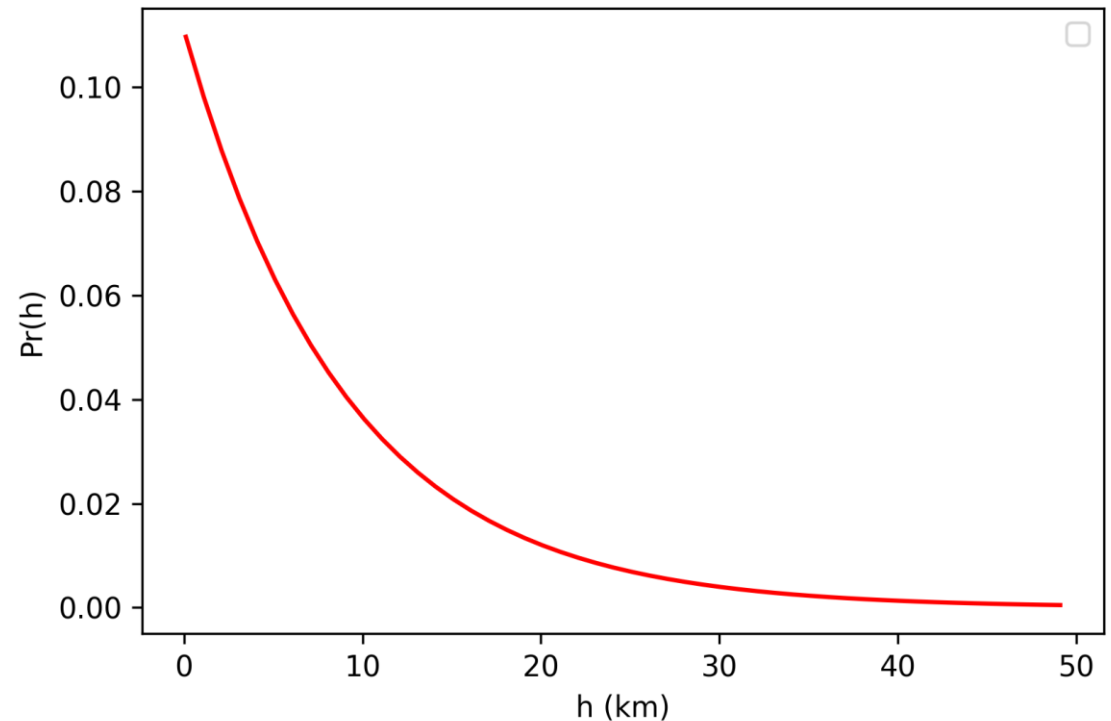


Recap from last time

We can predict the **microscopic behaviour** of a system, e.g. our ideal gas that makes up the atmosphere, using a probability density function defined using **macroscopic terms**

$$Pr(h) = \frac{mg}{k_B T} e^{-\left(\frac{mgh}{k_B T}\right)}$$



More complicated quantum systems

For an atomic system with 2 levels E_0 and E_1 (with $E_1 < E_0$), we have

$$Pr(E_i) = \frac{e^{-\frac{E_i}{k_B T}}}{e^{-\frac{E_0}{k_B T}} + e^{-\frac{E_1}{k_B T}}}$$

Increasing to N levels, we have

$$Pr(E_i) = \frac{e^{-\frac{E_i}{k_B T}}}{\sum_{j=0}^{N-1} e^{-\frac{E_j}{k_B T}}}$$

Interesting cases:

1) $T \rightarrow 0$: $Pr(E_0) = 1$,
 $Pr(E_{n \neq 0}) = 0$

2) $T \rightarrow \infty$: $Pr(E_0) = 1/N$,
 $Pr(E_{n \neq 0}) = 1/N$
(unbiased)

Example question

A type of atom has 4 possible energy levels, $E_0 = 0$, $E_1 = 0.08$ meV, $E_2 = 0.24$ meV and $E_3 = 0.48$ meV

For a single mole of atoms with a temperature at 50 K, how many of the atoms are in the E_2 (second excited state)?

$$\text{Pr}(E_i) = \frac{e^{-\frac{E_i}{k_B T}}}{\sum_{j=0}^{N-1} e^{-\frac{E_j}{k_B T}}} = \frac{e^{-\frac{E_2}{50k_B}}}{\sum_{j=0}^3 e^{-\frac{E_j}{50k_B}}} = \frac{e^{-\frac{E_2}{50k_B}}}{e^{-\frac{E_0}{50k_B}} + e^{-\frac{E_1}{50k_B}} + e^{-\frac{E_2}{50k_B}} + e^{-\frac{E_3}{50k_B}}}$$

