Accessible Configurations/States: 2 particles in 1D (ideal gas)

- We will first consider two particles in a box of size L, with total energy between E and $E+\delta E$. Let's take, for example, $\delta E/E = 10^{-4}$ as the precision in our total energy

- The "microstates" are the positions and momenta of the two particles:

$$x_1, p_1, \quad x_2, p_2$$

- These coordinates are not totally arbitrary since we must have

$$0 < x_1, x_2 < L$$

and they share the energy

$$E < \frac{p_1^2}{2m} + \frac{p_2^2}{2m} < E + \delta E$$

- Let us try to find the number of accessible (i.e. possible) microstates, which partition the total E

- We divide up the coordinate space into small bins of size Δx, and momentum space into bins of size Δp. Defining

$$h_0 = \Delta x \, \Delta p \qquad \text{(see slide)}$$

- The parameter h_0 was arbitrary in classical times, and only later was chosen as planck constant, h to make connection with quantum mechanics

- The number of "accessible" states is

$$\boxed{\Omega(E) \equiv \frac{1}{2!} \int_{[E, E+\delta E]} \frac{dx_1\, dp_1}{h_0} \frac{dx_2\, dp_2}{h_0}}$$

described below

This is visualized on the next slide. We are summing over all possible configurations wich satisfy the conditions:

$$2mE < p_1^2 + p_2^2 < 2m(E+\delta E)$$

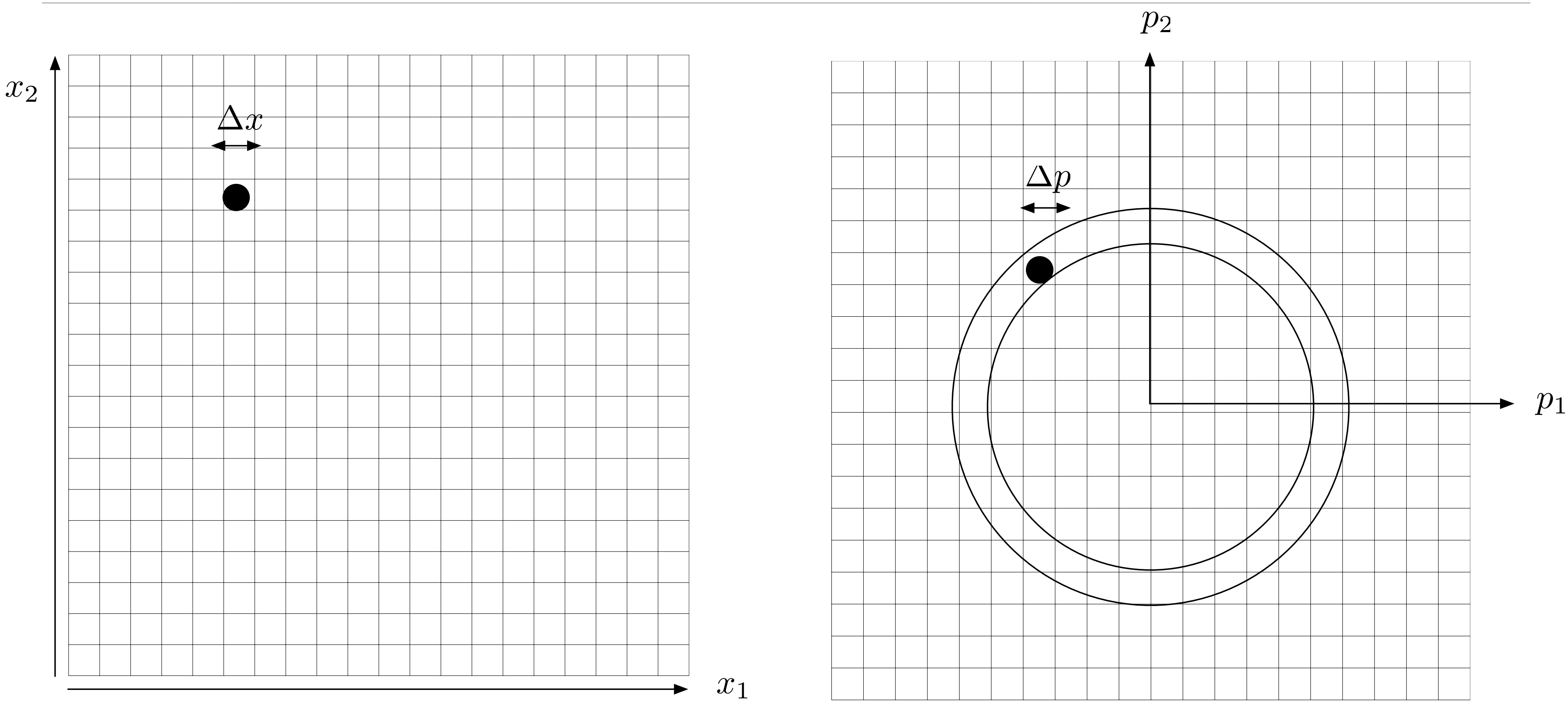
$$0 < x_1, x_2 < L$$

- This is a shell of inner radius $\rho = \sqrt{p_1^2 + \vec{p}_2^{\,2}}$ equal to $\sqrt{2mE}$ and outer radius $\sqrt{2m(E+\delta E)}$

