Kinetic theory

Using kinetic theory we wish to derive the equations for an ideal gas.

$pV = nRT$

Energy of:

$$U = \frac{3}{2}nRT = \frac{3}{2}pV$$

The ideal gas equations make assumptions:

- Particles have no size (point like) and do not collide with each other
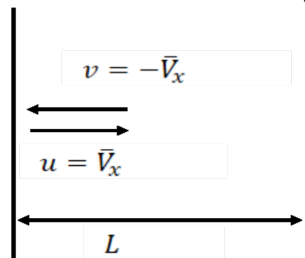- All collisions with walls are elastic
- All energy is kinetic energy:
  - We ignore potential energy and intermolecular forces
- The volume of each partial is much smaller than the total volume

We can calculate the energy of the gas with these rules:

If we have a box enclosing our gas of size $L * L * L$, each wall will have an area of $A = L^2$

If we look at one axis, the x axis, first, we can say the average velocity of the particles is $\bar{V}_x$

After a collision, a particles velocity is $-\bar{V}_x$, and so a change of momentum of:

$\Delta p = 2m\bar{V}_x$ occurs

The particle travels as a speed $\bar{V}_x$ and travels a distance 2L between collisions on the same wall. This means the time between collisions is

$$\Delta t = \frac{2L}{\bar{V}_x}$$

The force felt by the wall from a single particle therefore is:

$$F = \frac{\Delta p}{\Delta t} = \frac{m\bar{V}_x^2}{L}$$

The force felt by a number N particles is:

$$F_N = N\frac{m\bar{V}_x^2}{L}$$

The particles actually move in 3 dimensions, but we can assume that the speed of any given particle is distributed as:

$$\bar{S}^2 = \bar{V}_x^2 + \bar{V}_y^2 + \bar{V}_z^2$$

With $\bar{V}_x^2 \approx \bar{V}_y^2 \approx \bar{V}_z^2$

Therefore:

$$\bar{S}^2 = 3\bar{V}_x^2$$

$$F_{average} = mN\frac{\bar{S}^2}{3L}$$

We can then find pressure exerted on the walls of the box:

$$p = \frac{F}{A} = mN\frac{\bar{S}^2}{3L} * \frac{1}{L^2} = mN\frac{\bar{S}^2}{3L^3}$$

$$L^3 = V$$

$$p = mN\frac{\bar{S}^2}{3V} \rightarrow pV = \frac{mN\bar{S}^2}{3}$$

We want to find the energy of the gas, which we assume is all as kinetic energy:

$$U = KE = N * \frac{1}{2}mS^2$$

$$\bar{S}^2 = 3\frac{pV}{mN}$$

$$U = \frac{3}{2}pV$$

To derive the ideal gas equation, we must look at energy states

When we can calculate the kinetic energy of all particles in our gas, we can equate the value with the energy found above, and so find how pV relates to temperature.

Suppose we have N atoms that can only be in 2 energy states:

$$E = \epsilon, E = 0$$

If we have a total of N particles in our gas, and n have an energy of $E = \epsilon$, we can find the total energy U:

$$U = n\epsilon$$

We can also say that the probability of a particle having an energy of ϵ is:

$$P(E = \epsilon) = \frac{n}{N}$$

Now we wish to relate this idea to temperature.

Temperature can be found by:

$$T = \frac{dU}{dS} = \frac{\Delta U}{\Delta S}$$

Where ΔU is the change in energy, and ΔS is the change in entropy, with $S = kln(\Omega)$ Where k is the Boltzmann constant and Ω is the number of combinations that the energy can be distributed between all particles.

$$\Omega = \frac{N!}{n!\,(N-n)!}$$

(For example, if we have 4 particles, $[a, b, c, d]$, and 2 have energy of ϵ while the other two have an energy of 0, the total amount of ways the energy can be shared is:

$< \epsilon = a, b : 0 = c, d >, < \epsilon = a, c : 0 = b, d >, < \epsilon = a, d : 0 = c, b >,$
$< \epsilon = c, b : 0 = a, d >, < \epsilon = d, b : 0 = c, a >, < \epsilon = c, d : 0 = a, b >$

