Kinetic Theory of Gases

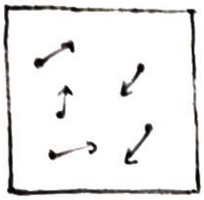
With this model, a gas is modelled by a group of many particles moving at high speed and bouncing off each other. Using this, we will develop microscopic understandings of macroscopic quantities like energy, temperature and pressure.

We will make many assumptions with this model:

1) gas is composed of large number of molecules N
2) Molecules are small compared to the separation distance
3) Molecules are uniformly distributed and move randomly
4) Molecules feel no force except when they collide elastically with other molecules or the walls of the container
5) Molecules obey Newton's Laws of Motion

Assumptions 2 and 4 fail when the molecules are close together so the Kinetic Theory cannot be used to describe liquids or gases. Assumption 5 is also wrong since quantum effects apply so there are quantum rules but these tend towards Newton's Laws if the de Broglie wavelength $\lambda = \frac{h}{mv}$ is much smaller than separation distance.

So the theory isn't perfect but for the purposes of developing an understanding of these concepts, it is good enough!



Consider a box with very many molecules of gas inside

N : number of molecules

$\underline{v}_i$: velocity of i^{th} molecule

$\underline{r}_i$: position of i^{th} molecule

V : volume of the box

We can set the total momentum of the molecules to be 0. This makes sense if we think about the fact the velocities are random and have an equal probability of being in all directions.

$\therefore$ Total Momentum $\sum_i^N m\underline{v}_i = 0$ This momentum is also conserved.

So what is the internal energy of the gas? This is the energy stored in the molecules' movements and is simply the total kinetic energy of the molecules

$\therefore$ Total Kinetic Energy $K = \sum_i^N \frac{1}{2} m |\underline{v}_i|^2$

But we don't know $\underline{v}_i$ for every particle and it would be impossible to measure! So we need to think statistically. What really matters to us is the ensemble average so we can say:

$$U = \langle K \rangle$$

where $\langle\ \rangle$ means "expected value" and U is internal energy

$$= \sum_i^N \frac{1}{2} m \langle |\underline{v}_i|^2 \rangle$$

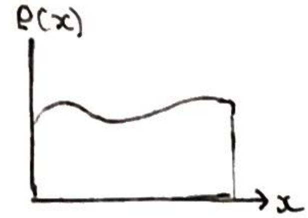
$$\therefore \boxed{U = \frac{1}{2} N m \langle |\underline{v}|^2 \rangle}$$

expectation value in this case:

$$\langle |\underline{v}|^2 \rangle = \int_{\mathbb{R}^3} |\underline{v}|^2 \rho(\underline{v})\, d^3v$$

A note on expectation values

For continuous random variables, the probability of a value x is given by the continuous probability distribution $\rho(x)$



Since the total probability of all scenarios must add up to 1, the total area under the graph must be 1:

$$\int_{-\infty}^{\infty} \rho(x)\,dx = 1$$

The probability that a random variable x will be found in an interval $[a, b]$ is given by:

$$P_{[a,b]} = \int_a^b \rho(x)\,dx$$

The probability of an infinitesimal interval $[x, x+dx]$ is:

$$P_{[x,x+dx]} = \int_x^{x+dx} \rho(x)\,dx = \rho(x)dx$$

Note that this $\to 0$ since it is physically impossible to be at an exact point in a continuous distribution.

The expectation value is simply the correct weighted average from a scenario. For a discrete distribution it is given by:

$$\langle x \rangle = \sum_i x_i P_i$$

where x_i is every measurement and P_i is the probability of that measurement.

For example, take the scenario: You roll a die. You get £12 if you roll a 6 and £0 otherwise. Or you can roll a die and get £3 if you roll 1, 2 or 3 and £0 otherwise. Which is better?

We can use expectation values to work this out.

For the first one: $\langle x \rangle = £0. \times \frac{5}{6} + £12 \times \frac{1}{6} = £2$

For the second: $\langle x \rangle = £3 \times \frac{1}{2} + £0 \times \frac{1}{2} = £1.50$

So the first is better!

For a continuous probability distribution, we can do the same thing but replace the sum by an integral and the probabilities by the probability distribution:

$$\langle x \rangle = \int x \rho(x)\, dx$$

The expectation value of a function is expressed in the same way:

$$\langle f \rangle = \int f(x) \rho(x)\, dx$$

The integration limits for both are given by the interval you are finding the expectation value for.

<u>Back to the topic</u>

From now on we will write $\langle |\underline{v}|^2 \rangle$ as $\langle v^2 \rangle$ for convenience:

$$U = \frac{1}{2} N m \langle v^2 \rangle$$

Remember that this is only valid within the assumptions of the Kinetic Theory of Gases since we are neglecting other energies such as rotational energy for poly-atomic molecules and attractive and repulsive forces between molecules.

example: What is the total internal energy in a balloon containing 10^{23} helium atoms if $v_{RMS} = 1300\,ms^{-1}$ and $m = 6.6 \times 10^{-27}\,kg$

v_{RMS} is the root mean square velocity defined as $v_{RMS} = \sqrt{\langle v^2 \rangle}$

So $U = \frac{1}{2} N m \langle v^2 \rangle = \frac{1}{2}(10^{23})(6.6 \times 10^{-27})(1300)^2$

$$= \underline{\underline{560\,J}}$$

Extensive and Intensive Quantities

The internal energy scales with the number of particles. For example, if a gas with a certain number of particles has energy U, then a gas with twice the number of particles has internal energy $2U$. Quantities that scale with the amount of material are called extensive quantities.

On the other hand, those that do not scale this way are called intensive, like Temperature. The ratio of extensive quantities is intensive.

Internal Energy and Vectors

You may have noticed that $\langle v^2 \rangle$ is the expectation value of the magnitude of a <u>vector</u> squared. But what if we are only given 1 component of the velocity vector?

$$\langle |v|^2 \rangle = \langle v_x^2 + v_y^2 + v_z^2 \rangle = \int_{\mathbb{R}^3} (v_x^2 + v_y^2 + v_z^2)\, \rho(v_x)\, \rho(v_y)\, \rho(v_z)\, dv_x\, dv_y\, dv_z$$

$$= \int_{-\infty}^{\infty} v_x^2 \rho(v_x)\, dv_x + \int_{-\infty}^{\infty} v_y^2 \rho(v_y)\, dv_y + \int_{-\infty}^{\infty} v_z^2 \rho(v_z)\, dv_z$$

$$= 3 \int_{-\infty}^{\infty} v_x^2 \rho(v_x)\, dv_x$$ since each component can be approximated to be equal

$$= 3 \langle v_x^2 \rangle$$

$$\therefore \text{Internal Energy } U = \frac{1}{2} Nm \langle v^2 \rangle = \frac{3}{2} Nm \langle v_x^2 \rangle$$