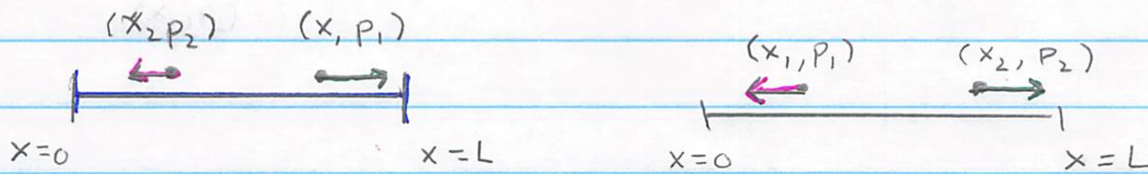
- This is called the "accessible" phase space, because if the two particles are moving around their energy $p_1^2/2m + p_2^2/2m$ remains fixed, and $p_1 + p_2$ are not arbitrary.

- The $\frac{1}{2!}$ is because we dont wish to count twice two states that

Accessible phase space of two particles in one dimension.
Dot represents one configuration.



Correspond to just a relabelling (or interchange) of the particles, particles one and two. That is we dont want to count these two states twice



• Integrating over the shell we find

$$\Omega(E) = \frac{1}{2!}\frac{1}{h_0^2} L^2 \, 2\pi p \, \delta p \leftarrow \text{thickness of shell}$$

Here δp is related to δE. For mometum p we have energy $E = p^2/2m$. For momentum $p + \delta p$ we have

$$E + \delta E = \frac{(p+\delta p)^2}{2m} \simeq \frac{p^2}{2m} + \frac{p}{m}\delta p$$

So

$$\delta E = \frac{p}{m}\delta p \qquad \text{i.e.} \qquad \delta E = \frac{dE}{dp}\delta p$$

Using $E = p^2/2m$ we write

$$\delta p = p \frac{\delta E}{2E}$$

- So the number of configurations is

$$\Omega(E) = \frac{1}{2!}\frac{1}{h_0^2} L^2\, 2\pi p^2 \frac{\delta E}{2E}$$

$$\propto \underbrace{L^2 p^2}_{\text{units of phase volume}} \underbrace{\frac{\delta E}{E}}_{\text{precision in energy}}$$

Accessible States: N particles in 3D

$$\boxed{\Omega(E) = \frac{1}{N!}\int_{\text{possible}} \frac{d^3r_1\, d^3p_1}{h_0^3} \cdots\cdots \frac{d^3r_N\, d^3p_N}{h_0^3}}$$

- With "possible" meaning:

$$0 < \vec{r}_1, \vec{r}_2 \ldots \vec{r}_n < L \qquad \text{i.e. in box of volume } V = L^3$$

- And the total energy is in $[E, E+\delta E]$

$$E < \underbrace{\frac{\vec{p}_1^{\,2}}{2m}}_{E_1} + \cdots + \underbrace{\frac{\vec{p}_N^{\,2}}{2m}}_{\varepsilon_n} < E + \delta E$$

$$\vec{p}_1 = p_{1x}^2 + p_{1y}^2 + p_{1z}^2$$

- The N particles are sharing the total available energy. Again we have

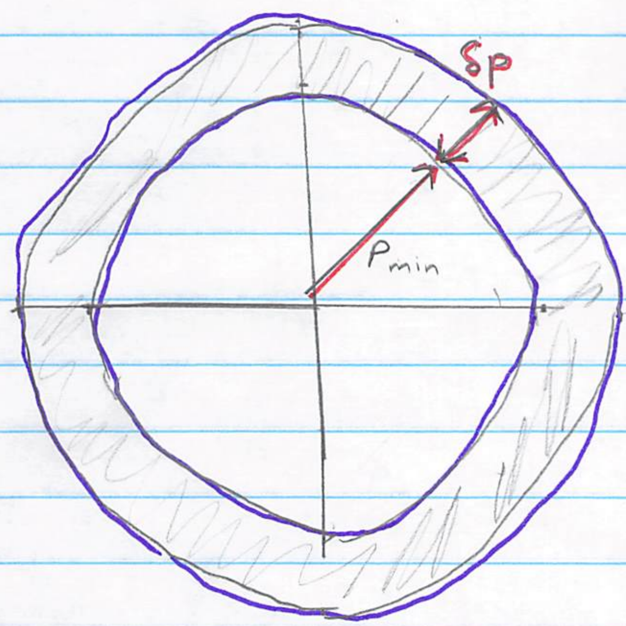
$$2mE < p^2 < 2m(E+\delta E)$$

with

$$p = (\vec{p}_1^{\,2} + \vec{p}_2^{\,2} + \ldots \vec{p}_N^{\,2})^{1/2}$$

being the "radius" of this 3N dimensional momentum space: $\underbrace{(p_{1x}, p_{1y}, p_{1z} \ldots\ldots p_{Nx}, p_{Ny}, p_{Nz})}_{\text{a vector of size } 3N}$