Degeneracies

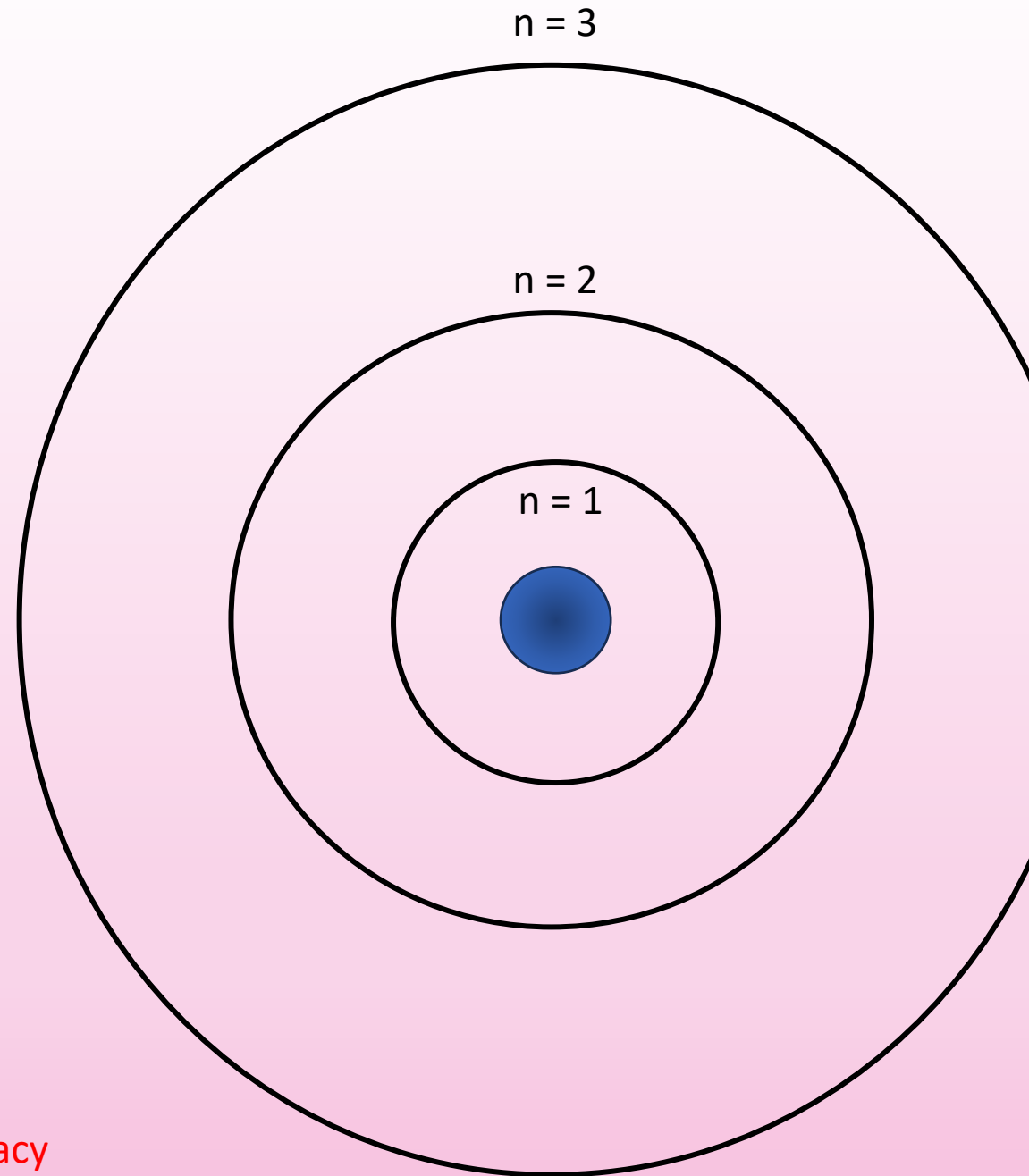
In reality, electrons in atoms can have the same energy in multiple ways (spin up vs spin down, for example).

There is a degeneracy of 2 (we can fit two electrons) in the $n=1$ subshell, 8 in the $n=2$ etc

Boltzmann factor changes accordingly:

