Graduate stat. Mech

HW # 4 - solution

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① a) $\mathcal{Z}(z,T) = \sum_{N=0}^{N_0} g(N)\, e^{-\alpha N} e^{-\beta N \varepsilon}$; $e^{-\alpha} = z$ fugacity

$g(N) \rightarrow$ degeneracy $= \binom{N_0}{N}$

$$= \sum_{N=0}^{N_0} \binom{N_0}{N} z^N \left(e^{-\beta\varepsilon}\right)^N = \sum_{N=0}^{N_0} \binom{N_0}{N} \left(z e^{-\beta\varepsilon}\right)^N$$

Binomial series

$$= \left(1 + z e^{-\beta\varepsilon}\right)^{N_0} \quad ; \quad \sum_{k=0}^{n} \binom{n}{k} r^k = (1+r)^n$$

b) fraction occupied $= \dfrac{\langle N \rangle}{N_0}$

but $\langle N \rangle = \dfrac{1}{\beta}\left(\dfrac{\partial \ln \mathcal{Z}}{\partial \mu}\right)_{T,V}$; where $z = e^{-\alpha} = e^{\beta\mu}$

$dz = \beta e^{\beta\mu} d\mu$

$\dfrac{\partial}{\partial z} = \dfrac{1}{\beta} e^{-\beta\mu} \dfrac{\partial}{\partial \mu}$

$\dfrac{\partial}{\partial \mu} = \beta e^{\beta\mu} \dfrac{\partial}{\partial z} = \beta z \dfrac{\partial}{\partial z}$

$$= \frac{1}{\beta} \beta z \left(\frac{\partial \ln \mathcal{Z}}{\partial z}\right)_{T,V}$$

$$= z \left(\frac{\partial \ln \mathcal{Z}}{\partial z}\right)_{T,V}$$

$$= z \left(N_0 \frac{e^{-\beta\varepsilon}}{1 + z e^{-\beta\varepsilon}}\right) = \frac{N_0}{z^{-1} e^{\beta\varepsilon} + 1}$$

$$\Rightarrow \frac{\langle N \rangle}{N_0} = \frac{1}{z^{-1} e^{\beta\varepsilon} + 1}$$

c) $E = -\dfrac{\partial}{\partial \beta} \ln \mathcal{Z} = \dfrac{N_0 \varepsilon}{z^{-1} e^{\beta\varepsilon} + 1}$

d) $C = \left(\dfrac{\partial E}{\partial T}\right)_V = \dfrac{N_0 k_B (\beta\varepsilon)^2 e^{\beta\varepsilon}}{z\left(z^{-1} e^{\beta\varepsilon} + 1\right)^2}$

② pathria 4.1

$$P_{r,s} = \frac{e^{-\alpha N - \beta E}}{\mathcal{Z}} \; ; \quad \alpha = -\mu\beta$$

now $\langle \ln P_{r,s} \rangle = -\alpha\bar{N} - \beta\bar{E} - \ln \mathcal{Z}$; but $\Omega = -k_B T \ln \mathcal{Z}$
$= -\frac{1}{\beta} \ln \mathcal{Z}$

let $\bar{N} \equiv N$ and $\bar{E} \equiv E$

$$\Rightarrow \langle \ln P_{r,s} \rangle = \beta\mu N - \beta E + \beta\Omega$$
$$= \beta(\mu N - E - PV)$$; where $\Omega = -PV$

now using $G = \mu N = E + PV - TS$, we have

$$\langle \ln P_{r,s} \rangle = \beta\left(\cancel{E} + \cancel{PV} - TS - \cancel{E} - \cancel{PV}\right) = -\beta TS$$
$$= -\frac{1}{k_B T} TS = -\frac{S}{k_B}$$

$$\Rightarrow S = -k_B \langle \ln P_{r,s} \rangle$$

but $\langle \ln P_{r,s} \rangle = \sum_{r,s} P_{r,s} \ln P_{r,s}$

so $S = -k_B \sum_{r,s} P_{r,s} \ln P_{r,s}$

Q.E.D

③ Pathria 4.4

In the G.C.E, the probability that a system is in a particular microstate with energy E_s and number of particles N_r is

$$P_{r,s} = \frac{e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}} = \frac{e^{-\alpha N_r - \beta E_s}}{\mathcal{Z}} = \frac{z^{N_r} e^{-\beta E_s}}{\mathcal{Z}} ;$$

where $\alpha = -\frac{\mu}{k_B T} = -\beta\mu$ and $z = e^{-\alpha} = e^{\beta\mu}$

now to find $P(N)$; the probability the system has a given number of particles N is found by summing the above probability over all possible microstates with the number of particles fixed to N

