# 1. Kinetic Theory of Gases

This is a statistical treatment of the large ensemble of molecules that make up a gas. We had expressed the ideal gas law as:

$$pV = nRT \qquad (1)$$

where $n$ is the number of moles. We can also express it as:

$$pV = NkT \qquad (2)$$

where $N$ is the number of molecules and $k$ is *Boltzmann's constant* $k = R/N_A \approx 1.381 \times 10^{-23} \, J/K$.

A volume of air the size of a birthday balloon contains some $10^{23}$ molecules. The very large number of molecules allows us to treat gases using statistics, in which averages of quantities such as speed appear rather than their values for individual molecules.

# 2. Pressure and Molecular Motion

Consider a container of dilute gas that consists of $N$ independent molecules each of mass $m$. Pressure is due to molecular collisions with the walls of the container. We need to calculate the average rate of momentum transfer. Suppose we have a container in thermal equilibrium at temperature $T$ with volume $V$. The molecules are moving in random directions and the *average velocity of the molecules is zero* (as many are moving in one direction as the other). $\langle \mathbf{v} \rangle = 0$

$$\langle v_x \rangle = \langle v_y \rangle = \langle v_z \rangle \qquad (3)$$

While the average velocity is zero, the average speed is not zero. We will concentrate on $\sqrt{\langle v^2 \rangle}$ which is the *root mean square (rms) speed*.

The internal energy $U$ consists mainly of the kinetic energies of the molecules so

$$U = N \langle K \rangle = N \left( \frac{1}{2} m \langle v^2 \rangle \right) \qquad (4)$$

where $\langle K \rangle$ is the average kinetic energy per molecule and $N$ is the total number of molecules. The average of a sum of terms is the sum of the averages of those terms so

$$\langle v^2 \rangle = \langle v_x^2 + v_y^2 + v_z^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle \tag{5}$$

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle \tag{6}$$

So we can relate the average of the components of the velocity squared to the thermal energy of the gas:

$$\langle v^2 \rangle = 3 \langle v_x^2 \rangle \tag{7}$$

$$\langle v_x^2 \rangle = \frac{1}{3} \langle v^2 \rangle = \frac{2}{3} \frac{U}{mN} \tag{8}$$

**2a.** *The Origin of Pressure*

Pressure arises from the multiple collisions the molecules of a gas have with the walls that contain the gas. First we compute the momentum transfer to a wall due to a single collision, and then find the number of molecules that strike the wall per unit time. A molecule colliding elastically with the right-hand wall of a box, only the x-component of velocity changes so the velocity before collision is:

$$\vec{v_i} = v_x \hat{i} + v_y \hat{j} + v_z \hat{k} \tag{9}$$

the velocity after collision is:

$$\vec{v_f} = -v_x \hat{i} + v_y \hat{j} + v_z \hat{k} \tag{10}$$

The momentum change of the molecule $\Delta \vec{P}_{mol}$ is

$$\Delta \vec{P}_{mol} = m\vec{v_f} - m\vec{v_i} = -2mv_x \hat{i} \tag{11}$$

and the momentum transfer to the wall is

$$\Delta \vec{P} = 2mv_x \hat{i} \tag{12}$$

The number of collisions with the wall that occur per unit time is calculated as follows. Consider the number of molecules that with an x-component velocity $v_x$

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that strike an area $A$ in a time interval $dt$ is the number of molecules contained in an imaginary cylinder whose base is against the wall of area $A$ and length $v_x dt$. If the number of molecules per unit volume is $N/V$, the total number of molecules in the cylinder is $(N/V(v_x dt)A$ and the number of collisions in time $dt$ will be half this number as $1/2$ of the molecules are moving to the right and $1/2$ to the left.

$$N_{coll} = \frac{1}{2}\frac{N}{V}(v_x dt)A \tag{13}$$

We can multiply this by the individual collision momentum transfer to find the momentum $dP_x$ transferred in time $dt$.

$$dP_x = (2mv_x)\left(\frac{1}{2}\frac{N}{V}(v_x dt)A\right) = mv_x^2 \frac{N}{V}A dt \tag{14}$$