$$Pr(E_i) \propto g(E) e^{-\left(\frac{E_i}{\kappa_B T}\right)}$$

$n = 1, g(E) = 2; n = 2, g(E) = 8 \dots g(E)$ represents the degeneracy



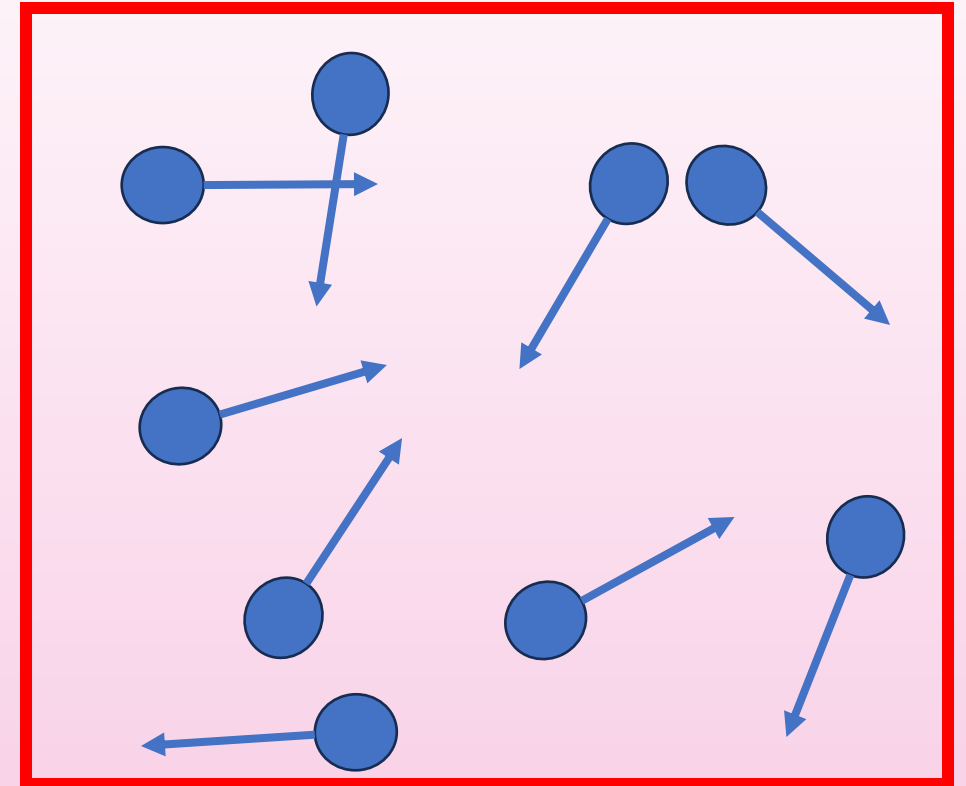
Boltzmann factors meet an ideal gas

Most important assumption for an ideal gas (in terms of energy):

Internal energy all comes from the average kinetic energy of the molecules, E_K (i.e. temperature)

Boltzmann factor for an ideal gas hence takes the form

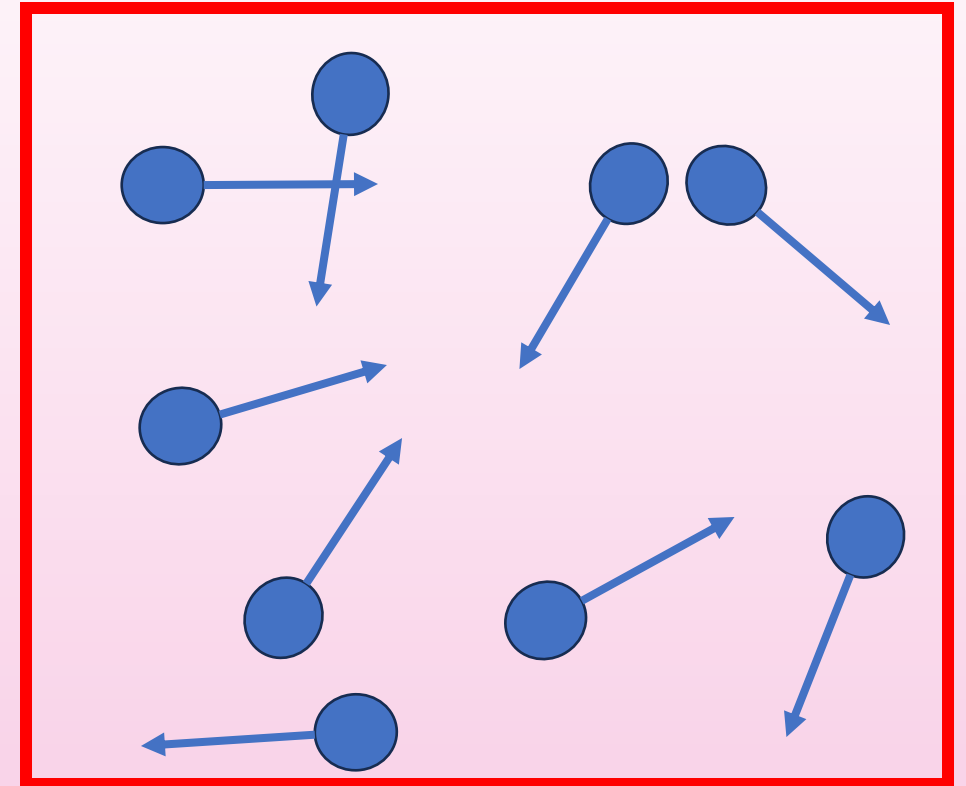
$$Pr(E_i) \propto e^{-\frac{E_K}{k_B T}}$$



Boltzmann factors meet an ideal gas

Other assumptions for an ideal gas:

- Thermal equilibrium (average KE does not change) and no gravity
- Molecules are much smaller than their average separation
- Huge number of molecules ($\sim 10^{23}$)
- Molecules have the same mass and size
- Directions of molecules are essentially “random”
- Molecules can collide, but do so infrequently and elastically (no energy loss)
- The molecules are non-relativistic (we can say that $E_K = 0.5 m v^2$)

