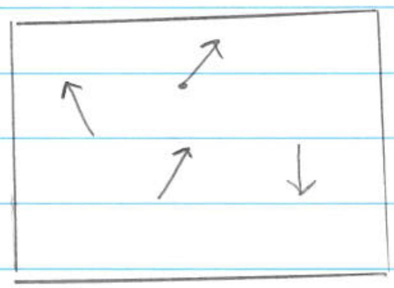
The Micro Canonical Algorithm For the Ideal Gas

- We first need to count all configurations of N particles in volume V



Energy E known with precision $\frac{\delta E}{E} \sim 10^{-4}$

Volume V

- The states are labelled by the positions and momenta of the particle $(\vec{r}_1, \vec{p}_1, \vec{r}_2, \vec{p}_2, \ldots\ldots \vec{r}_N, \vec{p}_N)$

- We need to count these states by integrating over configurations whose total energy is between E and $E + \delta E$, or briefly in $[E, \delta E]$.

$$E < \frac{\vec{p}_1^{\,2}}{2m} + \frac{\vec{p}_2^{\,2}}{2m} + \ldots\ldots + \frac{\vec{p}_N^{\,2}}{2m} < E + \delta E$$

- We will show (in the next pages)

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

grows with E and V (makes sense!)

So

and $\ln \Omega$ scales linearly with N

$$\boxed{S = k_B \ln \Omega = \text{const} + \frac{3}{2} N k_B \ln E + N k_B \ln V}$$

- Then we can find the relation between E and T

$$\frac{1}{k_B T} = \frac{1}{k_B}\left(\frac{\partial S}{\partial E}\right)_V = \frac{3}{2}\frac{N}{E}$$

Or more familiarly

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

Comments

- Of course we derived this using partition functions by finding the speed distribution, and then calculating $\langle \varepsilon \rangle \doteq \langle \frac{1}{2} m \vec{v}^2 \rangle = \frac{3}{2} kT$. Then

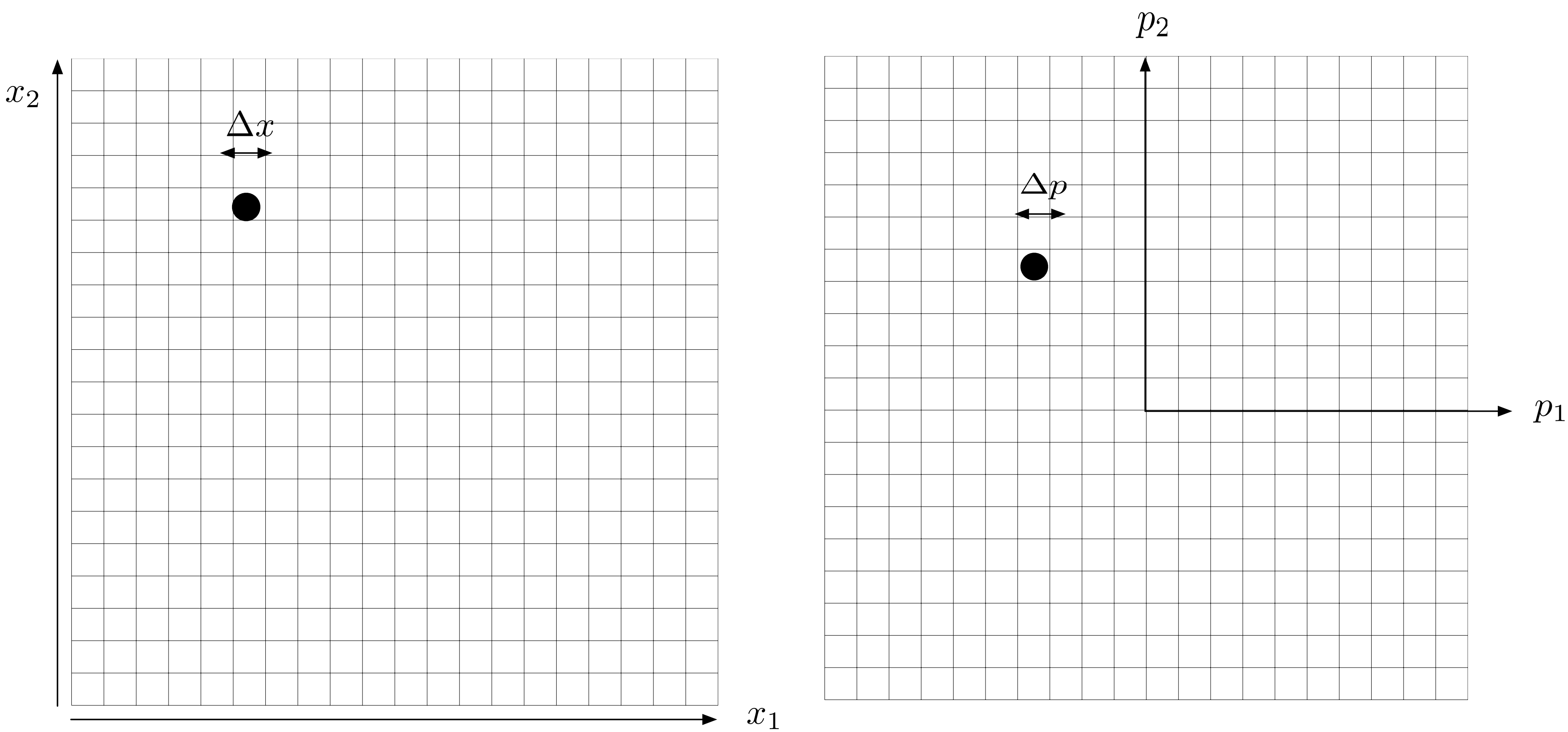
$$E = N \langle \varepsilon \rangle = \frac{3}{2} N k T$$