$$P(N) = \sum_{s, N_r = N} P_{r,s} = \frac{z^N \sum_s e^{-\beta E_s}}{\mathcal{Z}} = \frac{z^N Q_N(V,T)}{\mathcal{Z}(z,V,T)}$$

when $Q_N(V,T) = \sum_s e^{-\beta E_s}$ is the canonical partion function

so for classical ideal gas, we found

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

$$\text{and } \mu = k_B T \ln\left[\frac{\bar{N}}{V}\left(\frac{h^2}{2\pi m k_B T}\right)^{3/2}\right] = k_B T \ln\left[\frac{\bar{N}}{V}\lambda^3\right]$$

$$\Rightarrow \frac{\mu}{k_B T} = \ln\left(\frac{\bar{N}}{V}\lambda^3\right) \Rightarrow \mu\beta = \ln\left(\frac{\bar{N}}{V}\lambda^3\right)$$

$$\Rightarrow \underbrace{e^{\mu\beta}}_{z} = \frac{\bar{N}}{V}\lambda^3 \Rightarrow z = \frac{\bar{N}\lambda^3}{V} \Rightarrow \boxed{\bar{N} = \frac{zV}{\lambda^3}}$$

and $\Omega = -k_B T \ln Z \Rightarrow -\beta\Omega = \ln Z \Rightarrow \beta P V = \ln Z$

$$\Rightarrow e^{\beta P V} = Z \quad \Rightarrow \quad e^{\frac{PV}{k_B T}} = Z \quad \Rightarrow \quad e^{\bar{N}} = Z$$

where $\frac{PV}{k_B T} = \bar{N}$

$$\therefore P(N) = \frac{\left(\frac{\bar{N}\lambda^3}{V}\right)^N \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N}{e^{\bar{N}}} = \frac{1}{N!}\bar{N}^N e^{-\bar{N}} \quad \text{--- (1)} \quad \text{Poisson distribution}$$

as expected for a gas of N particles that are uncorrelated in the G.C.E

Now $\overline{\Delta N^2} = \overline{N^2} - \bar{N}^2 = k_B T \left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V}$

for an ideal gas $\bar{N} = \frac{zV}{\lambda^3} \Rightarrow \frac{\partial \bar{N}}{\partial \mu} = \frac{\partial \bar{N}}{\partial z}\frac{\partial z}{\partial \mu} = \frac{V}{\lambda^3}\beta z$

where $z = e^{\beta\mu}$

$\frac{\partial z}{\partial \mu} = \beta e^{\beta \mu} = \beta z$

$$\therefore \overline{\Delta N^2} = k_B T\left(\frac{V z \beta}{\lambda^3}\right)$$

$$= \frac{1}{\beta}\frac{V z \beta}{\lambda^3} = \frac{zV}{\lambda^3} = \frac{\bar{N}\lambda^3}{V}\frac{V}{\lambda^3} = \bar{N} \quad \text{--- (2)}$$

on the other hand $\overline{\Delta N^2}$ can be calculated using the Poisson distribution as follows

$$\overline{\Delta N^2} = \overline{N^2} - \bar{N}^2$$

$$\bar{N} = \sum_{N=0}^{\infty} N P(N) = e^{-\bar{N}} \sum \frac{N \bar{N}^N}{N!} = e^{-\bar{N}} \sum_{N=0}^{\infty} \frac{N \bar{N}^N}{N(N-1)!}$$

$$= e^{-\bar{N}} \sum_{N=1}^{\infty} \frac{\bar{N}^N}{(N-1)!}$$

can not start from $N=0$ as $(0-1)! = (-1)!$ is not defined

$$\bar{N} = e^{-\bar{N}} \sum_{N=1}^{\infty} \frac{\bar{N}^N}{(N-1)!} = \bar{N} e^{-\bar{N}} \sum_{N=1}^{\infty} \frac{\bar{N}^{N-1}}{(N-1)!} = \bar{N} e^{-\bar{N}} \underbrace{\sum_{N=0}^{\infty} \frac{\bar{N}^N}{N!}}_{e^{+\bar{N}}}$$

$$= \bar{N} e^{-\bar{N}} e^{+\bar{N}} = \bar{N}$$

and

$$\overline{N^2} = \sum_{N=0}^{\infty} N^2 p(N) = e^{-\bar{N}} \sum_{N=0}^{\infty} N^2 \frac{\bar{N}^N}{N!} = e^{-\bar{N}} \sum_{N=1}^{\infty} \frac{N^2 \bar{N}^N}{N(N-1)!}$$

$$= e^{-\bar{N}} \sum_{N=1}^{\infty} \frac{N \bar{N}^N}{(N-1)!} = e^{-\bar{N}} \sum_{N=1}^{\infty} \frac{(N-1+1) \bar{N}^N}{(N-1)!}$$