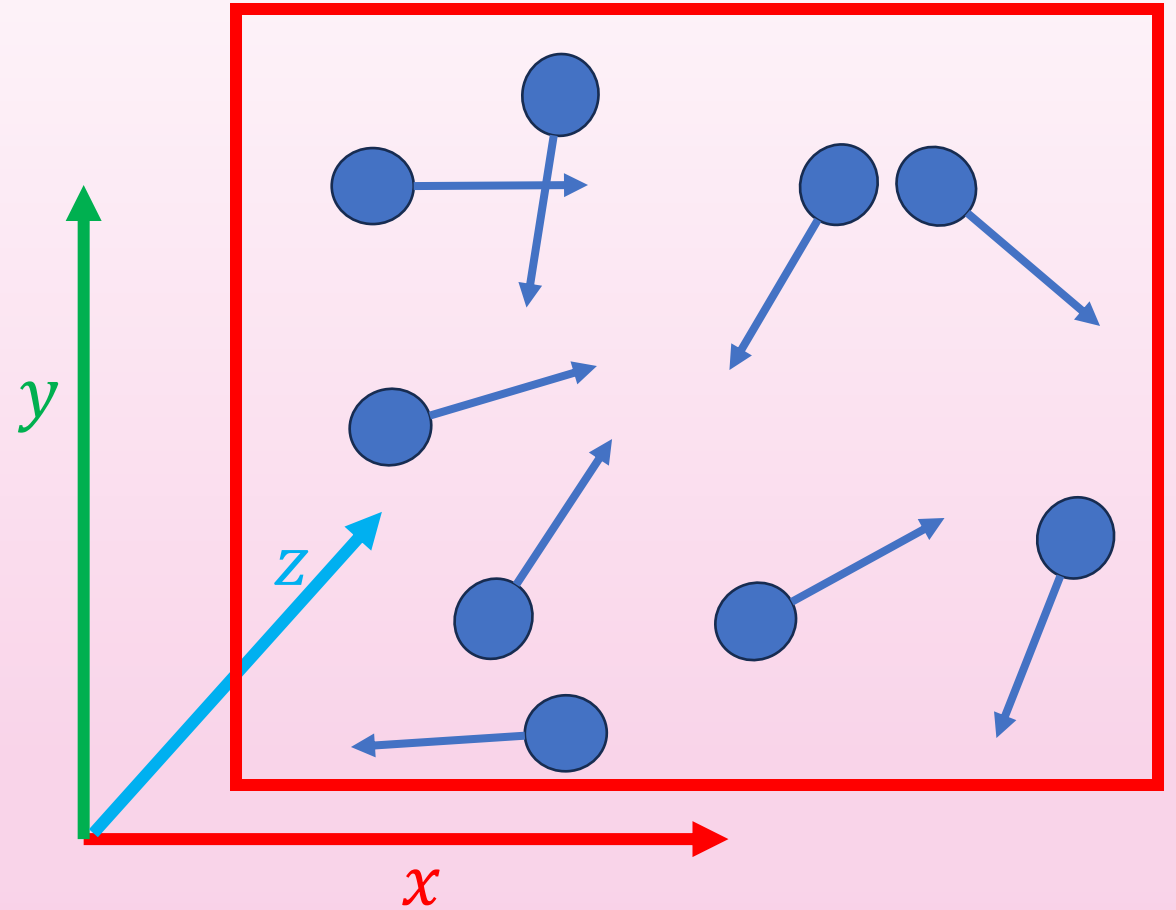


“1 dimensional” ideal gas

The velocity of a gas can be split into three components in each cartesian direction:

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

Easiest to start just considering the x direction

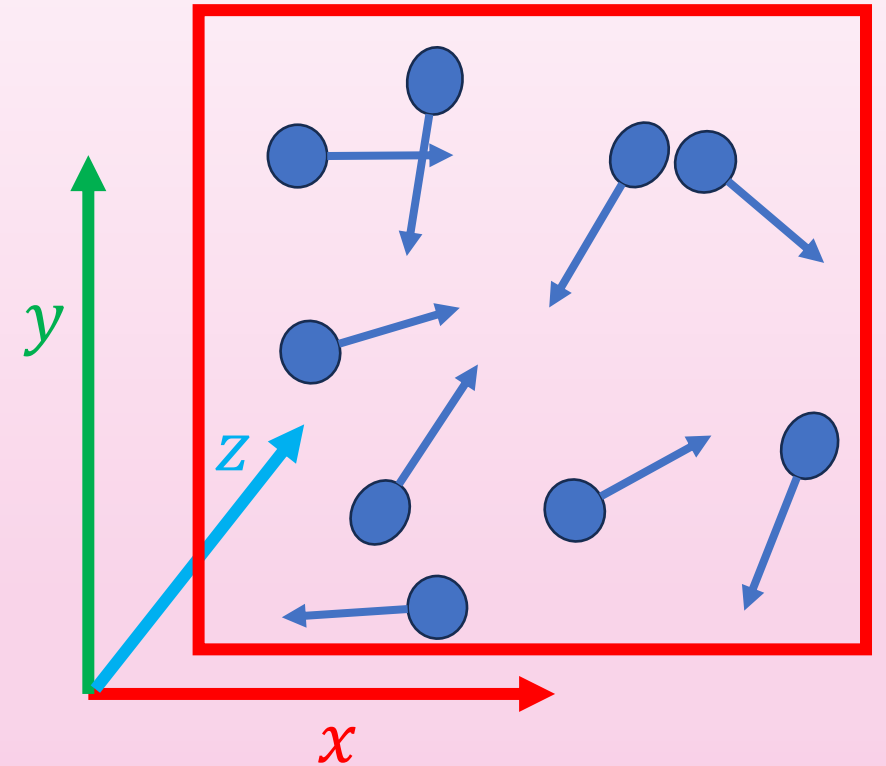


Boltzmann factor for the x direction

Need to consider the probability of having a velocity somewhere between

v_x and $v_x + dv_x$:

