamma(E)}{h^2} = \frac{2\pi m A E}{h^2} \frac{\delta E}{E}$$

$$S = k_B \ln \Omega$$

$$= k_B \ln \left[\frac{2\pi A E}{h^2} \frac{\delta E}{E} \right)$$

small as $\delta E \ll E$

$$= k_B \left[\ln \frac{2\pi A E m}{h^2} + \ln \frac{\delta E}{E} \right]$$

$$\approx k_B \ln \left(\frac{2\pi m A E}{h^2} \right)$$

c) 3D : $\quad \epsilon_p = \frac{p^2}{2m}$

$$w(E) = \int d^3q\, d^3p\, \delta(\epsilon - \epsilon_p) \quad ; \quad d^3p = p^2 dp\, d\Phi$$

solid angle

$0 < p < \infty$

$$= V \int_0^{4\pi} d\sigma \int_0^{\infty} p^2 dp\, \delta(\epsilon - \epsilon_p)$$

$$= 4\pi V \int_0^{\infty} p^2 dp\, \delta(\epsilon - \epsilon_p)$$

$$= 4\pi V (2m)^{3/2} \cdot \frac{1}{2} \int_0^{\infty} \epsilon_p^{1/2}\, d\epsilon_p\, \delta(E - \epsilon_p)$$

$$= 2\pi V (2m)^{3/2} E^{1/2}$$

Now $\Sigma(E) = \int_0^E w(\epsilon)\, dE = \frac{4\pi}{3} V (2m)^{3/2} E^{3/2}$

$$\Gamma(E) = w(E)\, \delta E = 2\pi V (2m)^{3/2} E^{1/2} \delta E$$

$$\Omega = \frac{\Gamma(E)}{h^3} = \frac{2\pi V (2m)^{3/2}}{h^3} E^{1/2} \delta E \times \frac{E}{E} = \frac{2\pi V (2m)^{3/2}}{h^3} E^{3/2} \frac{\delta E}{E}$$

small as $\delta E \ll E$

$$S = k_B \ln \Omega$$

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

$$\approx k_B \ln \left[\frac{2\pi V}{h^3} (2mE)^{3/2} \right]$$

⑥ Pathria 2.7

i)

we have N 1D H.Os with $\varepsilon(n_r) = (n_r + \frac{1}{2})\hbar\omega_0$; $n_r = 0, 1, 2, \ldots$

total energy $E = \sum_{r=1}^{N} \varepsilon(n_r) = \sum_{r=1}^{N} (n_r + \frac{1}{2})\hbar\omega_0$

$$= \sum_r n_r \hbar\omega_0 + \frac{1}{2} N \hbar\omega_0$$

$\Rightarrow \frac{E - \frac{1}{2} N \hbar\omega_0}{\hbar\omega_0} = \sum_{r=1}^{N} n_r \equiv R$ total # of quanta to be distributed among N 1D H.Os. in the classical limit, the average energy per oscillator $\frac{E}{N}$ is much larger than the energy quantum $\hbar\omega_0$

i.e $\frac{E}{N} \gg \hbar\omega_0$

so $R = \frac{1}{\hbar\omega_0}\left(E - \frac{1}{2} N \hbar\omega_0\right) = \frac{N}{\hbar\omega_0}\left(\frac{E}{N} - \frac{1}{2}\hbar\omega_0\right)$

$$\approx \frac{E}{\hbar\omega_0} \qquad \text{—— (1)}$$

which is similar to the case of ignoring the zero point energy of all oscillators.

$\Omega = \frac{(R+N-1)!}{R!\,(N-1)!}$ the # of ways of distributing R quanta among N oscillators

$\ln\Omega = R \ln\frac{(R+N)}{R} + N \ln\left(\frac{R+N}{N}\right)$; where $\ln R! = R\ln R - R$, $\ln N! = N\ln N - N$

where I used $R \gg 1$ and $N \gg 1$

hence $R+N-1 \to R+N$

$N-1 \to N$

in the classical limit $R >> N$

$$\ln \Omega \approx R \cancelto{0}{\ln\left(\frac{R}{R}\right)} + N \ln\left(\frac{R}{N}\right) = \ln\left(\frac{R}{N}\right)^N = \ln \frac{R^N}{N^N}$$

now $\ln N! \approx N \ln N - N = \ln N^N - N \approx \ln N^N$

$\Rightarrow N! \approx N^N$ $\quad$ ↳ where $\ln N^N >> N$

$$\Rightarrow \ln \Omega \approx \ln \frac{R^N}{N!} = \ln \frac{(E/\hbar\omega_0)^N}{N!} \Rightarrow \Omega = \frac{(E/\hbar\omega_0)^N}{N!} \quad \text{---(2)}$$

ii) for a single oscillator, we have $\varepsilon_r = \frac{p_r^2}{2m} + \frac{1}{2} m\omega_0^2 q_r^2$

for N oscillators $E = \sum_{r=1}^{N} \frac{p_r^2}{2m} + \frac{1}{2} m\omega_0^2 q_r^2$

↳ 2N-dimensional hyperelipse

Recall that for each oscillator we need to coordinates (p_x, q_x), so for N 1D oscillators, we need $2N$ coordinates
-now we need to calculate the volume enclosed by this hyperelipse, for an energy $<E$. practically, it is very hard to integrate over this elipse, but we can convert this elipse to a hypersphere having the same volume using the following transformation.

$$p_r' = \frac{p_r}{\sqrt{2m}} \quad \text{and} \quad q_r' = \frac{q_r}{\sqrt{2/m\omega_0^2}}$$

$$dp_r' = \left(\frac{1}{2m}\right)^{1/2} dp_r \quad \text{and} \quad dq_r' = \left(\frac{1}{2/m\omega_0^2}\right)^{1/2} dq_r$$

$$\Rightarrow E = \sum_{r=1}^{N} p_r'^2 + q_r'^2$$ this is now a hypersphere with radius $\sqrt{E}$

with $dp_r^N = (2m)^{N/2} dp_r'$ and $dq_r^N = \left(\frac{2}{m\omega_0^2}\right)^{N/2} dq_r'$

$$\Rightarrow \Sigma(E) = \int dq^{2N} dp^{2N} = \left(\frac{4}{\omega_0^2}\right)^{N/2} \underbrace{\int dq'^{2N} dp'^{2N}}_{\text{volume of hypersphere with radius } R=\sqrt{E}}$$

using

$$V_n = \frac{\pi^{n/2}}{(n/2)!} R^n \quad ; \text{with } n = 2N, \; R = \sqrt{E}$$

$$= \frac{\pi^N}{N!} (E)^N \Rightarrow \Sigma(E) = \left(\frac{4}{\omega_0^2}\right)^{N/2} \frac{\pi^N}{N!} E^N = \left(\frac{2}{\omega_0}\right)^N \frac{\pi^N E^N}{N!}$$

$$= \frac{1}{N!} \left(\frac{2\pi E}{\omega_0}\right)^N$$

Now $\Sigma(E) \propto \Omega$

$\Rightarrow \Sigma(E) = c\,\Omega$; c is a constant

$$\cancel{\frac{1}{N!}\left(\frac{2\pi E}{\omega_0}\right)^N} = c\left(E/\hbar\omega_0\right)^N \frac{1}{N!} = \frac{1}{N!} c \left(\frac{2\pi E}{h\omega_0}\right)^N$$

$$= \frac{c}{h^N} \cancel{\frac{1}{N!}\left(\frac{2\pi E}{\omega_0}\right)^N}$$

$$\Rightarrow \frac{c}{h^N} = 1 \Rightarrow \boxed{c = h^N}$$

as expected