$$= e^{-\bar{N}} \sum_{1} (N-1) \frac{\bar{N}^N}{(N-1)!} + e^{-\bar{N}} \sum_{1} \frac{\bar{N}^N}{(N-1)!}$$

$$= e^{-\bar{N}} \sum_{N=2}^{\infty} \frac{(N-1) \bar{N}^N}{(N-1)(N-2)!} + \bar{N} e^{-\bar{N}} \underbrace{\sum_{N=0} \frac{\bar{N}^N}{N!}}_{e^{+\bar{N}}}$$

can not start from 1

$$= e^{-\bar{N}} \sum_{N=2} \frac{\bar{N}^N}{(N-2)!} + \bar{N} e^{-\bar{N}} e^{+\bar{N}} = \bar{N}^2 e^{-\bar{N}} \sum_{N=2} \frac{\bar{N}^{N-2}}{(N-2)!} + \bar{N}$$

$$= \bar{N}^2 e^{-\bar{N}} \underbrace{\sum_{N=0}^{\infty} \frac{\bar{N}^N}{N!}}_{e^{+\bar{N}}} + \bar{N} = \bar{N}^2 + \bar{N}$$

$$\Rightarrow \overline{\Delta N^2} = \overline{N^2} - \bar{N}^2 = (\cancel{\bar{N}^2} + \bar{N}) - \cancel{\bar{N}^2} = \bar{N} \quad \text{--- (3)}$$

same result of (2)

④ <u>Pathria 4.12</u>

starting from $\bar{N} = \sum_{r,s} N_r e^{-\alpha N_r - \beta E_s} \Big/ \sum_{r,s} e^{-\alpha N_r - \beta E_s}$, we have

$$\left(\frac{\partial \bar{N}}{\partial \beta}\right)_{\alpha,V} = \sum_{r,s} N_r (-E_s) e^{-\alpha N_r - \beta E_s} \sum_{r,s} e^{-\alpha N_r - \beta E_s} \Big/ \left(\sum_{r,s} e^{-\alpha N_r - \beta E_s}\right)^2$$

$$- \sum_{r,s} N_r e^{-\alpha N_r - \beta E_s} \sum_{r,s} (-E_s) e^{-\alpha N_r - \beta E_s} \Big/ \left(\sum_{r,s} e^{-\alpha N_r - \beta E_s}\right)^2$$

$$= -\overline{NE} + \bar{N}\bar{E}$$

also $\left(\frac{\partial \bar{N}}{\partial \beta}\right) = -k_B T^2 \left(\frac{\partial \bar{N}}{\partial T}\right)$ when $\frac{\partial}{\partial \beta} = -k_B T^2 \frac{\partial}{\partial T}$

now from pathria 4.5.12, we have $\left(\frac{\partial N}{\partial T}\right)_{z,V} = \frac{1}{T}\left(\frac{\partial E}{\partial \mu}\right)_{T,V}$

so $\left(\frac{\partial \bar{N}}{\partial \beta}\right) = -k_B T^2 \frac{1}{T}\left(\frac{\partial E}{\partial \mu}\right)_{T,V} = -k_B T \left(\frac{\partial E}{\partial \mu}\right)_{T,V}$

$$= -k_B T \left(\frac{\partial E}{\partial \bar{N}}\right)_{T,V} \underbrace{\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V}}$$ chain rule

using pathria 4.5.3 $\overline{\Delta N^2} = k_B T \left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V}$

$$= -k_B T \left(\frac{\partial E}{\partial \bar{N}}\right)_{T,V} \frac{\overline{\Delta N^2}}{k_B T} = -\left(\frac{\partial E}{\partial \bar{N}}\right)_{T,V} \overline{\Delta N^2}$$

Q.E.D

(5)

$$\mathcal{Z} = \sum_{r,s} e^{-\alpha N_r - \beta E_s} = \sum_{N_r=0}^{\infty} z^N \underbrace{\sum_s e^{-\beta E_s}}_{Q_{N_r}}$$

$$= \sum_{N_r=0}^{\infty} z^{N_r} Q_{N_r}$$; let us replace N_r by N

$$= \sum_{N=0}^{\infty} z^N Q_N$$

for an ideal gas $Q_N = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N$

$$\Rightarrow \mathcal{Z} = \sum_{N=0}^{\infty} z^N \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N = \sum_{N=0}^{\infty} \frac{1}{N!}\left(\frac{zV}{\lambda^3}\right)^N$$

$$= \exp\left(\frac{zV}{\lambda^3}\right) = \exp\left(e^{\beta\mu}\frac{V}{\lambda^3}\right)$$; where $z = e^{\beta\mu}$

Q.E.D