Last Time / Recap

(1) $dE = đQ + đW \Leftarrow$ First Law

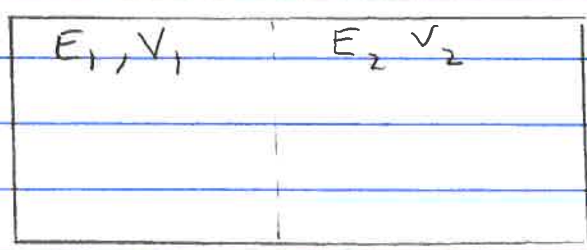
For a full equlibrated (or "reversible" process)
$đQ_{rev} = T\,dS$ (second law):

2) $dE = T\,dS - p\,dV$

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

☆ $$dS = \frac{1}{T}\,dE + \frac{p}{T}\,dV \Longrightarrow \frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_E$$

) We studied maximization of Entropy for two systems sharing the energy and volume:



$E = E_1 + E_2$

$V = V_1 + V_2$

$$S_{TOT} = S_1(E_1, V_1) + S_2(E_2, V_2)$$

$$\frac{dS_{TOT}}{dt} = \left(\frac{\partial S_1}{\partial E_1}\right)_V \frac{dE_1}{dt} + \left(\frac{\partial S_1}{\partial V_1}\right)_{E_1} \frac{dV_1}{dt}$$

$$+ \left(\frac{\partial S_2}{\partial E_2}\right)_{V_2} \frac{dE_2}{dt} + \left(\frac{\partial S_2}{\partial V_2}\right)_{E_2} \frac{dV_2}{dt}$$

Or Since $E_1 + E_2 = \text{const}$ and $V_1 + V_2 = \text{const}$

$$\frac{dE_1}{dt} = -\frac{dE_2}{dt} \qquad \frac{dV_1}{dt} = -\frac{dV_2}{dt}$$

And using the thermodynamic relations

$$\frac{dS}{dt} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\frac{dE_1}{dt} + \left(\frac{p_1}{T} - \frac{p_2}{T}\right)\frac{dV_1}{dt} > 0$$

Entropy is maximized when

$$T_1 = T_2 \quad \text{and} \quad p_1 = p_2$$

4) We talked about the entropy of an ideal mono-atomic gas, $T = \frac{2}{3}\frac{E}{Nk}$, $\frac{p}{T} = \frac{Nk}{V}$, and using eqn (★)

$$dS = \frac{3}{2} Nk \frac{dE}{E} + Nk \frac{dV}{V}$$

$$S/k = \frac{3}{2} Nk \ln E + Nk \ln V + \text{const}$$

So the numer of configurations (i.e. the number of ways for N partices to share the energy and volume) is

$$\Omega(E,V) = e^{S/k_B} = (\text{Const})\, E^{3N/2}\, V^N$$

Today we will go in reverse. We will count up the ways N particles can share the available Energy and Volume $\Omega(E,V)$

Then $S = k_B \ln \Omega$, and the pressure and energy and temperature relation will follow:

