For N particles

Assume all ni dependent (noninteracting, & gas classical)

If all N particles of gas were distinguishable, we'd obtain Z_1^N for Z_N.

=BUT= they're not distinguishable ⇒ we overcounted.

By how much did we overcount?

For a fixed set of energy levels, there are N! ways of arranging the system.

$$\Rightarrow \boxed{Z_N = \frac{Z_1^N}{N!}}$$

Using our result for Z_1, we have

$$Z_N = \frac{1}{N!} V^N \left(\frac{M\tau}{2\pi\hbar^2}\right)^{\frac{3N}{2}}$$

Now we will find
- the energy U
- the Helmholtz free energy F
- the pressure p

and we use this fundamental information to DERIVE the ideal gas law - from first principles!!

a) By how much did we overcount?

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* Let's find some quantities of thermodynamic interest.

Average energy U.

$$U = \tau^2 \frac{\partial \log Z_N}{\partial \tau}$$

What's $\log Z_N$?

$$\log Z_N = \log\left(\frac{Z_1^N}{N!}\right) = N \log Z_1 - \log N!$$

$$\cong N \log Z_1 - N \log N + N \quad \text{using Stirling's approx}$$

($N \log Z_1$: depends on τ; $-N \log N + N$: doesn't)

So $$U = \tau^2 \frac{\partial (N \log Z_1)}{\partial \tau} = \frac{\tau^2 N}{Z_1} \frac{\partial Z_1}{\partial \tau}$$

Now, $Z_1 \propto \tau^{3/2}$

So $\frac{1}{Z_1}\frac{\partial Z_1}{\partial \tau} = \frac{3}{2\tau}$

and so

$$U = \tau^2 N\left(\frac{3}{2\tau}\right) \quad \text{or} \quad \boxed{U = \frac{3}{2}N\tau}$$

- Specific heat @ constant V

$$C_V \equiv \left(\frac{\partial U}{\partial \tau}\right)_V$$

↑ (physically this results in no change to ε levels!)

i.e. $\boxed{C_V = \frac{3}{2}N}$ The $\frac{3}{2}$ came directly from the $\tau^{3/2}$ dependence of Z_1.

- Pressure

$$P = -\left(\frac{\partial F}{\partial V}\right)_\tau \quad \text{with} \quad F = -\tau \log Z_N$$

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

$$= -\tau N \log V + (V\text{-independent terms}).$$

Therefore,

$$p = -\left(\frac{\partial F}{\partial V}\right)_\tau$$

$$= \tau N \left(\frac{1}{V}\right)$$

and so $\boxed{pV = N\tau = N k_B T}$

Woohoo! We derived the ideal gas law (bulk thermo) from fundamental stat mech.



- Entropy

$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V$ (or we can use $F = U - \tau\sigma$ $\Rightarrow \sigma = \left(\frac{U-F}{\tau}\right)$)

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

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

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

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

& $\Rightarrow \boxed{\sigma = N\left[\frac{5}{2} + \log\left(\frac{n_Q}{n}\right)\right]}$ since $n = \frac{N}{V}$ for N particles

"Sackur-Tetrode" eqn for ideal monatomic (structureless) gas

Photon Gas

The big difference here is that photons have ZERO MASS, and are always relativistic.

We'll do this in two steps;

(i) find the partition function for a single electromagnetic mode of frequency ω

(ii) work out the possible ω's for photons in boxes and sum over all possible modes to get the final answer.

(i) A single mode

Imagine there's a mode of frequency ω.

Then a photon @ ω has energy

$$\varepsilon = \hbar\omega$$

If there are s photons in this mode

then $$\varepsilon_s = s\hbar\omega.$$

(we ignore here the zero-point energy $\frac{1}{2}\hbar\omega$ because it would give only a constant factor in Z & we ignore it.)

Note: This system has the same possible energies as a harmonic oscillator, but the basic idea is very different.

Here we're talking about s photons having $\varepsilon = \hbar\omega$ where s photons are electromagnetic "waves" whereas the SHO is a single oscillator that can be in one of many possible energy levels!

- Partition function of mode, frequency ω

$$Z = \sum_{s=0}^{\infty} e^{-\varepsilon_s/\tau}$$
$$= \sum_{s=0}^{\infty} e^{-s\hbar\omega/\tau}$$

Let $x = \hbar\omega/\tau$. Then $Z = \sum_{s=0}^{\infty} e^{-sx} = 1 + e^{-x} + e^{-2x} + \cdots$

Note that $\tau \in [0, \infty)$ so $e^{-x} \in [0, 1)$

Indeed, e^{-x} is always less than 1.

$$\Rightarrow \quad Z = \frac{1}{1 - e^{-x}} \quad \text{i.e.} \quad \boxed{Z = \frac{1}{1 - e^{-\hbar\omega/\tau}}}$$

Let's find out how probable it is to have s photons at temperature $\tau \longrightarrow$

$$P(s) = \frac{e^{-\varepsilon}}{Z}$$

$$= \frac{e^{-s(\hbar\omega/\tau)}}{Z}$$

- **Average photon # s**

$$\langle s \rangle = \sum_{s=0}^{\infty} s\, P(s)$$

$$= \frac{1}{Z} \sum_{s=0}^{\infty} s\, e^{-s(\hbar\omega/\tau)}$$

$$= \frac{1}{Z} \frac{-\partial}{\partial(\hbar\omega/\tau)} \underbrace{\sum_{s=0}^{\infty} e^{-s(\hbar\omega/\tau)}}_{Z}$$

$$= -\frac{1}{Z} \frac{\partial Z}{\partial(\hbar\omega/\tau)}$$

Now $Z = \dfrac{1}{1 - e^{-(\hbar\omega/\tau)}}$

So $\dfrac{\partial Z}{\partial\left(\frac{\hbar\omega}{\tau}\right)} = \dfrac{-1}{\left(1 - e^{-(\hbar\omega/\tau)}\right)^2} \cdot e^{-(\hbar\omega/\tau)}$.

$$\Rightarrow \boxed{\langle s \rangle = \frac{e^{-(\hbar\omega/\tau)}}{1 - e^{-(\hbar\omega/\tau)}} = \frac{1}{e^{\hbar\omega/\tau} - 1}}$$

"Planck distribution function"

- Average Energy

$\langle \mathcal{E} \rangle = \langle s \rangle \hbar\omega$

$\langle s \rangle$: average photon #; $\hbar\omega$: energy of 1 photon

So $\langle \mathcal{E} \rangle = \dfrac{\hbar\omega}{e^{\hbar\omega/\tau} - 1}$

What happens at <u>high τ</u>?

$\frac{\hbar\omega}{\tau}$ becomes small, so $e^{\hbar\omega/\tau} - 1$

$\cong \left(1 + \frac{\hbar\omega}{\tau} + \mathcal{O}\left(\frac{\hbar\omega}{\tau}\right)^2\right) - 1$

$\cong \frac{\hbar\omega}{\tau}$

$\Rightarrow \langle \mathcal{E} \rangle \underset{\tau \to \infty}{\longrightarrow} \tau$

At high τ, s (# photons) $\to \infty$

This is the limit where photons "blur" and we safely talk about a <u>classical electromagnetic field</u>.