The partition fcn way is easier

- Later we will see that $S(E, V)$ also determines the pressure.

- Ok, Lets count and find Ω

Two particle phase space: the dot represents a micro state
To count the phase space we divide it in bins of size $h = \Delta x \Delta p$



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:

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

- 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 and Volume V.

- 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

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

described below

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

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

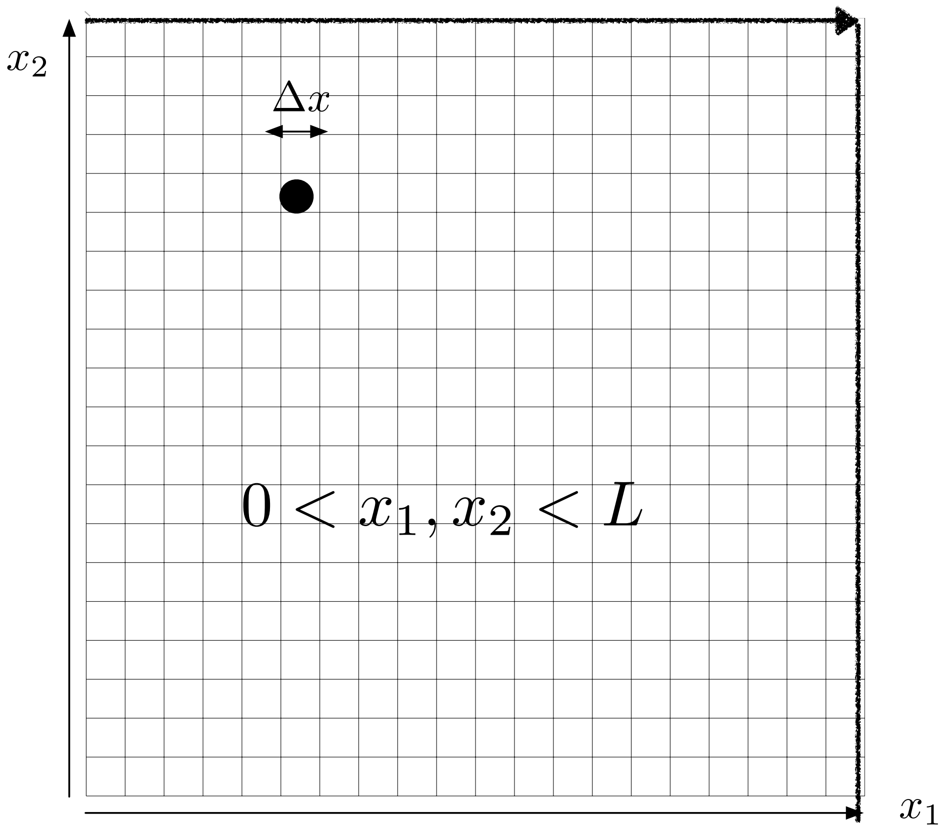
$$0 < x_1, x_2 < L$$

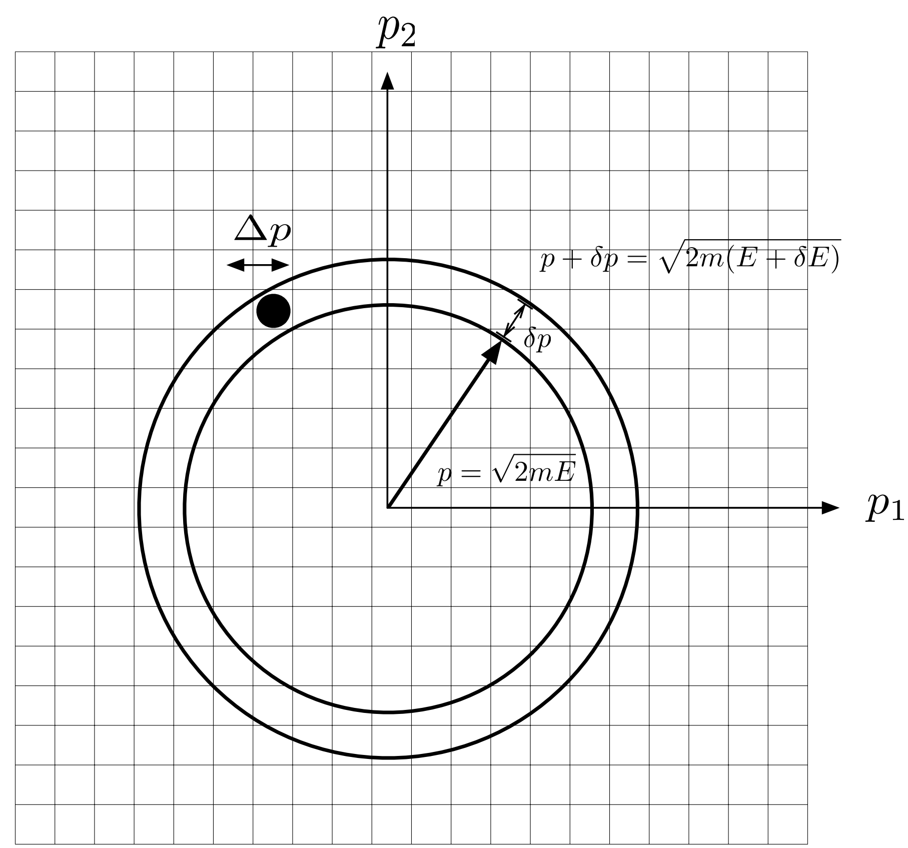
- This is a shell of inner radius $p = \sqrt{p_1^2 + p_2^2}$ equal to $\sqrt{2mE}$ and outer radius $\sqrt{2m(E+\delta E)}$

- 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

Number of configurations of two particles in one dimension





correspond to just a relabelling (or interchange) of the particles, #1 and #2.

- Integrating we find

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

$$= \frac{1}{2!}\frac{1}{h^2} L^2\, 2\pi\, p^2 \left(\frac{\delta p}{p}\right)$$

precision in momenta

The momentum interval determines the energy interval.
$E = p^2/2m$, so $dE = \frac{p}{m}dp$ or $\frac{dE}{E} = 2\frac{\delta p}{p}$

Thus

$$\Omega(E) = \frac{1}{2!}\underbrace{\frac{L^2\, 2\pi\, p^2}{h^2}}_{\text{dimensionless} \sim (Lp)^2/h^2}\left(\frac{\delta E}{2E}\right)$$

corresponding precision in energy.

So now $p = \sqrt{2mE}$ so in terms of E

$$\Omega(E) = \frac{\pi}{2}\frac{L^2(2mE)}{h^2}\frac{\delta E}{E}$$

