Kinetic Theory

Kinetic theory is one of the great achievements of physics and has led to both tremendous improvement in the quality of life and to advances in a wide range of physics fields.

Several theoretical models were posed in the 1800’s to explain the ideal gas law and eventually discrete. It was the Scottish physicist James Clerk Maxwell and Austrian physicist Ludwig Boltzmann who used the concept of the atom, statistics, and classical mechanics to correctly describe the properties of gases. However, their work remained controversial for several decades as the concept of the atom was not universally accepted among scientists until the 20th Century. Boltzmann who suffered from depression committed suicide in 1905 influenced by attacks upon his theory by German scientists. Unfortunately, he didn’t know that a young German physicist has published his PhD thesis in 1905 showing that Brownian Motion was due to the random motion of atoms. This result finally convinced the scientific community of the existence of atoms. The physicist’s name was Albert Einstein.

I. Derivation of the Ideal Gas Law

Assumptions:

1. Gas consists of large numbers of molecules
2. Molecules/atoms move in continuous random motion
3. Separation between molecules is large (Equivalent to low density)
4. Molecules do not act on one another at a distance (i.e. Free particles)
5. All collisions between molecules and molecules/wall are elastic (i.e. treat molecules like hard spheres)
Consider a cube with sides of length L containing a gas as shown:

The momentum in the x-direction of a particle about to strike the right-hand wall is

Since the wall is much more massive, the particle’s momentum in the x-direction after the collision is

Thus, the momentum transferred to the wall by the particle is

Using Newton’s second law, the force applied to wall is given by

The force at the wall will be changing rapidly as a large number of particles (say $10^{26}$) are striking it at various different times and at different speeds. Any macroscopic instrument used for measurement would not respond at this high rate and would measure an average force. Thus, the interaction
time can be considered to be the time between repeat collisions by the same molecule.

This gives us an average force by a single molecule as

To find the total force on the wall due to all molecules in the gas, we multiply the average force by the number of molecules, N.

Using the definition of pressure, we have the gas pressure as

But $L^3$ is the volume of the container so we can rearrange our result as
In general, a gas molecule will be moving in all three directions. Thus, the average kinetic of a molecule is

Since there is no preference for one direction over another, the averages of the square of the speed component in each direction must be equal. Thus, we have:

Substituting this relationship for kinetic energy into our gas result gives us

The gas’ only type of energy is kinetic energy so the average kinetic energy per molecule is the same thing as the internal energy per molecule of the gas.
The Zeroth Law of Thermodynamics hinted at a connection between temperature and the internal energy per molecule of a system. Comparing our results to the experimental work on gases, we now see what that connection is:

\[ T \text{ (Kelvin)} = \frac{\text{Temperature}}{\text{Absolute Scale}} \]

Temperature is a measure of the internal energy per molecule of a gas provided we use the Kelvin (absolute) temperature scale. No other scale has this physical meaning!!

When we measure \( T \) & \( N \), we are finding the internal energy of a gas without measuring the energy of each molecule individually!!

The ideal gas law doesn’t hold for all gases. Our results were based upon the assumption that the molecules were free except for when they collide and had no other energy storage modes like vibration or rotation. At higher densities, the particles interact and our derivation is not valid. This is why the ideal gas law fails in these situations. However, if we can model the forces in the system, we could always in principle always determine the equation of state for that system. Usually, we do the opposite. Experimental physicists determine experimentally the equation of state and theoretical physicists determine the interaction required to fit the data. This is how we discover atomic forces since we can’t build atomic force meters.
II. Speed Distribution

The molecules in a gas travel at a variety of speeds and velocities. Maxwell and Boltzmann worked out this physics.

A. Average Velocity

The average velocity of gas molecules is zero!!

B. Maxwell-Boltzman Distribution of Speeds

In statistics, we usually describe a distribution by the following quantities (average value, rms value (measure of spread), and most probably value).

C. Root Mean Square Speed - (RMS Speed)

Our kinetic theory enables us to calculate the rms speed

\[ v_{RMS} = \sqrt{\frac{3 k T}{2 m}} \]

This represents how much our speeds vary about the average speed.
D. Most Probable Speed

The most probably (likely) speed of a gas molecule is

\[ v_{mp} = \sqrt{\frac{2kT}{m}} \]

E. Average Speed

The average speed of a gas molecule is given by

\[ v_{av} = \sqrt{\frac{8kT}{\pi m}} \]