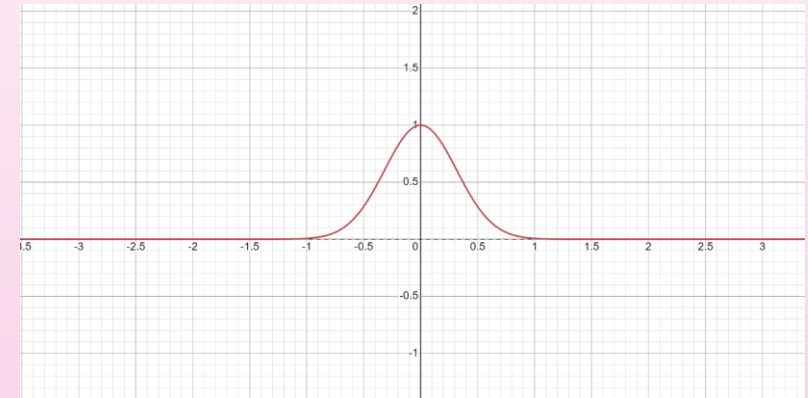
$$Pr(v_x \rightarrow v_x + dv_x) = \int_{v_x}^{v_x + dv_x} Pr(v_x) dv_x$$



Boltzmann factor for the x direction

$$\int_{v_x}^{v_x+dv_x} Pr(v_x) dv_x = \int_{v_x}^{v_x+dv_x} C e^{-\left(\frac{0.5m(v_x)^2}{k_B T}\right)} dv_x \quad (\text{which we should normalise})$$

Standard integral: $\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$



$$C = \sqrt{\frac{m}{2\pi k_B T}}$$

and therefore

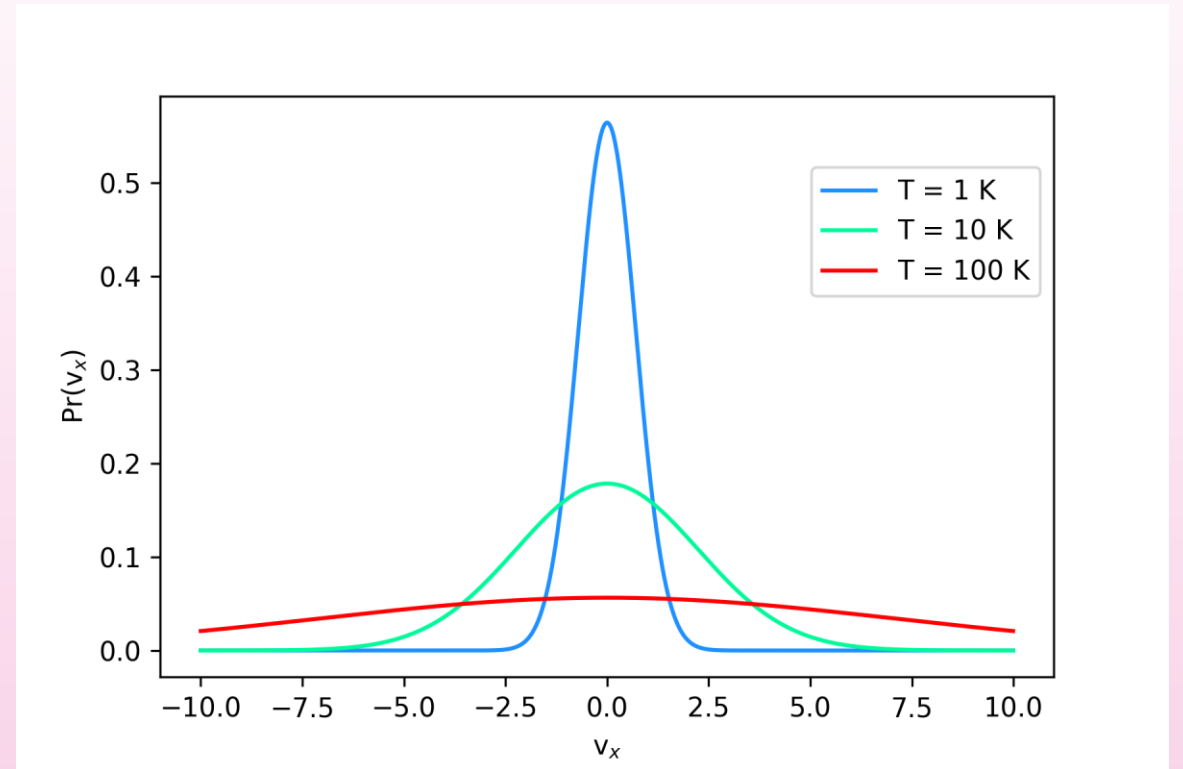
$$Pr(v_x) = \sqrt{\frac{m}{2\pi k_B T}} e^{-\left(\frac{0.5m(v_x)^2}{k_B T}\right)}$$