We will generalize this to more particles and three dimension

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

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

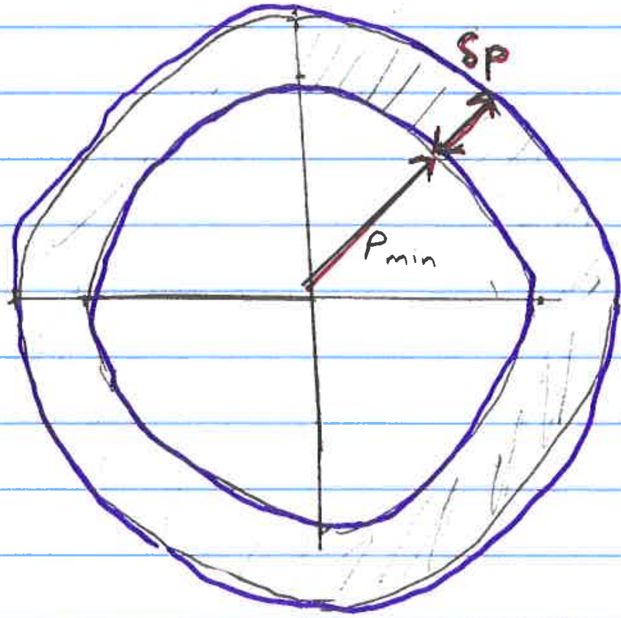
with

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

being the "radius" of this 3N dimensional momentum space:

$$\underbrace{(p_{1x}, p_{1y}, p_{1z} \cdots\cdots p_{Nx}, p_{Ny}, p_{Nz})}_{\text{a vector of size } 3N}$$

- The picture is the same



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

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

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

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

$$= \frac{1}{N!}\frac{V^N}{h_0^{3N}}\, C_{3N}\, p^{3N-1}\, \delta p \qquad p = \sqrt{2mE}$$

Where $C_{3N} = 2\pi^{3N/2}/\Gamma(3N/2)$. Let us neglect all constants and focus on the dependence on energy and volume. $C(N)$ will mean some N-dependent constant, which you will keep track of in homework.

$$\Omega(E,V) = C(N)\, V^N\, p^{3N-1}\, \delta p$$

$$= C(N)\, V^N\, p^{3N}\, \frac{\delta p}{p}$$

Now $p = \sqrt{2mE} \propto E^{1/2}$ and $\delta p/p = \delta E/2E$ as before. so

a new constant

$$\Omega(E,V) = C(N)\, V^N\, E^{3N/2}\, \frac{\delta E}{E}$$

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

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

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

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

Or exponentiating

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

- 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,

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

$$\simeq e^N$$