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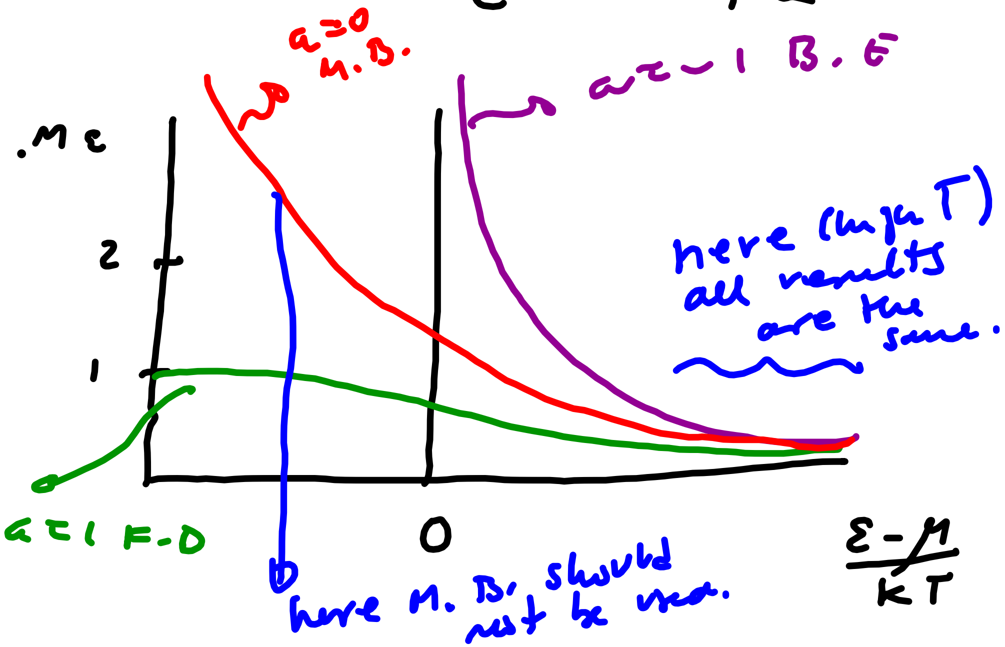
Statistics of the occupation numbers.

$$\langle n_\varepsilon \rangle = \frac{1}{e^{(\varepsilon-\mu)/kT} + a}$$

$a = -1$ B.E

$a = 1$ F.D

$a = 0$ M.B



B.E:

$\varepsilon - \mu \geq 0$

$\therefore \varepsilon \geq \mu$

If $\varepsilon_0 = 0$ it means that

$\mu \leq 0$.

If $\langle n_\varepsilon \rangle \ll 1 \ \forall \ \varepsilon \Rightarrow g_{MB}\{n_\varepsilon\} = \prod_\varepsilon \frac{1}{(n_\varepsilon)!} \approx 1$

Then in the classical limit $\frac{\varepsilon - \mu}{kT}$ is very large $\therefore$ μ is negative and large.

$$z = e^{\mu/kT} \ll 1$$

For ideal gas $N = zVf(T) = zV\left(\frac{2\pi m kT}{h^2}\right)^{3/2}$

$$= \frac{V}{\lambda^3} z$$

$\therefore$ $z = \frac{N}{V}\lambda^3 \ll 1$ condition for validity of M-B.

Fluctuations:

$$\mathcal{Z} = \sum_{N_r=0}^{\infty} \left[z^{N_r} \sum_{\{n_{\varepsilon_s}\}}' e^{-\beta \sum_{\varepsilon_s} n_{\varepsilon_s} \varepsilon_s} \right]$$

$$\langle n_{\varepsilon_r} \rangle = \frac{1}{\mathcal{Z}} \left(-\frac{1}{\beta} \frac{\partial \mathcal{Z}}{\partial \varepsilon_r} \bigg|_{z, T, \varepsilon_s \neq \varepsilon_r} \right)$$

$$\langle n_{\varepsilon_r}^2 \rangle = \frac{1}{\mathcal{Z}} \left(-\frac{1}{\beta} \frac{\partial}{\partial \varepsilon_r} \right)^2 \mathcal{Z} \bigg|_{z, T, \varepsilon_s \neq \varepsilon_r}$$

$$\langle n_{\varepsilon_r}^2\rangle - \langle n_{\varepsilon_r}\rangle^2 = \left[\left(-\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_r}\right)^2 \ln \mathcal{Z}\right]_{z,T,\varepsilon_s\neq\varepsilon_r} =$$