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

$$\left(\frac{\partial S}{\partial V}\right)_E = \frac{Nk}{V} = \frac{P}{T}$$

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

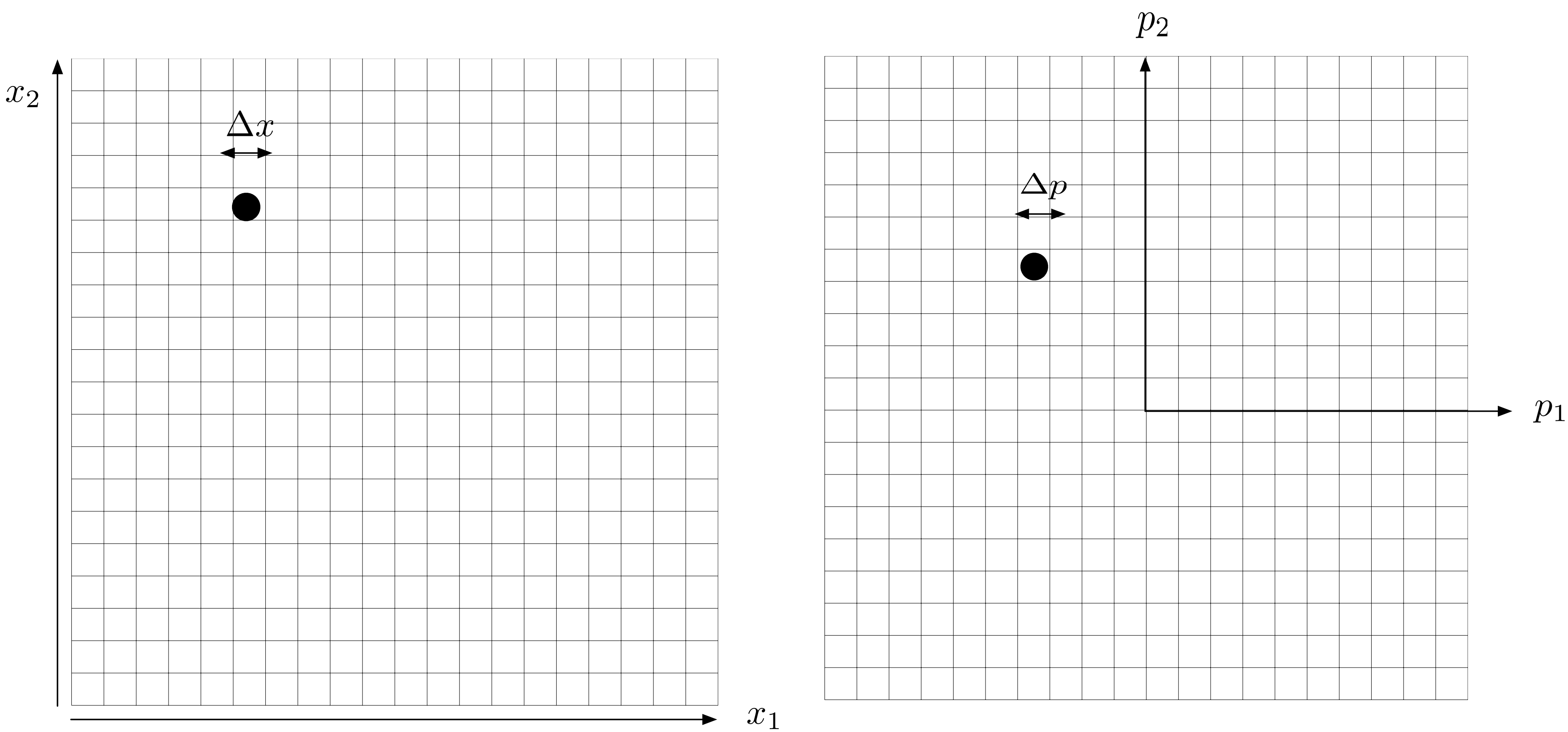
$$E < \frac{p_1^2}{2m} + \frac{p_2^2}{2m} < E + \delta E$$

- 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

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

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



- 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:

