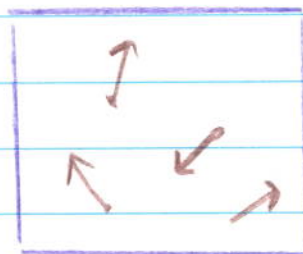## Ex 2    The Ideal Gas Again

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

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

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

- The partition function is

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

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

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

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

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 $l_o \equiv \left(\frac{V}{N}\right)$

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

First note

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

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

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

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

- 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

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

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

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

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

- An Alternate method starts with $\ln Z$

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

$\curvearrowright$ only $Z_1$ depends on $\beta = 1/kT$

Then

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

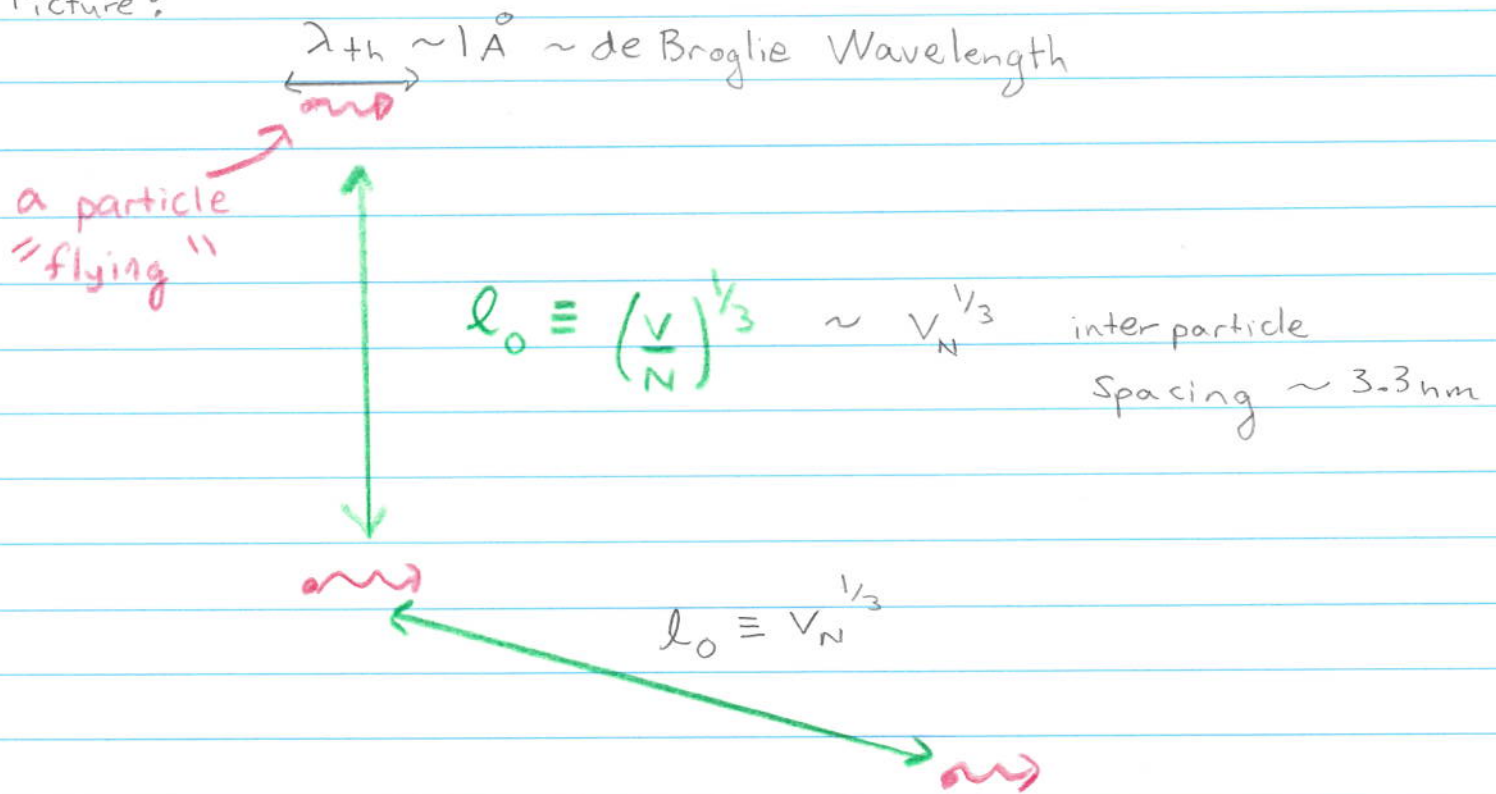Now $Z_1 = \frac{V}{\lambda^3} \propto \beta^{-3/2}$ since $\lambda \propto T^{-1/2}$

So

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

$$\boxed{u = \frac{3}{2} \frac{N}{\beta} = \frac{3}{2} NkT} \quad \leftarrow once \ again$$

Discussion of Sackur Tetrode Eqn

Picture:

$\lambda_{th} \sim 1 \overset{\circ}{A} \sim$ de Broglie Wavelength

a particle "flying"

$\ell_0 \equiv \left(\dfrac{V}{N}\right)^{1/3} \sim V_N^{1/3}$ inter-particle spacing $\sim 3.3$ nm

$\ell_0 \equiv V_N^{1/3}$

- 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 $h$

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

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

So $\qquad \dfrac{S}{Nk_B} \sim \ln\left(\dfrac{V_N}{\lambda^3}\right) \sim \ln\left(\dfrac{\ell_0^3}{\lambda^3}\right) \sim 10$

So the entropy per particle is about 10.