A total of 6, the same value from the equation

We can find the change in entropy for a given change in energy. If we add an energy of ϵ, there are now $n + 1$ particles with an energy of ϵ, and so can find the change in entropy:

$$S_i = kln\left(\frac{N!}{n!\,(N-n)!}\right)$$

$$S_f = kln\left(\frac{N!}{(n+1)!\,(N-n-1)!}\right)$$

$$\Delta S = S_f - S_i = kln\left(\frac{N-n}{n+1}\right)$$

Next, assuming that $n \gg 1$, we can simplify this:

$$n + 1 \approx n$$

$$\Delta S = kln\left(\frac{N-n}{n}\right) = kln\left(\frac{N}{n} - 1\right)$$

Now that we have a change in entropy associated with an energy change, we can show:

$$T = \frac{\Delta U}{\Delta S} = \frac{\epsilon}{kln\left(\frac{N}{n} - 1\right)} \rightarrow ln\left(\frac{N}{n} - 1\right) = \frac{\epsilon}{kT}$$

$$\frac{N}{n} - 1 = e^{\frac{\epsilon}{kT}} \rightarrow \frac{N}{n} = e^{\frac{\epsilon}{kT}} + 1$$

$$\rightarrow \frac{n}{N} = \frac{1}{e^{\frac{\epsilon}{kT}} + 1} = \frac{e^{-\frac{\epsilon}{kT}}}{1 + e^{-\frac{\epsilon}{kT}}}$$

This is the same as the probability of a particle having an energy of ϵ:

$$P(E = \epsilon) = \frac{n}{N} = \frac{e^{-\frac{\epsilon}{kT}}}{1 + e^{-\frac{\epsilon}{kT}}}$$

This is a simple but important case, as we can find the probability of a particle having any energy E_i in a system where N energy states are allowed:

$$P(E = E_i) = \frac{e^{-\frac{E_i}{kT}}}{\sum_{j=0}^{N} e^{-\frac{E_j}{kT}}}$$

We now want to find the probability that a particle has an energy E_j when a total of E_N states are allowed:

$$P(E = E_i) = c(T)e^{-\left(\frac{E_i}{kT}\right)}$$

ASK LECTURER ABOUT THESE PROBABILITIES

We can now find the velocity of a particle using its kinetic energy:

$$\boldsymbol{v} = (v_x, v_y, v_z) \rightarrow |v^2| = v_x^2 + v_y^2 + v_z^2$$
$$E = KE = \frac{1}{2}m|v^2|$$

However, we want to know the energy of the whole system, so we look at the average velocity and the associated energy state:

$$E_i = \frac{1}{2}m|\bar{v}^2|$$

We can now use the Boltzmann distribution to find the probability of a particle having this energy, and so the probability of it having this velocity:

$$P(E = E_i) = c(T)e^{-\frac{m(v_x^2+v_y^2+v_z^2)}{2kT}}$$
$$P(v_x, v_y, v_z) = c(T)e^{-\frac{m|\bar{v}^2|}{2kT}}$$

We can find $c(T)$ as we know the sum of all possible energies must be 1, therefore:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} c(T)\, e^{-\frac{m(v_x^2+v_y^2+v_z^2)}{2kT}}\, dv_x\, dv_y\, dv_z = 1$$

We can find the solution to this by using the standard integral:

$$I_n(a) = \int_{-\infty}^{\infty} e^{-ax^2} \cdot x^n dx$$

For $n = 0$,

$$I_0(a) = \sqrt{\frac{\pi}{a}}$$

For $n > 0$,

$$I_n(a) = \frac{(n-1)!!}{2^{\frac{n}{2}}a^{\frac{n}{2}}}\sqrt{\frac{\pi}{a}}$$

We can use this to solve the integral and so find $c(T)$:

$$\frac{1}{c(T)} = \int_{-\infty}^{\infty} e^{-\frac{m}{2kT}v_x^2}\, dv_x \cdot \int_{-\infty}^{\infty} e^{-\frac{m}{2kT}v_y^2}\, dv_y \cdot \int_{-\infty}^{\infty} e^{-\frac{m}{2kT}v_z^2}\, dv_z$$

$$\int_{-\infty}^{\infty} e^{-\frac{m}{2kT}v_x^2}\, dv_x = \sqrt{\frac{2kT\pi}{m}}$$
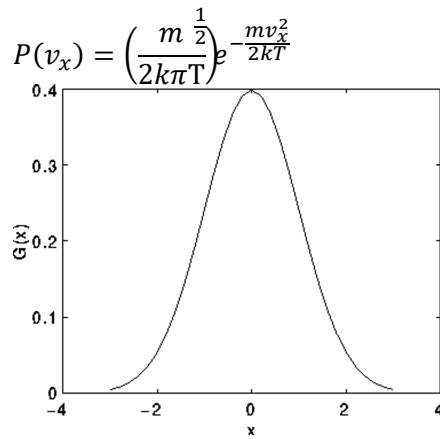
We can see that each integral is equal, and so:

$$\frac{1}{c(T)} = \left(\frac{2kT\pi}{m}\right)^{\frac{3}{2}} \rightarrow c(T) = \left(\frac{m}{2kT\pi}\right)^{\frac{3}{2}}$$