Boltzmann factor for the x direction

$$Pr(v_x) = \sqrt{\frac{m}{2\pi k_B T}} e^{-\left(\frac{0.5m(v_x)^2}{k_B T}\right)}$$

A distribution centred around 0 is expected, as velocity can be either positive or negative

As we increase temperature, we increase the chance of occupying higher energy states (higher v_x)



No degeneracy in this distribution: only one way to have a specific v_x

Interesting cases: 1) $T \rightarrow 0 : Pr(E_0) = 1, Pr(E_1) = 0$
2) $T \rightarrow \infty : Pr(E_0) = 0.5, Pr(E_1)$

Boltzmann factor for 3D space

Logically,

$$Pr(v_x) = \sqrt{\frac{m}{2\pi k_B T}} e^{-\left(\frac{0.5m(v_x)^2}{k_B T}\right)}$$

$$Pr(v) = Pr(v_x)Pr(v_y)Pr(v_z)$$

Hence ,

$$Pr(v) = g(v) \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\left(\frac{0.5m(v_x^2 + v_y^2 + v_z^2)}{k_B T}\right)}$$

Degeneracy!

Say that $v^2 = 100...$

$$v_x = 10$$

$$v_y = 0$$

$$v_z = 0$$

$$v_x = 0$$

$$v_y = 10$$

$$v_z = 0$$

$$v_x = 0$$

$$v_y = 0$$

$$v_z = 10$$

$$v_x = 5$$

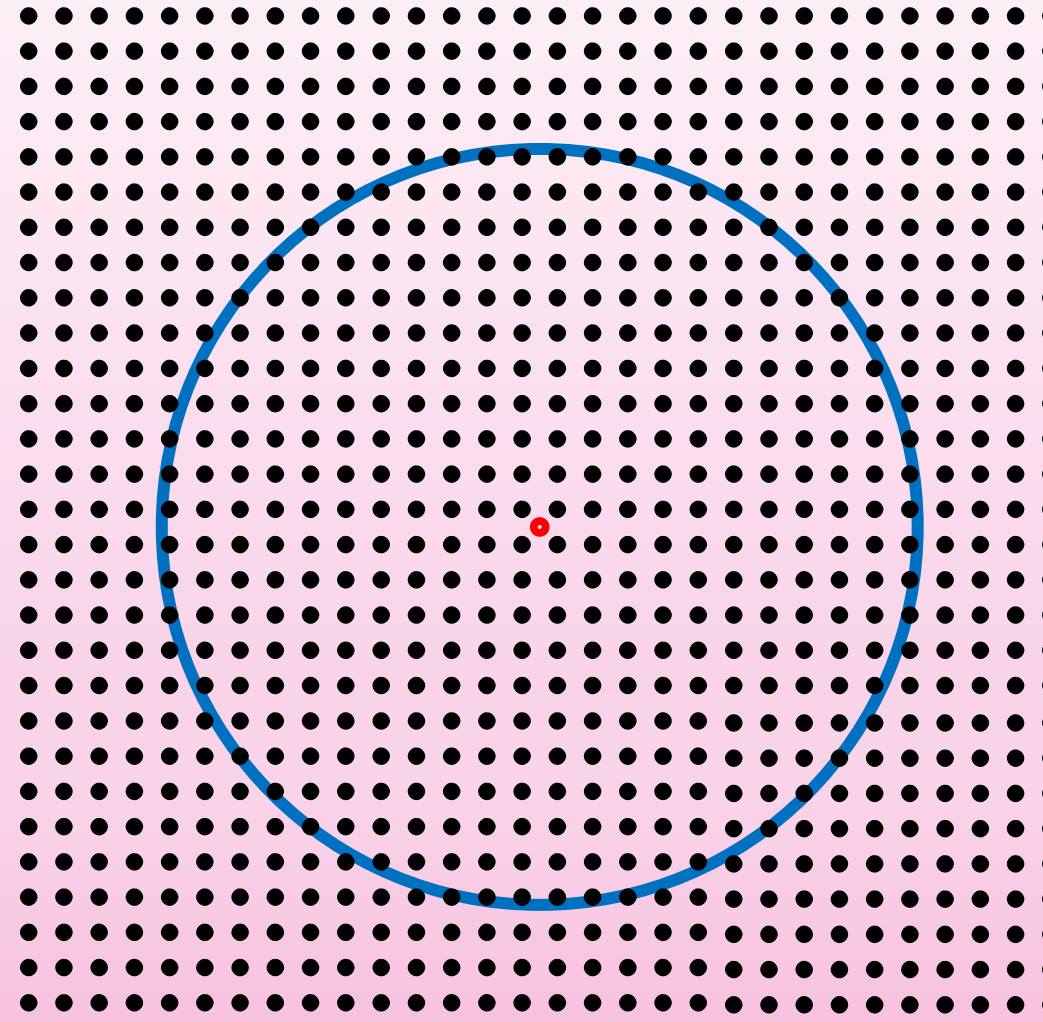
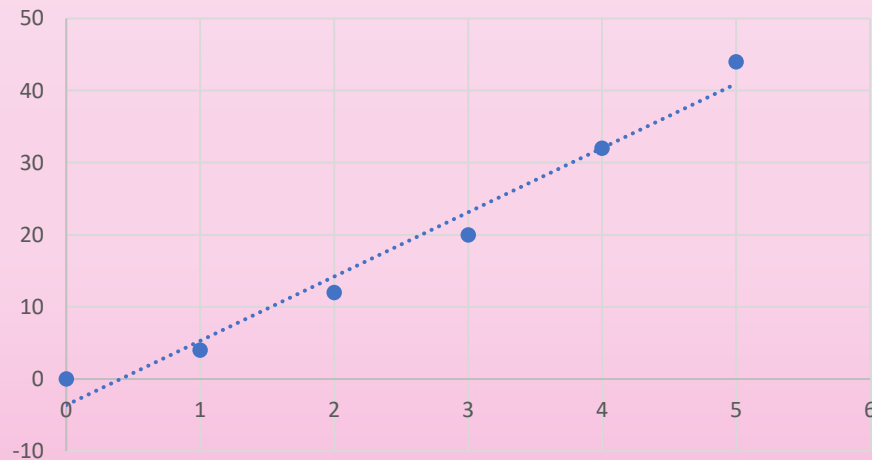
$$v_y = 8$$

