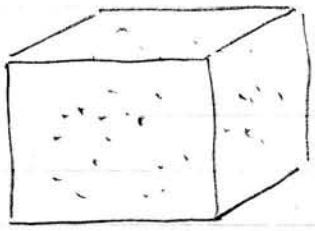
Lecture 4

Ideal gas (assume monatomic for now) – free, independent



N atoms in box of volume
$V = L_x L_y L_z$

The one tool we have (so far) is $\Omega(E)$

How do we count states?
Treat gas as particles in a box (from Quantum Mechanics)

Wavefunction for free particle

$$\Psi(r) = \frac{1}{\sqrt{V}} e^{i\bar{k}\cdot\bar{r}} e^{-i\omega t}$$

(Note that $P = |\Psi|^2 = \frac{1}{V}$ = probability of being in volume V)

$$E = \frac{p^2}{2m} = \frac{\hbar^2 |\bar{k}|^2}{2m}$$ only kinetic energy, no potential energy

Walls impose reflecting boundary conditions, so

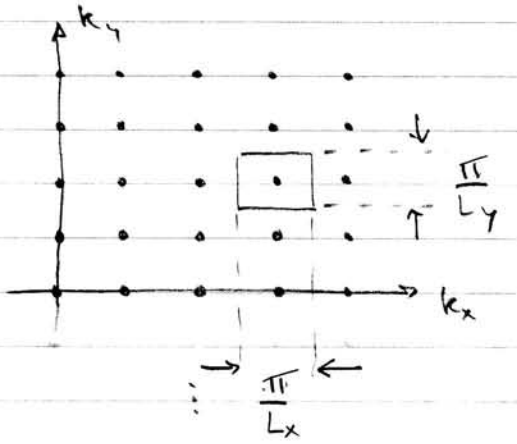
$$k_x = \frac{\pi n_x}{L_x}, \quad k_y = \frac{\pi n_y}{L_y}, \quad k_z = \frac{\pi n_z}{L_z}$$

$$n_x, n_y, n_z = 1, 2, 3 \ldots$$

Energy is <u>quantized</u>

$$E_n = \frac{\hbar^2 k^2}{2m}, \quad k^2 = k_x^2 + k_y^2 + k_z^2$$

In k-space, each quantum state is a point on a lattice



Each state occupies a volume in k-space:

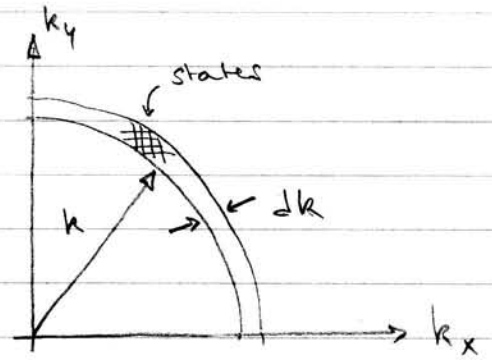
$$\frac{\pi}{L_x} \cdot \frac{\pi}{L_y} \cdot \frac{\pi}{L_z} = \frac{\pi^3}{V}$$

So in a volume $dk_x\, dk_y\, dk_z \equiv d^3k$ there are:

$$\frac{V}{\pi^3} d^3k \quad \text{states}$$

∴ To count states, we'll sum up volume in k-space and divide by volume of one state.

We want $\Omega(E)$, i.e. states with same energy $E = \frac{\hbar k^2}{2m}$
These will sit on surface of a sphere in k-space with radius $k = \sqrt{k_x^2 + k_y^2 + k_z^2}$



We need to give this some volume to count states so consider a shell in k-space with thickness dk
(Note that $k_x, k_y, k_z > 0$)

So # states with energy E, $E + dE$ is

$$\Omega_1(E, E+dE) = \frac{V}{\pi^3} V_{shell} = \frac{V}{\pi^3} \frac{4\pi}{8} k^2 dk = \frac{V}{(2\pi)^3} 4\pi k^2 dk$$

surface area of 1/8 sphere

we will consider limit where $n_x, n_y, n_z \gg 1$ so $k \gg \Delta k$
($\Delta k \sim \frac{\pi}{L}$ spacing between states)