So we can find the probability of a given velocity to be:

$$P(v_x, v_y, v_z) = \left(\frac{m}{2k\pi T}\right)^{\frac{3}{2}}e^{-\frac{m(v_x^2+v_y^2+v_z^2)}{2kT}}$$

If we look at just 1 dimension, we can plot the probability with respect to the velocity for a given temperature:

$$P(v_x) = \left(\frac{m^{\frac{1}{2}}}{2k\pi\mathrm{T}}\right)e^{-\frac{mv_x^2}{2kT}}$$

If the temperature is increased, the distribution gets wide and the peak has a lower probability, however the most probably point will always be at $v_x = 0$

This distribution is the Maxwell-Boltzmann distribution

The total number of particles with a velocity in the range:

$$v_0 = \begin{pmatrix} v_x \\ v_y \\ v_z \end{pmatrix} \to v_1 = \begin{pmatrix} v_x + \delta v_x \\ v_y + \delta v_y \\ v_z + \delta v_z \end{pmatrix}$$

Is proportional to the probability at the velocity v_0 multiplied with the total range of velocities:

$$P(v = v_1) = P(v = v_0) \cdot (\delta v_x \delta v_y \delta v_z)$$

Sometimes we wish to find the distribution of particle speeds rather than velocities.

$$s = |\boldsymbol{v}| = \sqrt{v_x^2 + v_y^2 + v_z^2}$$

Because the same speed can occur with multiple velocities ($|v_x, v_y, v_z| = |-v_x, -v_y, -v_z|$) , we must define a shell for a given speed.

A sphere of radius r, $r = s = \sqrt{v_x^2 + v_y^2 + v_z^2}$

If the sphere has a thickness ds, the total volume is surface area * ds:

$$dV = 4\pi s^2 * ds$$

This means we can write:

$$P(s) = c(T) * 4\pi s^2 e^{-\left(\frac{ms^2}{2kT}\right)}$$

To find the constant $c(T)$ we again integrate over all speeds and set this value to 1:

$$\int_0^\infty c(T)4\pi s^2 e^{-\frac{ms^2}{2kT}} \, ds = 1$$

If we look at the defined integral earlier:

$$I_n(a) = \int_{-\infty}^\infty e^{-ax^2} x^n dx = \frac{(n-1)!!}{2^{\frac{n}{2}} \cdot a^{\frac{n}{2}}} \cdot \sqrt{\frac{\pi}{a}}$$

We also know that this function is symmetric, and for a symmetric function $f(x)$:

$$\int_{-\infty}^\infty f(x)dx = 2\int_0^\infty f(x)dx$$

So we can look back at our original integral and say:

$$\int_0^\infty c(T)4\pi s^2 e^{-\frac{ms^2}{2kT}} \, ds = \frac{1}{2}\int_{-\infty}^\infty c(T)4\pi s^2 e^{-\frac{ms^2}{2kT}} \, ds = 1$$

We can now find the constant $c(T)$:

$$1 = \int_0^\infty c(T)4\pi s^2 e^{-\frac{ms^2}{2kT}} \, ds = \frac{1}{2}\int_{-\infty}^\infty c(T)4\pi s^2 e^{-\frac{ms^2}{2kT}} \, ds$$

$$\frac{2}{4\pi c(T)} = \int_{-\infty}^\infty s^2 e^{-\frac{ms^2}{2kT}} \, ds = I_n(a) \quad \left(n = 2, a = \frac{m}{2kT}\right)$$

$$\frac{1}{2\pi c(T)} = I_2\left(\frac{m}{2kT}\right) = \frac{(2-1)!!}{2 \cdot \frac{m}{2kT}} \cdot \sqrt{\frac{2\pi kT}{m}} = \sqrt{2\pi} \cdot \left(\frac{kT}{m}\right)^{\frac{3}{2}}$$
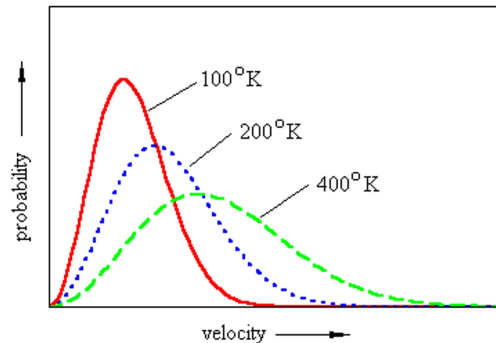
$$2\pi c(T) = \left(\frac{1}{2\pi}\right)^{\frac{1}{2}} \cdot \left(\frac{m}{kT}\right)^{\frac{3}{2}}$$

$$\to c(T) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}$$

And so:

$$P(s) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} 4\pi s^2 e^{-\left(\frac{ms^2}{2kT}\right)}$$