$$= -\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_r}\overbrace{\left[\frac{\frac{1}{\beta}\beta\sum_{N_i=0}^{\infty}\left[z^{N_i}\sum'_{\{n_{\varepsilon_s}\}} n_r e^{-\beta\sum_s n_{\varepsilon_s}\varepsilon_s}\right]}{\mathcal{Z}}\right]}^{\langle n_{\varepsilon_r}\rangle} =$$

$$= \frac{\sum_{N_i=0}^{\infty} z^{N_i}\sum'_{\{n_{\varepsilon_s}\}} n_r^2 e^{-\beta\Sigma\cdots}}{\mathcal{Z}} - \left[\frac{\sum_{N_i=0}^{\infty} z^{N_i}\sum_{\{n_{\varepsilon_s}\}} n_r e^{-\beta(\cdots)}}{\mathcal{Z}}\right]^2$$

$$\Rightarrow \langle n_{\varepsilon_r}^2\rangle - \langle n_{\varepsilon_r}\rangle^2 = -\frac{1}{\beta}\frac{\partial\langle n_{\varepsilon_r}\rangle}{\partial\varepsilon_r}\Bigg|_{z,T} \tag{1}$$

We know that

$$\langle n_\varepsilon \rangle = \frac{1}{e^{\frac{\varepsilon-\mu}{kT}} + a} \Rightarrow e^{\frac{\varepsilon-\mu}{kT}} = \frac{1}{\langle n_\varepsilon \rangle} - a \quad (3)$$

Then

$$\frac{\langle n_\varepsilon^2 \rangle - \langle n_\varepsilon \rangle^2}{\langle n_\varepsilon \rangle^2} = \left(\frac{1}{\beta} \frac{\partial}{\partial \varepsilon} \left\{ \frac{1}{\langle n_\varepsilon \rangle} \right\} \right) \overset{(2)}{=}$$

$$= \frac{1}{\beta} \left[- \frac{1}{\langle n_\varepsilon \rangle^2} \frac{\partial \langle n_\varepsilon \rangle}{\partial \varepsilon} \right] \overset{(1)}{=} \frac{1}{\langle n_\varepsilon \rangle^2} \left[\langle n_\varepsilon^2 \rangle - \langle n_\varepsilon \rangle^2 \right]$$

$$\overset{(2),(3)}{=} \frac{1}{\beta} \frac{\partial}{\partial \varepsilon} \left(e^{\frac{\varepsilon-\mu}{kT}} + a \right) = \frac{1}{\cancel{\beta}} \frac{1}{\cancel{kT}} e^{\frac{\varepsilon-\mu}{kT}} \overset{(3)}{=} \frac{1}{\langle n_\varepsilon \rangle} - a$$

$$\therefore \quad \frac{(\Delta n_\varepsilon)^2}{\langle n_\varepsilon \rangle^2} = \begin{cases} \dfrac{1}{\langle n_\varepsilon \rangle} + 1 & \text{B.E. (larger than "normal").} \\ \dfrac{1}{\langle n_\varepsilon \rangle} & \text{M.B. ("normal" relative fluctuations.} \\ \dfrac{1}{\langle n_\varepsilon \rangle} - 1 & \text{F.D. (smaller than "normal" go to zero when } \langle n_\varepsilon \rangle \to 1. \end{cases}$$

Kinetic theory.

$$q = \frac{PV}{kT} = \frac{1}{a} \sum_{\varepsilon_s} \ln\left(1 + az e^{-\beta \varepsilon_s}\right)$$

or $$P = \frac{kT}{aV} \sum_{\varepsilon_s} \ln\left(1 + az e^{-\beta \varepsilon_s}\right) \longrightarrow$$

go to an integral since $\Delta k \ll 1$

$$\frac{kT}{aV} \int \ln\left(1 + az e^{-\beta \varepsilon_s(p)}\right) \underbrace{g(p)\,dp}_{\frac{V}{h^3} \underbrace{4\pi}\, p^2 dp \;(2.4.5)} =$$

$$\int d\Omega$$

$$= \frac{\cancel{V} kT}{a h^3} \frac{4\pi}{\cancel{V}} \int_0^\infty \underbrace{p^2}_{u'} \underbrace{\ln\left(1 + az e^{-\beta \varepsilon_s(p)}\right)}_{v} dp =$$

integrating by parts.