$$v_z = \sqrt{11}$$

etc

Establishing the degeneracy: Density of states

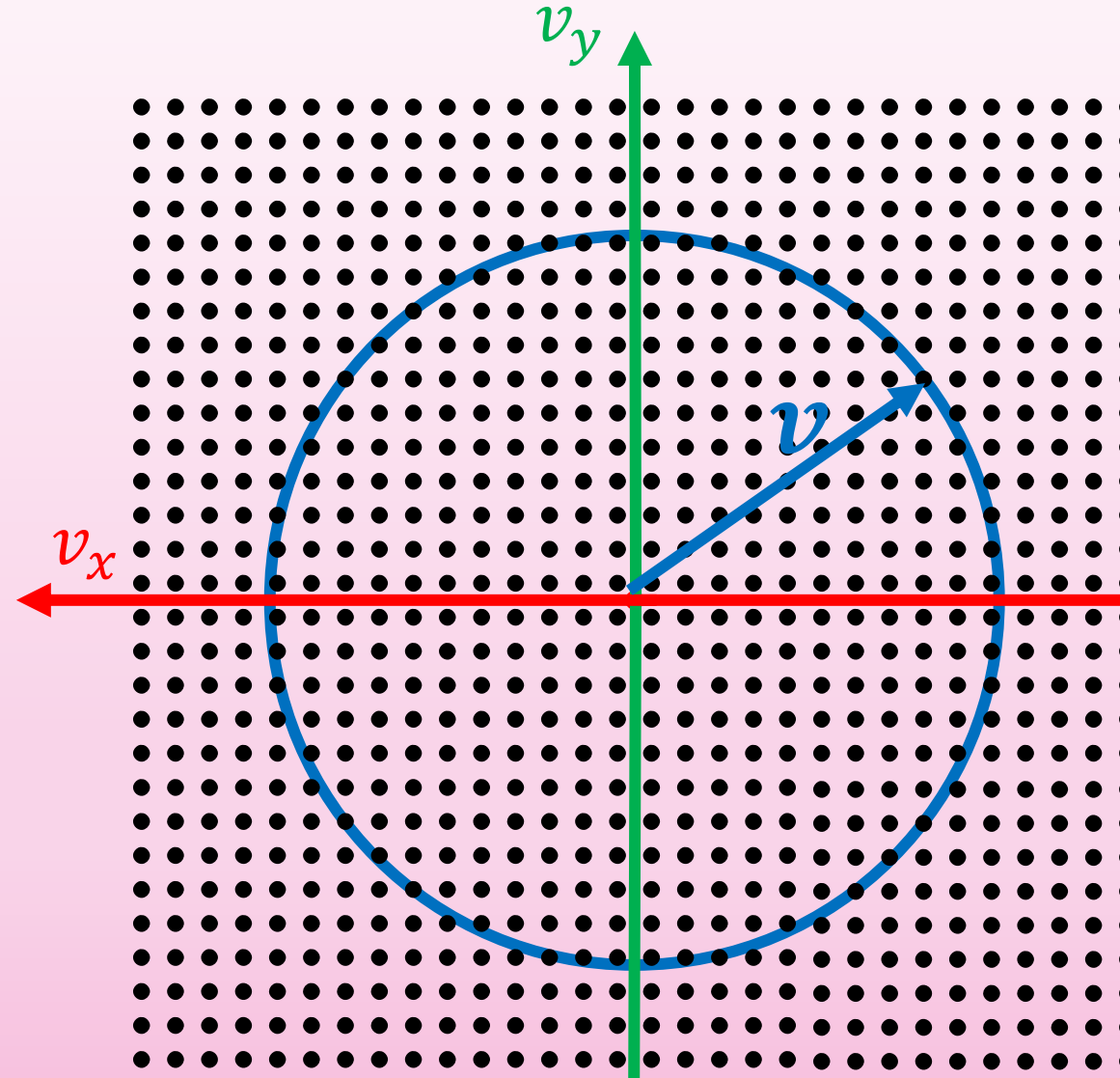
Radius (cm)	Number of dots on circumference
0	0
1	4
2	12
3	20
4	32
5	44