For all practical purposes $\Delta k \to dk$

$$dE = \frac{\hbar^2 k}{m} dk \ll \frac{\hbar^2 k^2}{2m} = E$$

$$\Omega_1(E, E+dE) = \frac{V}{(2\pi)^3} 4\pi k\, dk \qquad k = \sqrt{\frac{2m}{\hbar^2}E}, \quad dk = \sqrt{\frac{2m}{\hbar^2}}\frac{dE}{2\sqrt{E}}$$

$$= \frac{V}{(2\pi)^3} 4\pi \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{\sqrt{E}}{2} dE$$

= # of states for 1 particle in V with energy in range $E, E+dE$

Now consider 2 particles

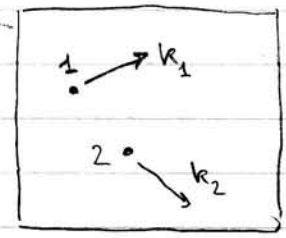
Double the # of variables: $k_{1x}, k_{1y}, k_{1z}, k_{2x}, k_{2y}, k_{2z}$

$$E = \frac{\hbar^2 k^2}{2m} \qquad k^2 = k_{1x}^2 + k_{1y}^2 + k_{1z}^2 + k_{2x}^2 + k_{2y}^2 + k_{2z}^2$$

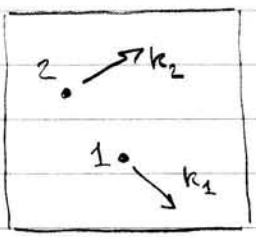
Now we have 1 quantum state per volume $\left(\frac{\pi^3}{V}\right)^2$
And shell is in $2\times 3 = 6$-dimensional k-space

$$\Omega_2(E, E+dE) = \left(\frac{V}{\pi^3}\right)^2 V_{shell}$$

Actually, this overcounts # states because particles are indistinguishable



is same state as



So we have to divide by 2

For N indistinguishable particles, divide by $N!$

$$\Omega_N(E, E+dE) = \left(\frac{V}{\pi^3}\right)^N \frac{V_{shell}}{N!}$$

where V_{shell} is a hypershell in $3\times N$-dimensional k-space with radius $k = \sqrt{\frac{2mE}{\hbar^2}}$

How do we determine V_{shell}? Use dimensional analysis:

Volume has units of k^{3N}

so: $V_{shell} \propto k^{3N-1}\,dk = g_N\, k^{3N-1}\,dk$

↑ geometrical factor $g_1 = 4\pi/8$
Let's not worry about it for now

$$\therefore \Omega_N(E, E+dE) = V^N \frac{g_N}{2N!}\left(\frac{2m}{\hbar^2}\right)^{3N/2} E^{3N/2-1}\,dE$$

Note that dE does not contribute very much. Look at entropy

$$S = k_B \ln\Omega \sim \left(\frac{3N}{2}-1\right)\ln E + \ln dE = \frac{3N}{2}\ln E + \ln\frac{dE}{E}$$

↓ ↓

when $N \sim 10^{20}$, this term is negligible ($dE \ll E$)

$$\therefore \Omega_N \sim E^{3N/2}$$

(Recall for Einstein solid $\Omega \sim E^N$
For many systems we get $\Omega \sim E^{f/2}$ where
f = # of degrees of freedom
Here for ideal gas $f = (3\text{-dimensions of } k) \times (N \text{ particles}) = 3N$

$$\Omega_N = f(N)\, V^N\, E^{3N/2}$$

Ω depends on E like Einstein solid, also on V.
If $V \uparrow$ there are more microstates available for each particle
$\therefore \Omega \sim V^N$