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

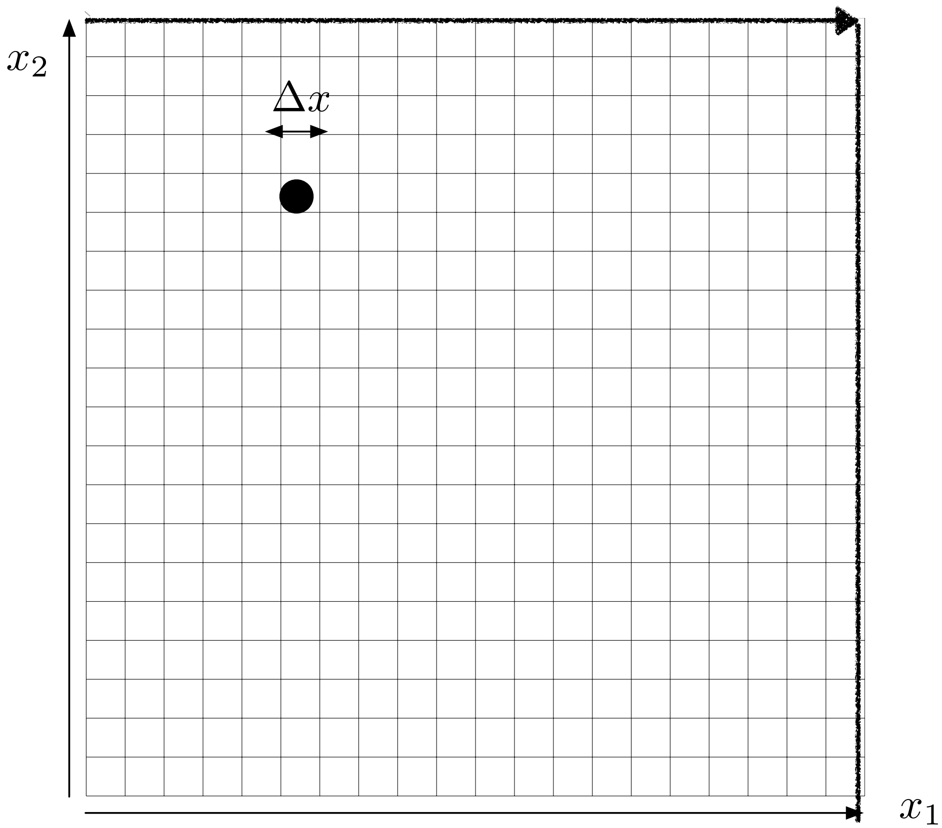
$$0 < x_1, x_2 < L$$

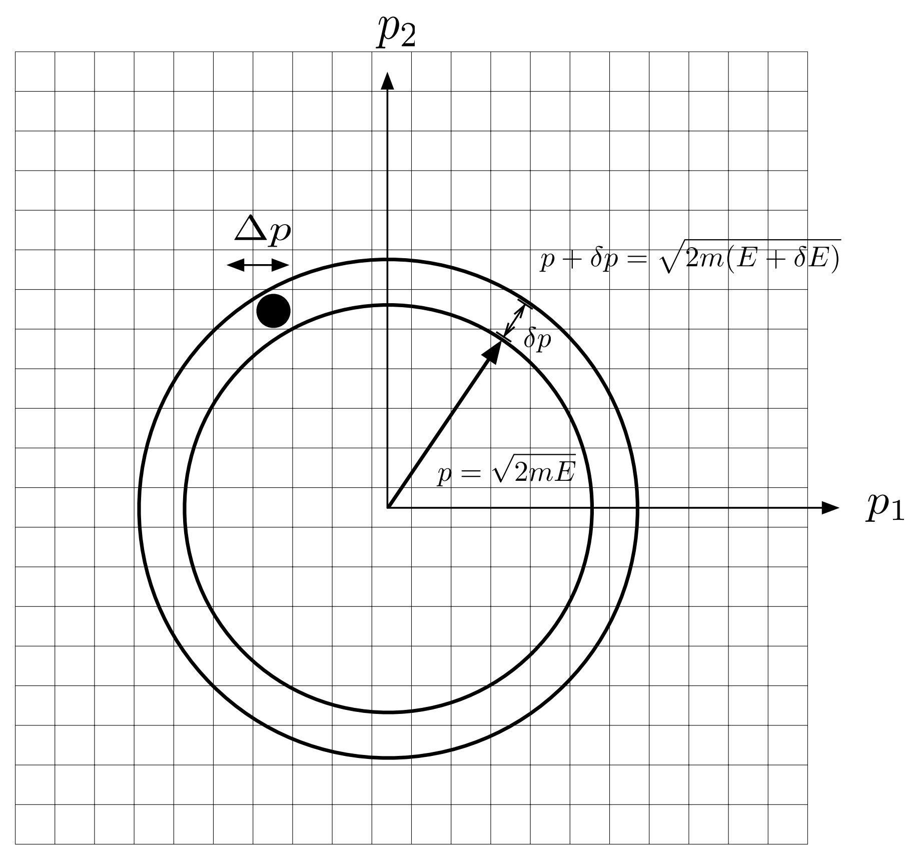
- This is a shell of inner radius $\rho = \sqrt{p_1^2 + p_2^2}$ equal to $\sqrt{2mE}$ and outer radius $\sqrt{2m(E+\delta E)}$