Establishing the degeneracy: Density of states

As we increase the size of the circle, more dots get enclosed within the circumference (seems directly proportional to radius)

We can relate the grid to the velocity plane, where the different ways to combine v_x and v_y to make v are shown by a circle, as $v_x^2 + v_y^2 = v^2$ (like $x^2 + y^2 = r^2$)

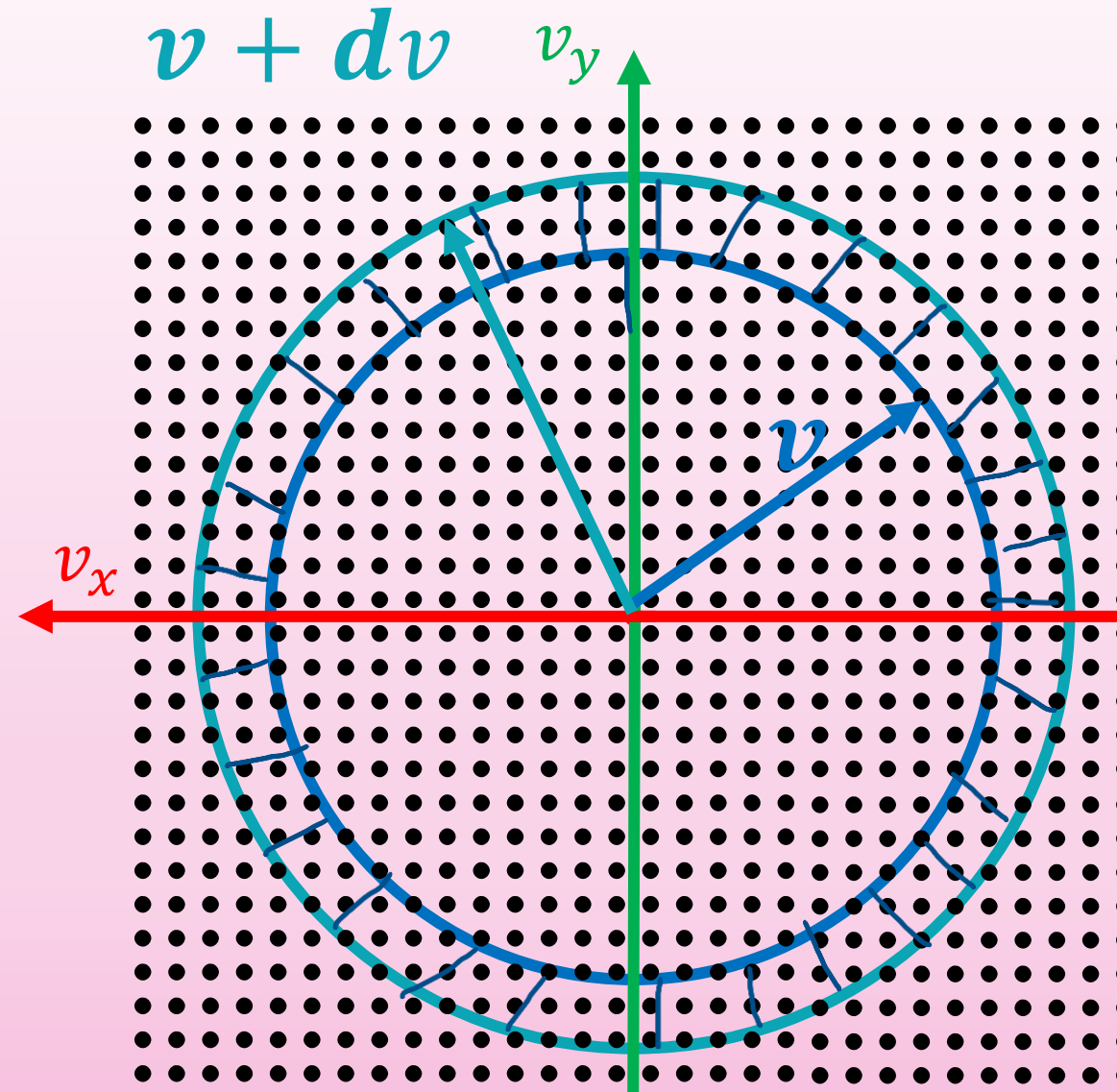


Establishing the degeneracy: Density of states

Density of states, $g(v) dv$, is given by the area of the ring between v and $v + dv$

In 2 dimensions this is given by
 $g(v) dv = 2\pi v dv$

For 3 dimensions, we could do the same of the spherical shell surface area: $g(v) dv = 4\pi v^2 dv$



Maxwell-Boltzmann distribution in full swing

$$Pr(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-\left(\frac{0.5m(v^2)}{k_B T} \right)}$$

and now we know the density of states, such that $g(v) = 4\pi v^2$

and that

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