- The picture is the same



- The allowed phase space is a shell in the 3N dimensional momentum space

$$\sqrt{2mE} < p^2 < \sqrt{2m(E+\delta E)}$$

The area of a sphere in d dimensions is proportional to r^{d-1}. For example

2D: $A_2 = C_2\, r$ $\qquad C_2 \equiv 2\pi$

3D: $A_3 = C_3\, r^2$ $\qquad C_3 \equiv 4\pi$

dD: $A_d = C_d\, r^{d-1}$ $\qquad C_d \equiv \dfrac{2\pi^{d/2}}{\Gamma(d/2)}$

You should check that this gives the right result in two dimensions and three dimensions

- So again we have

$$\Omega(E) = \frac{1}{N!} \frac{V^N}{h_0^{3N}} \int_{\substack{\text{shell} \\ \text{of dimension } 3N}} d^3p_1 \cdots d^3p_N$$

$$= \frac{1}{N!} \frac{V^N}{h_0^{3N}} \quad C_{3N} \; p^{3N-1} \quad \delta p$$

- Again with $C_{3N} = 2\pi^{3N/2} / \Gamma(3N/2)$ and $\delta p = p \frac{\delta E}{2E}$ we have

$$\Omega(E) = \frac{1}{N!} \frac{\hat{C}_{3N}}{h_0^{3N}} \quad V^N p^{3N} \quad \frac{\delta E}{2E}$$

$$\propto V^N p^{3N} \frac{\delta E}{E}$$

$$p = (2mE)^{1/2}$$

$$\propto V^N E^{3N/2} \frac{\delta E}{E}$$

- So

$$\Omega(E) = C_0^N V^N E^{3N/2} \frac{\delta E}{E} \qquad C_0 = \text{some constant}$$

You can work out the constant C_0 (see homework)

- Actually, you can ignore the $\delta E/E$ factor since:

$$\ln \Omega(E) = N \ln C_0 + N \ln V + \frac{3N}{2} \ln E + \ln\left(\frac{\delta E}{E}\right)$$

So, $N \sim 6 \times 10^{23}$, while if $\delta E/E = 10^{-6}$ then $\ln 10^{-6} = -13.8$. So, we have $6 \times 10^{23} \gg 13.8$ and the $\ln \delta E/E$ term can be dropped. So

$$\ln \Omega(E) = \underbrace{N \ln C_0}_{\text{const}} + N \ln V + \frac{3N}{2} \ln E$$

Or exponentiating

$$\boxed{\Omega(E) = C_0^N V^N E^{3N/2}}$$

- We say that $\delta E/E$ is not exponentially large (or small) and thus can be set to unity when multiplying exponentially large numbers eg.

$$e^N \frac{\delta E}{E} = e^N e^{\ln \delta E/E} = e^{6\times 10^{23} - 14} \simeq e^{6\times 10^{23}}$$

$$\simeq e^N$$

Computing the constant

- Usually we are only interested in changes in entropy ΔS and then the constants don't matter.

- But you can keep track of the constants (homework)

$$\Omega(E) = \frac{1}{N!}\,\hat{C}_{3N}\,V^N\left(\frac{p}{h_0}\right)^{3N}\frac{\delta E}{2E} \qquad p=\sqrt{2mE}$$

with $\hat{C}_{3N} = \dfrac{2\pi^{3N/2}}{\Gamma(3N/2)}$

- Using

$$N! \cong \left(\frac{N}{e}\right)^N \quad \text{and}$$

$$\Gamma(3N/2) = \left(\frac{3N}{2}-1\right)! \simeq \left(\frac{3N}{2}\right)! \simeq \left(\frac{3N}{2e}\right)^{3N/2}$$

we have after some algebra and setting $\delta E/E \simeq 1$ as before:

$$\boxed{\Omega(E) = e^{\frac{5}{2}N}\left(\frac{V}{N}\right)^{5/2 N}\left(\frac{4\pi m E}{3Nh_0^2}\right)^{3N/2}}$$

So the entropy is

$$\boxed{\frac{S}{k_B} = N\left[\log\left(\frac{V}{N}\left(\frac{4\pi m E}{3Nh_0^2}\right)^{3/2}\right) + \frac{5}{2}\right]}$$

Sackur Tetrode Eqn.