- Last time, starting from the Schrödinger equation of non-relativistic Quantum Mechanics, we derived (for $|\Delta\varepsilon| \gg \tau$) :-

(1.1) $$\boxed{Z_1(1\text{-}d) = \sqrt{\frac{m\tau}{2\pi\hbar^2}}\, L}$$

- For our (non-relativistic) molecules in 3-d, each direction is independent; (also, kinetic energy is additive) $\Rightarrow$

(1.2) $$\Rightarrow \quad \boxed{Z_1(3\text{-}d) = \left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2} V}$$

Dimensions, & Quantum Concentration.

Consider $Z_1(1\text{-}d) = L\sqrt{\frac{m\tau}{2\pi\hbar^2}}$

This is a pure number. (recall: $Z = \sum_s e^{-\varepsilon_s/\tau}$)

$\Rightarrow \sqrt{\frac{m\tau}{2\pi\hbar^2}}$ has dimensions of inverse length.

(1.3) Let's define $\boxed{\lambda_* \equiv \sqrt{\frac{2\pi\hbar^2}{m\tau}}} = \lambda_*(\tau)$.

(1.4)
$$[\hbar] = J.s = (kg\, m^2 s^{-2})s = kg\, m^2 s^{-1} = (kg\, m)(m s^{-1})$$
$$[k_B] = J.K^{-1} = kg\, m^2 s^{-2} K^{-1}$$
$$[m] = kg$$
$$[T] = K$$

$$\Rightarrow [\lambda_*] = \{(kg\, m^2 s^{-1})^2\} / \{(kg)(kg\, m^2 s^{-2} K^{-1})(K)\}^{1/2}$$
$$= (kg)^0 (m)^1 (s)^0 (K)^0 \quad ✓ ☺$$

Now consider

(1.5) $$\lambda_* = \sqrt{\frac{2\pi\hbar^2}{m\tau}} \sim \frac{h}{\sqrt{m\tau}} \qquad ([\lambda_*] = m)$$

(2.1) • de Broglie wavelength $\boxed{\lambda_{deB} = \frac{h}{p}}$ $\circledast$

• Here, momentum comes from thermal/kinetic side:

(2.2) $\langle \frac{1}{2} m v^2 \rangle \sim (\text{energy}) \sim \tau$ ← (only energy scale available, thermally)

so $m \langle v^2 \rangle \sim \tau$

(2.3) so $m\sqrt{\langle v^2 \rangle} \sim \sqrt{m\tau} \sim p(\text{thermal})$

(2.4) i.e. $\lambda_{deB}(\text{thermal}) \sim \frac{h}{\sqrt{m\tau}} \sim \lambda_*$

(2.5) ⇒ "Quantum concentration" $\boxed{n_Q := \frac{1}{\lambda_*^3}}$

$\Leftrightarrow \frac{1 \text{ particle}}{(\text{box side} = \lambda_{deB}^{(\text{thermal})})}$

Exercise: check that, for a regular box of side 10cm at 300 K, the condition $|n| \ll n_Q$ is met. (I get ~10^{-6} → fine ✓)

$n_Q = n_* = \frac{1}{\lambda_*^3}$.

(2.6) • When $\left|\frac{n}{n_Q}\right| \ll 1$ ⇒ "classical régime"

(2.7) • Non-interacting molecules ⇒ "ideal gas"

N >> 1 molecules of ideal gas

Non-interacting molecules: two steps to understanding finding of Z_N:

(2.8) (a) independence
(b) indistinguishability!

(3.1) $$\Rightarrow \boxed{Z_N(3\text{-}d) = \frac{[Z_1(3\text{-}d)]^N}{N!}}$$ Ideal Gas Partition Fn in 3-d

- (3.2) ✪ $$\boxed{Z_N(3\text{-}d) = \frac{1}{N!}\left(\sqrt{\frac{m\tau}{2\pi\hbar^2}}\,L\right)^{3N}}$$

- Let's find $F = -\tau \log Z = +\tau \log(N!) - 3\frac{N\tau}{2}\log\left(\frac{m\tau}{2\pi\hbar^2}\right) - N\tau\log V$

- Then $U = \frac{\tau^2}{Z}\frac{\partial Z}{\partial \tau}$

$$= \tau^2 \frac{\partial \log Z}{\partial \tau} = \tau^2 \frac{\partial}{\partial \tau}\left\{\log\left(\tau^{3N/2}\cdot(\text{etc})\right)\right\} = \frac{3}{2}N\tau$$

(3.3) i.e. $\boxed{U = \frac{3}{2}N\tau}$ Ideal Gas energy

- (3.4) Heat capacity $\boxed{C_V = \left(\frac{\partial U}{\partial \tau}\right)_{V,N} = \frac{3}{2}N}$

- (3.5) pressure $p = -\left(\frac{\partial F}{\partial V}\right)_{\tau,N} = +\frac{\tau N}{V} \Rightarrow \boxed{pV = N\tau}$ Yeehaa! Ideal Gas equation

- entropy $\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_{V,N}$, and

$$F = -\tau \log\left\{\frac{1}{N!}V^N\left(\frac{m\tau}{2\pi\hbar^2}\right)^{\frac{3N}{2}}\right\}$$

$$\Rightarrow -\left(\frac{\partial F}{\partial \tau}\right)_V = +\log\left\{\frac{1}{N!}V^N\left(\frac{m\tau}{2\pi\hbar^2}\right)^{\frac{3N}{2}}\right\} + \frac{\tau}{\tau}\frac{3N}{2}$$

$$= (-N\log N + N) + (N\log V) + \frac{3N}{2} + \frac{3N}{2}\log\left(\frac{m\tau}{2\pi\hbar^2}\right)$$

$$= \frac{5N}{2} + N\log\left(\frac{V}{N}\left(\frac{m\tau}{2\pi\hbar^2}\right)^{\frac{3}{2}}\right)$$

$n := N/V$

(3.6) $$\boxed{\sigma = N\left[\frac{5}{2} + \log\left(\frac{n_Q}{n}\right)\right]}$$ (Ideal Gas entropy) (Sackur-Tetrode eqn)

N.B.! valid for ideal monatomic ideal gas
We will do diatomics & polyatomics soon ☺