The force exerted on the area $A$ is

$$\frac{dP_x}{dt} = F_x = mv_x^2 \frac{N}{V}A \tag{15}$$

and the pressure on the wall $p$ is the force per unit area

$$p = \frac{F_x}{A} = mv_x^2 \frac{N}{V} \tag{16}$$

Finally, recall that we have employed the average x-component of velocity squared for each molecule. We make this explicit by employing the notation $\langle v_x^2 \rangle$ and find

$$p = m\langle v_x^2 \rangle \frac{N}{V} = m\left(\frac{2U}{3mN}\right)\frac{N}{V} = \frac{2}{3}\frac{U}{V} \tag{17}$$

$$pV = \frac{2}{3}U \tag{18}$$

This is an important derivation, as we have used the microscopic properties of a gas to find a relation between macroscopic thermodynamic variables.

## 2b. *The Meaning of Temperature*

The fact that the energy is the sum of the kinetic energy of all the molecules $U = \frac{1}{2}M, \langle v^2 \rangle$, and the fact that energy is related to pressure $U = (3/2)pV$ provides a link to temperature.

$$U = \frac{3}{2}nRT = \frac{3}{2}NkT \qquad (19)$$

to give the microscopic interpretation of temperature:

$$kT = \frac{2}{3}\frac{U}{N} = \frac{2}{3}\langle K \rangle \qquad (20)$$

*The temperature of an ideal gas is a measure of the average kinetic energy of the constituents.* Because the number of molecules canceled, $T$ is independent of the amount of gas.

note: absolute zero in the Kelvin scale is the point at which the pressure drops to zero. In the microscopic view of an ideal gas, the temperature is zero when the average kinetic energy of the ideal gas is zero. Pressure vanished because the molecules no longer mover around and bounce against the walls.

**2c.** *Specific Heat of the Perfect Gas*

We will consider the energy and specific heat at vanishing density (perfect gases). The energy of the molecules of a gas can be divided into:

1. Translatory kinetic energy

2. Rotational kinetic energy

3. Energy of vibration of atoms relative to center of mass of whole molecule

4. Mutual potential energy (not relevant for ideal gasses)

**i. Equipartition** The total average energy per molecule depends on how many independent motions a molecule can have.

**Point mass** Energy has three terms propotional to $v_x^2, v_y^2$ and $v_z^2$

**Diatomic** With rotational inertia about axes $x$ and $y$ we have two new terms in the energy (making it five).

**Vibration** Brings two more terms related to the relative speed of the atomic constituents and separation (making it seven).

Every term in the energy expression that is quadrati in an independent dynamical variable designates a *degree of freedom. The contribution of each degree of freedom to the average energy of a molecule is $kT/2$. This is the equipartition theorem.*

$$\langle E \rangle = \frac{s}{2}kT \tag{21}$$

and E can contain contributions associated with translation, rotation and vibration.

**Translatory Energy**  $U = U_t$ and in specific quantities $u = u_t = \frac{3}{2}kT = \frac{3}{2}RT$.
This is exactly the same as the example we had done above.

$$u = \frac{3}{2}RT \tag{22}$$

$$c_v = \frac{3}{2}R \tag{23}$$

$$c_p = R + c_v = \frac{5}{2}R \tag{24}$$

$$\gamma = c_p/c_v = 5/3 \tag{25}$$

Helium, Neon Argon, Krypton, Xenon.

**Rotational Energy**  For *two atoms* rigidly united we have two more degrees of freedom $u = u_t + u_r = \frac{5}{2}kT = \frac{5}{2}RT$

$$u = \frac{5}{2}RT \tag{26}$$

$$c_v = \frac{5}{2}R \tag{27}$$

$$c_p = R + c_v = \frac{7}{2}R \tag{28}$$

$$\gamma = c_p/c_v = 7/5 \tag{29}$$

$H_2, HCl, N_2, CO, O_2, NO$

For *three atoms* rigidly united we have three more degrees of freedom $u =$

$$u_t + u_r = 3kT = 3RT$$

$$
\begin{align}
u &= 3RT \tag{30} \\
c_v &= 3R \tag{31} \\
c_p &= R + c_v = 4R \tag{32} \\
\gamma &= c_p/c_v = 4/3 \tag{33}
\end{align}
$$

However, classical theory breaks down for this.