$$= \frac{kT\,4\pi}{a h^3}\left[\underbrace{\frac{p^3}{3} \ln\left(1 + a z e^{-\beta \varepsilon(p)}\right)\Big|_0^\infty}_{0} + \right.$$

$$\left. + \int_0^\infty \frac{p^3}{3} \frac{a z e^{-\beta \varepsilon(p)}}{1 + a z e^{-\beta \varepsilon(p)}} \beta \frac{d\varepsilon}{dp}\, dp \right] =$$

$$= \frac{\cancel{kT}\,4\pi}{\cancel{a} h^3} \frac{\cancel{a}}{3\cancel{kT}} \int_0^\infty \frac{p}{z^{-1} e^{\beta \varepsilon(p)} + a} \frac{d\varepsilon}{dp} p^2\, dp =$$

$$= \frac{4\pi}{3h^3} \int_0^\infty \frac{p\, d\varepsilon/dp}{z^{-1} e^{\beta \varepsilon(p)} + a} p^2\, dp = P \qquad 4$$

Notice that

$$N = \sum_{\varepsilon} \langle n_\varepsilon \rangle = \sum_{\varepsilon} \frac{1}{z^{-1} e^{\beta \varepsilon(p)} + a} \xrightarrow[(2.4.5)]{}$$

$$\rightarrow \frac{4\pi V}{h^3} \int_0^\infty \frac{p^2 \, dp}{z^{-1} e^{\beta \varepsilon(p)} + a}$$

$$\therefore \quad \frac{4\pi}{h^3} = \frac{N}{V} \frac{1}{\int_0^\infty \frac{p^2 \, dp}{z^{-1} e^{\beta \varepsilon(p)} + a}} \qquad (5)$$

Replacing (5) in (4) we obtain:

$$P = \frac{N}{3V} \frac{\int_0^\infty \frac{p\, d\varepsilon/dp}{z^{-1} e^{\beta \varepsilon(p)} + a} p^2\, dp}{\int_0^\infty \frac{p^2\, dp}{z^{-1} e^{\beta\varepsilon(p)} + a}} = \frac{N}{3V} \left\langle p \frac{d\varepsilon}{dp} \right\rangle$$

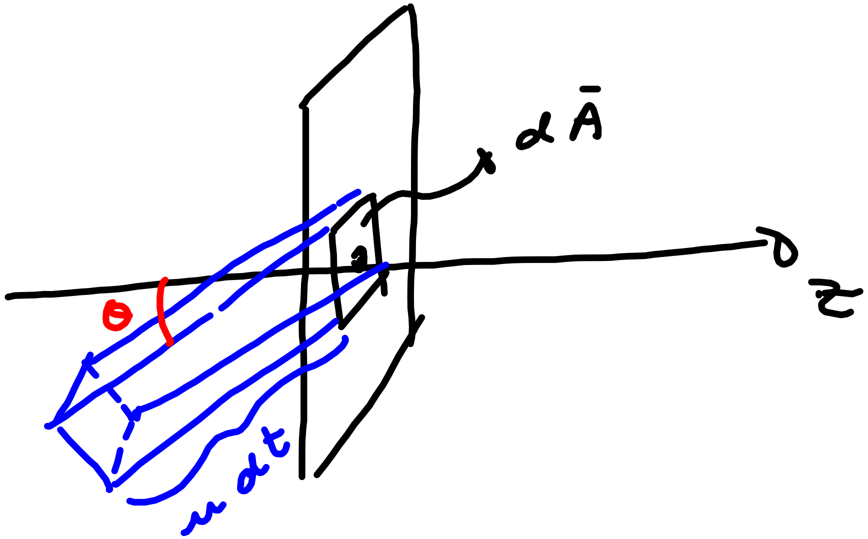
$$= \frac{1}{3} n \left\langle p \frac{d\varepsilon}{dp} \right\rangle = \frac{1}{3} n \langle p u \rangle$$

$$\varepsilon = \frac{p^2}{2m} \Rightarrow \frac{d\varepsilon}{dp} = \frac{2p}{2m} = \frac{p}{m} = \frac{mu}{m} = u$$ (speed of the molecule)

