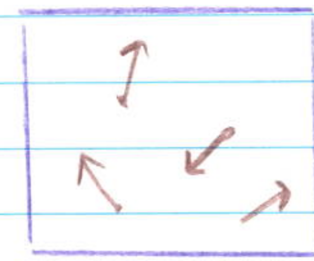
Ex 2 The Ideal Gas Again

- Then we have N particles in a box at temperature T and Volume V



$$E = \frac{\vec{p}_1^{\,2}}{2m} + \cdots\cdots + \frac{p_N^2}{2m}$$

$$= \varepsilon_1 + \cdots\cdots + \varepsilon_N$$

- The partition function is

$$Z_{TOT} = \frac{1}{N!} \int \frac{d^3\vec{r}_1\, d^3\vec{p}_1}{h^3} \cdots\cdots \frac{d^3\vec{r}_N\, d^3\vec{p}_N}{h^3}\; e^{-E/kT}$$

Since the energy is a sum the integrals factorize

$$Z_{TOT} = \frac{1}{N!} \left[\int \frac{d^3\vec{r}_1\, d^3\vec{p}_1}{h^3}\; e^{-\varepsilon_1/kT} \right]^N$$

$$= \frac{1}{N!} Z_1^N$$

The particles are identical / indistinguishable. This "extra" factor is because an exchange of particles does not change the state.

with

$$Z_1 = \int \frac{d^3r\, d^3p}{h^3}\; e^{-\varepsilon/kT}$$

- Now Z_1 can be evaluated as follows

$$Z_1 = \frac{V}{h^3}\int dp_x\, dp_y\, dp_z\, e^{-(p_x^2+p_y^2+p_z^2)/2mkT}$$

$$Z_1 = \frac{V}{h^3}(2\pi mkT)^{3/2} = \boxed{\frac{V}{\lambda^3} = Z_1}$$

In this we integrated over p_x, p_y, and p_z separately. Each integral is a gaussian form with width $\sigma^2 = mkT$.
The quantity

$$\boxed{\lambda \equiv \frac{h}{(2\pi mkT)^{1/2}}}$$

is known as the thermal debroglie wavelength. It is of order an angstrom and was discussed throughout the course. It is short compared to the typical spacing $l_0 \equiv \left(\frac{V}{N}\right.$

- Now we will determine the free energy of the system, using $F = -kT\ln Z$

First note

$$Z = \frac{Z_1^N}{N!} \simeq \left(\frac{eZ_1}{N}\right)^N$$ using the Sterling approximation $N! = \left(\frac{N}{e}\right)^N$

Now define $n \equiv N/V$ and $V_N = V/N$ so

$$F = -kT \ln Z$$

$$F = -NkT \ln\left(\frac{eV}{N\lambda^3}\right) = -NkT\left[\ln\left(\frac{V_N}{\lambda^3}\right) + 1\right]$$

- The Free energy as a function of Temperature and volume determines everything using thermodynamics

$$dF = -S\,dT - p\,dV$$

- From its dependence on volume:

$$p = -\frac{\partial F}{\partial V} = -\frac{\partial}{\partial V}\left[-NkT\left(\ln V + \text{const}\right)\right]$$

$$\boxed{p = \frac{NkT}{V}}$$

- Thus we have recovered the ideal gas law. The entropy follows by differentiation too

$$S = -\frac{\partial F}{\partial T} = -\frac{\partial}{\partial T}\left(-NkT\left[\ln\left(V_N/\lambda_{th}^3\right) + 1\right]\right)$$

Since $\lambda_{th} \propto T^{-1/2}$ we find

$$S = Nk\left[\ln\left(V_N/\lambda_{th}^3\right) + 1\right] + NkT \frac{\partial}{\partial T}\left(\ln T^{3/2} + \text{const}\right)$$

So Finally we find

$$\boxed{S = Nk\left(\ln\left(V_N/\lambda_{th}^3\right) + \frac{5}{2}\right)}$$

The entropy per particle is

$$\boxed{\frac{S}{Nk} = \ln\left(V_N/\lambda_{th}^3\right) + \frac{5}{2}}$$

This is the Sackur-Tetrode equation again. Now we derived it using the canonical ensemble. See discussion below.

- Finally note

$$F = U - TS \quad \text{so} \quad U = F + TS$$

Thus

$$U = -NkT\left(\ln\left(V_N/\lambda_{th}^3\right) + 1\right) + NkT\left(\ln\left(V_N/\lambda^3\right) + \frac{5}{2}\right)$$

$$\boxed{U = \frac{3}{2}NkT}$$

- An Alternate method starts with $\ln Z$

$$\ln Z = N \ln(e Z_1 / N)$$

only Z_1 depends on $\beta \equiv 1/kT$

Then

$$U = -N \frac{\partial}{\partial \beta}(\ln Z_1 + \text{const})$$

Now $Z_1 = \frac{V}{\lambda^3} \propto \beta^{-3/2}$ since $\lambda \propto T^{-1/2}$