Consequences:

$$S = k_B \ln \Omega = k_B\left(N \ln V + \frac{3N}{2} \ln E + \ln f(N)\right)$$

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{N,V} = \frac{3N}{2}\,\frac{k_B}{E}$$

$$\therefore \quad E = \frac{3}{2} N k_B T$$

We'll derive this from Equipartition theorem later

One final note: $f(N)$ includes geometrical factor g_N
It turns out:

$$g_N = \frac{2\pi^{3N/2}}{\left(\frac{3N}{2}-1\right)!} \cdot \frac{1}{2^{3N}}$$

If you plug this in, then,

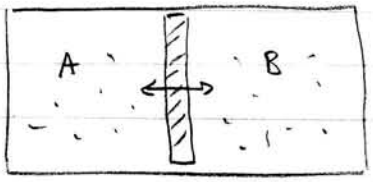
$$S = N k_B \left[\ln\left[\frac{V}{N}\left(\frac{4\pi m E}{3Nh^2}\right)^{3/2}\right] + \frac{5}{2}\right]$$

assume $N \gg 1$ (applying Stirling's approximation)

This is called the Sackur - Tetrode equation

Mechanical equilibrium

Consider two gases A, B with piston between the two



$V_{tot} = V_A + V_B$ fixed

But V_A, V_B can vary

Just like derivation of thermal equilibrium, S_{tot} of total system A+B is maximized

$$S_{tot} = S_A + S_B$$

$$\frac{\partial S_{tot}}{\partial V_A} = \frac{\partial S_A}{\partial V_A} + \frac{\partial S_B}{\partial V_A} = 0$$

$$= \frac{\partial S_A}{\partial V_A} + \frac{\partial S_B}{\partial V_B} \cdot \underbrace{\frac{\partial V_B}{\partial V_A}}_{=-1} = 0 \qquad \therefore \quad \frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}$$

Pressure is given by

$$p \equiv T\left(\frac{\partial S}{\partial V}\right)_{U,N}$$

At thermal equilibrium $T_A = T_B$, so $p_A = p_B$
This is called <u>mechanical equilibrium</u>

For ideal gas

$$p = T\frac{\partial S}{\partial V} = k_B T \frac{\partial}{\partial V}(N \ln V) = \frac{N k_B T}{V}$$

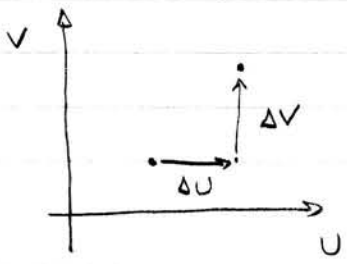
$$\therefore \quad pV = N k_B T \qquad \text{the } \underline{\text{ideal gas law}}!$$

Thermodynamic identity

$S = S(U, V)$ so

$$\Delta S = \left(\frac{\partial S}{\partial U}\right)_V \Delta U + \left(\frac{\partial S}{\partial V}\right)_U \Delta V$$

$$= \frac{1}{T}\Delta U + \frac{p}{T}\Delta V$$



or, in terms of ΔU

$$\Delta U = T\Delta S - p\Delta V$$

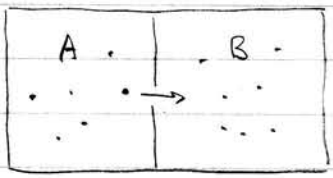
Thermodynamic identity (1st law)

$T\Delta S$: Heat; $p\Delta V$: Mechanical work

A teaser for a future lecture – diffusive equilibrium

$S = S(U, V, N)$

A, B can now exchange particles



$N_{tot} = N_A + N_B$ N_A, N_B vary

$$\Delta S = \left(\frac{\partial S}{\partial U}\right)_{V,N}\Delta U + \left(\frac{\partial S}{\partial V}\right)_{U,N}\Delta V + \left(\frac{\partial S}{\partial N}\right)_{U,V}\Delta N$$

$$= \frac{1}{T}\Delta U + \frac{p}{T}\Delta V - \frac{\mu}{T}\Delta N$$

μ = chemical potential

At diffusive equilibrium $\mu_A = \mu_B$

We'll come back to this later