If $\varepsilon \propto p^s \Rightarrow \frac{\partial \varepsilon}{\partial p} \propto s p^{s-1} \therefore p \frac{d\varepsilon}{dp} = s\varepsilon$

$$\therefore P = \frac{1}{3} n s \langle \varepsilon \rangle = \frac{s}{3} \frac{E}{V} = \begin{cases} \frac{E}{3V} & \text{if } s=1 \text{ (photons)} \\ \frac{2}{3}\frac{E}{V} & \text{if } s=2 \text{ (ideal gas)} \end{cases}$$

More explicit calculation for the pressure:



$n\,f(\bar{u})\,d\bar{u}$ = # of particles per unit volume tha have velocity between $(\bar{u}, \bar{u}+d\bar{u})$.

$$\int_{\forall u} f(\bar{u})\,d\bar{u} = 4\pi \int_0^\infty f(u)\,u^2\,du = 1$$

since $\int_{\forall u} n\,f(\bar{u})\,d\bar{u} = n = \frac{N}{V} \Rightarrow$

How many particles with velocity in $(\bar{u}, \bar{u} + d\bar{u})$ reach ΔA during dt? All the particles inside $dV = d\bar{A} \cdot \bar{u}\, dt$

$$\therefore \quad N_{\bar{u}} = \bar{u} \cdot d\bar{A}\, dt\, n\, f(\bar{u})\, d\bar{u}$$

$\Delta p_z = 2 p_z$ (ellastic collision of the molecules with the wall $p_z \longrightarrow -p_z$).

Total normal momentum transpored to the wall per unit area and unit time is the pressure.

$$P = 2\int_{\bar{u}} p_z(\bar{u})\, N_{\bar{u}}\, d\bar{u} =$$

$$2m \int_{-\infty}^{\infty} du_x \int_{-\infty}^{\infty} du_y \int_{0}^{\infty} du_z\, p_z u_z f(\bar{u}) =$$

$\rightarrow$ only positive v_z allows to hit the wall

$$= 2m \int_{-\infty}^{\infty} du_x \int_{-\infty}^{\infty} du_y \frac{1}{2}\int_{-\infty}^{\infty} du_z\, \underbrace{p_z u_z}_{\text{even}} f(u) =$$

even function

$$= m \int_{\text{all } \bar{u}} p_z u_z f(u)\, d^3u = m \langle p_z v_z \rangle =$$

$$= m \langle p u \cos^2\theta \rangle \qquad 6$$

$$\langle pu\cos^2\theta\rangle = \frac{\int_0^\infty f(u)\, pu\, u^2\,du \underbrace{\int_0^\pi \cos^2\theta \sin\theta\, d\theta}_{2/3} \underbrace{\int_0^{2\pi} d\varphi}_{2\pi}}{\underbrace{\int_0^\infty f(u)\, u^2\,du \underbrace{\int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\varphi}_{4\pi}}_{1}}$$

$$= \frac{\int_0^\infty f(u)\, pu\, u^2\,du\, \frac{\cancel{2}}{3}\, \cancel{2}\cancel{\pi}}{\cancel{4}\cancel{\pi} \int_0^\infty f(u)\, u^2\,du} =$$

$$= \frac{1}{3}\, \frac{\int_0^\infty f(u)\, pu\, u^2\,du}{\int_0^\infty f(u)\, u^2\,du} = \frac{1}{3}\langle pu\rangle \qquad (7)$$

Plugging (7) in (6):

$P = \frac{n}{3}\langle pu \rangle$ as we found before.

<u>Effusion:</u> particles escaping through a hole of area dA.

$$\overset{\nearrow \text{rate}}{R} = n\int_{-\infty}^{\infty} du_x \int_{-\infty}^{\infty} du_y \int_{0}^{\infty} du_z \, u_z f(u) =$$

$$= n\int_0^{2\pi} d\varphi \underbrace{\int_0^{\pi/2 \, (u_z>0)} u\cos\theta \sin\theta \, d\theta}_{u/2} \int_0^{\infty} u^2 f(u)\, du =$$

$$= m\pi \int_0^\infty u^3 f(u)\, du$$

Since $\int_0^\infty f(u)\, 4\pi u^2\, du = 1$

$$\langle u \rangle = \frac{4\pi \int_0^\infty u\, f(u)\, u^2\, du}{\underbrace{4\pi \int f(u)\, u^2\, du}_{1}} \quad \therefore \quad \int_0^\infty u^3 f(u)\, du = \frac{\langle u \rangle}{4\pi}$$

$$\therefore \; R = \frac{m\pi \langle u \rangle}{4\pi} = \frac{m \langle u \rangle}{4}.$$