Which results in a Boltzmann distribution:

We can see that the probability of a particle having no speed is 0, for any temperature. The most probable speed occurs at the peak

To derive our ideal gas equation, we must find the mean squared speed of a gas
If we are given a probability distribution function $P(x)$, we can find the mean of the function the function $f(x)$ by:

$$< f(x) > = \int_{all\ x} f(x)p(x)dx$$

To find the mean energy of the gas we need to find the mean of the speed squared:

$$< E > = \frac{1}{2}m < s^2 >$$

Given our probability distribution found before, the Boltzmann distribution, we can find the mean speed:

$$P(s) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} 4\pi s^2 e^{-\left(\frac{ms^2}{2kT}\right)}, f(s) = s^2 \therefore$$

$$< s^2 > = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} 4\pi \int_0^\infty s^4 e^{-\left(\frac{ms^2}{2kT}\right)} ds$$

We can solve this using the standard integral again:

$$\int_{-\infty}^{\infty} x^n e^{-ax^2} dx = I_n(a) = \frac{(n-1)!!}{2^{\frac{n}{2}} a^{\frac{n}{2}}} \cdot \sqrt{\frac{\pi}{a}}, n = 4, a = \frac{m}{2kT}$$

$$\int_0^\infty g(x)\ dx = \frac{1}{2}\int_{-\infty}^\infty g(x)\ dx \text{(or symmetric } g(x))$$

$$< s^2 > = \frac{1}{2} * \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} 4\pi * \frac{3 \cdot 1}{2^2 \cdot \left(\frac{m}{2kT}\right)} \cdot \sqrt{\frac{2\pi kT}{m}}$$

$$< s^2 > = \frac{3kT}{m}$$

Now with this result we can form the ideal gas equation:

$$KE = U = \frac{1}{2}mv^2 = \frac{1}{2}m < s^2 >$$

The above is for 1 particle, given N particles:

$$U = \frac{3}{2}NkT = \frac{3}{2}nRT$$

If we equate our two equations for the energy of a gas we get the ideal gas equation:
$$U = \frac{3}{2}nRT = \frac{3}{2}pV$$
$$pV = nRT$$

The ideal gas equations only work for an ideal gas, one at a medium pressure and temperature. At higher temperatures, our assumption that all the energy is stored as kinetic energy breaks down. This is because energy is shared with the other degrees of freedom.

Each particle in a gas has multiple degrees for freedom. These are ways that the energy of the particle can be distributed. A molecule with m atoms will have $3m$ degrees of freedom.

There are 3 types of degree of freedom:

Translational - the velocity of the centre of mass of the particle. This takes up 3 degrees of freedom, 1 for each dimension the particle can travel in.

Rotational - if a molecule is linear it has 2 rotational degrees of freedom. If it is non linear, it has 3 rotational degrees of freedom.

Vibration - This takes up all remaining of the required degrees of freedom.

Each degree of freedom takes a share of the molecules energy:

Translation takes $\frac{1}{2}kT$ for each dimension, and so:
$$< E_{translation} > = \frac{3}{2}kT$$
Rotation takes the same amount, and so the total energy depends on if the particle has 2 or 3 degrees of freedom from rotation:
$$< E_{rotation} > = \frac{1}{2}kT$$
Vibration takes a total of kT per degree of vibrational freedom. This is because each vibration has $\frac{1}{2}kT$ for kinetic energy and potential energy

For example, we can calculate the degrees of freedom for water vapour:

Water is H_2O. This means it has 9 degrees of freedom.

3 are translational, 3 are rotational (non linear) and 3 are vibrational.

The total energy for N particles is therefore:
$$E = N\left(3*\frac{1}{2}kT + 3 *\frac{1}{2}kT + 3 * kT\right) = 6NkT$$
$$E = 6nRT$$

This partitioning of energy can be seen when measuring the heat capacity.

Head capacity is given by: $\frac{dQ}{dT}$ where Q is the added energy. For a constant volume:
$$c_v = \left(\frac{\partial U}{\partial T}\right)_V$$
We can find the heat capacity for each degree of freedom:
$$c_{v_{trans}} = \frac{3}{2}nR$$
$$c_{v_{rot}} = \frac{3}{2}nR$$
$$c_{v_{vib}} = 3nR$$
$$\therefore c_v = 6nR$$
At low temperatures, the heat capacity of a gas will simply be from the translational heat capacity. At larger temperatures, increasing temperature also increases rotational and vibrational energy of the particles.

At high temperatures, the ideal gas equation breaks down, as the Kinetic energy is not directly proportional to the temperature.