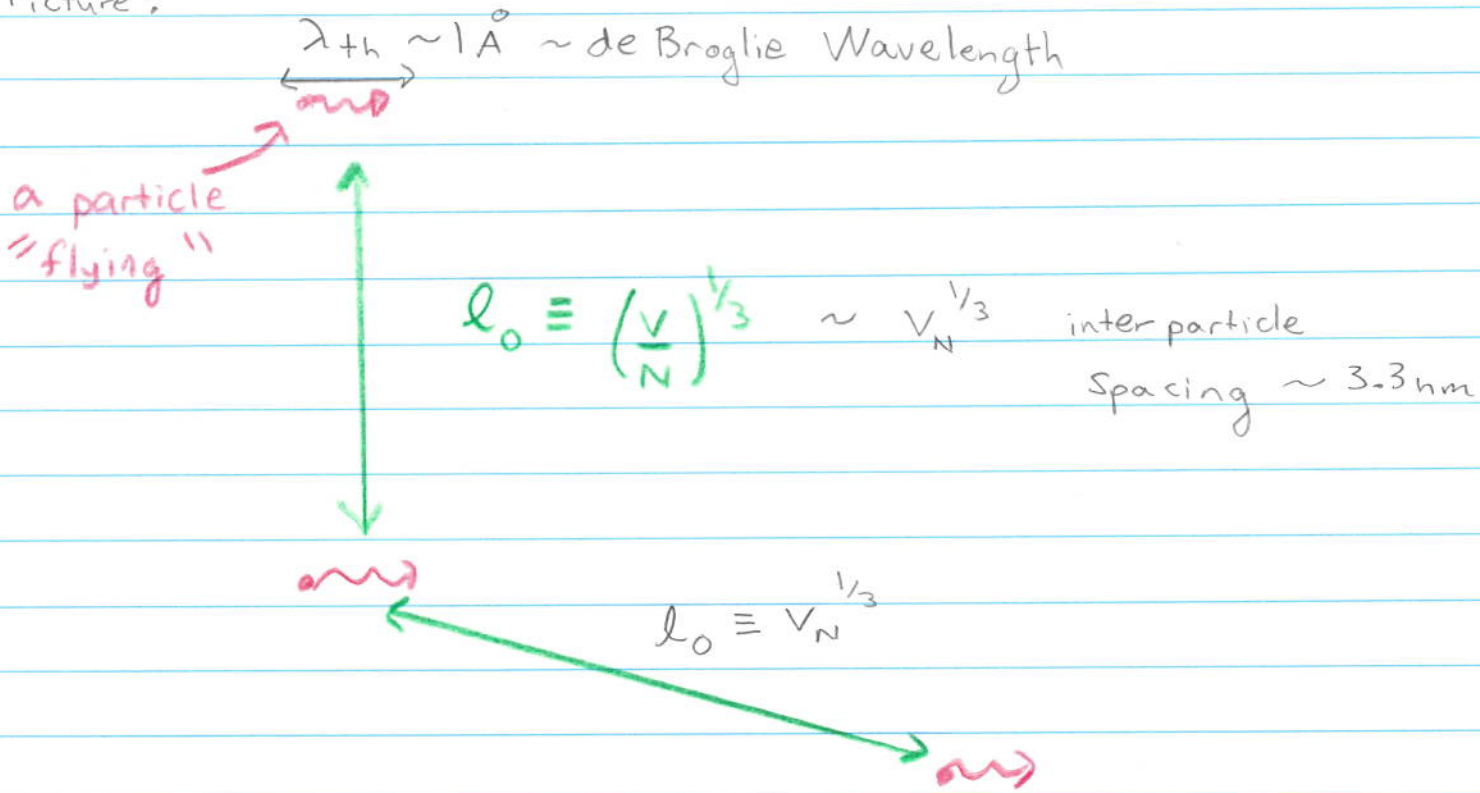
So

$$U = -N \frac{\partial}{\partial \beta}(\ln \beta^{-3/2} + \text{const})$$

$$\boxed{U = \frac{3}{2}\frac{N}{\beta} = \frac{3}{2} NkT}$$ ← once again

Discussion of Sackur Tetrode Eqn

Picture:



- The entropy per particle in units of k_B, is of order of the log of the typical phase space volume per particle in units of h

$$\boxed{\frac{\text{phase space per particle}}{h^3} \sim \frac{v_N\, p_{typ}^3}{h^3} \sim \frac{v_N\,(mkT)^{3/2}}{h^3}}$$

We used $p_{th}^2/2m \sim kT$. Now $(mkT)^{3/2}/h^3 \sim 1/\lambda^3$

So $$\boxed{\frac{S}{Nk_B} \sim \ln\left(\frac{v_N}{\lambda^3}\right) \sim \ln\left(\frac{\ell_0^3}{\lambda^3}\right) \sim 10}$$

So the entropy per particle is about 10.

We are estimating $S/Nk_B \sim \ln(v_N/\lambda^3)$ neglecting the 5/2 in the Sackur-Tetrode formula. The 5/2 is a quantum correction to the classical part. The classical part is the log of the phase space per particle.