- 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.

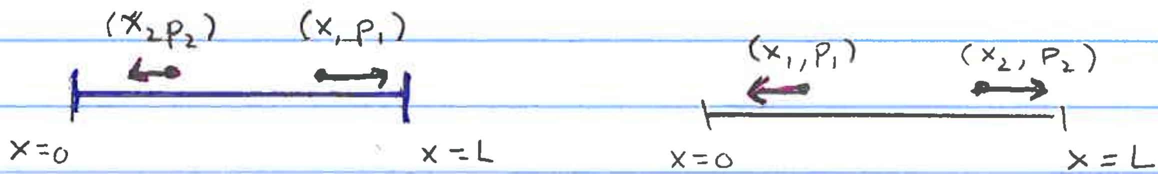
- The $\frac{1}{2!}$ is because we dont wish to count twice two states that

Number of configurations of two particles in one dimension





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



- Integrating over the shell we find

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

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

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

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

- With "possible" meaning:

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

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

$$E < \underbrace{\frac{\vec{p}_1^{\,2}}{2m}}_{E_1} + \cdots + \underbrace{\frac{\vec{p}_N^{\,2}}{2m}}_{\varepsilon_n} < E + \delta E \qquad \vec{p}_1 = p_{1x}^2 + p_{1y}^2 + p_{1z}^2$$

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

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

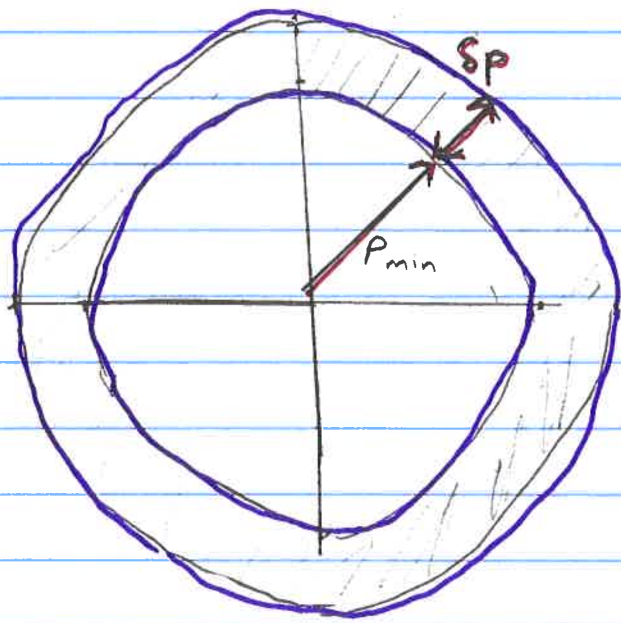
with

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

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

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

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

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

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

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.

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

Entropy as the Mother of All

Given the number of states $\Omega(E, V)$ we can find the entropy

$$S = k \ln \Omega = \frac{3}{2} N k \ln E + N k \ln V + \text{const}\,.$$

The derivates of the entropy determine both the relation between temperature and energy:

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

and the ideal gas law

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_E = \frac{N k}{V}$$