**Vibration**  For the temperatures of our atmosphere, we will not deal with this.

## 2d.  *Velocity Distribution of Gases*

We define the velocity distribution function $F(\vec{v})$ as the probability distribution for the velocities of the gas molecules. The probability of finding any particular velocity $\vec{v}$ is zero, so we start with a number distribution $N(\vec{v})$ such that $N(\vec{v})d^3v=$ number of molecules between $\vec{v}$ and $\vec{v} + d\vec{v}$ and $d^3v = dv_x dv_y dv_z$.

The total number of molecules is $N$ so that

$$\int N(\vec{v})d^3v = N \tag{34}$$

The probability distribution $F(\vec{v}) = \frac{1}{N}N(\vec{v})$, is defined such that $F(\vec{v})d^3v=$ is the probability that a gas molecule velocity is between $\vec{v}$ and $\vec{v} + d\vec{v}$. From here we can calculate the average velocity squared:

$$\langle v^2 \rangle = \int v^2 F(\vec{v})d^3v \tag{35}$$

To determine $F(\vec{v})$ we make the assumption that *any way in which a gas's total energy and total momentum (which is zero) can be shared among the molecules is equally likely*. When this is assumed, the distribution function is found to be:

$$F(\vec{v}) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT} \tag{36}$$

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# 3. Collisions and Transport Phenomena

Molecules follow a tortuous path in their container, colliding with one another and the walls. At STP an air molecule undergoes billions of collisions per second, but the average distance a molecule travels between collisions is a statistical quantity that can be calculated. By these collisions, molecules can carry thermal energy, odor, etc. The movement of molecules by random collisions is called diffusion. Molecules of diameter $D$ collide when the path of the center of one molecule lies within an area $\pi D^2$ presented by the second molecule. The area is the *collision cross section* $\sigma$. $\sigma = \pi D^2$.

A molecule that moves with speed $v$ and sweeps out an area $\sigma$ sweeps out a volume $V = \sigma d = \sigma v t$ in a time $t$. However, the molecule is not alone and encounters $N$ collisions, but even if the path is bent, the volume $V$ remains unchanged. There are on average a collision every $\tau = t/N$ seconds. $\tau$ is the *mean collision time*. Averaging over many molecules we replace $v$ with $v_{rms}$.

$$\tau = \frac{t}{N} = \frac{t}{nV} = \frac{t}{n\sigma v_{rms} t} = \frac{1}{n\sigma v_{rms}} \tag{37}$$

where $n = N/V$ is the number density (not the number of moles). A more precise calculation takes into account the fact that the other molecules are also moving

$$\tau = \frac{1}{\sqrt{2} n \sigma v_{rms}} \tag{38}$$

The average distance that a molecule travels before it is involved in a collision is the *mean free path* $\lambda$ where

$$\lambda = \tau v_{rms} = \frac{1}{\sqrt{2} n \sigma} \tag{39}$$

$\lambda$ is inversely proportional to both the density and the collision cross section.

**3a.** *Random Walk and Diffusion*

Molecules move through a gas by diffusion. The average distance moved by a molecule is similar to the *random walk* problem (or drunkard's walk). In this problem, a drunkard starts at a lamppost and takes steps that are equal in length but random in direction. We can find the average displacement of the molecule after

$N$ steps as follows. Let the successive displacements be $\vec{L}_1, \vec{L}_2...\vec{L}_n$ all of random directions but magnitude $L$. After $N$ steps the displacement of the molecule is $\vec{R}_N = \vec{L}_1 + \vec{L}_2 + ... + \vec{L}_n$. Squaring this quantity we have:

$$R_N^2 = L_1^2 + L_2^2 + ... + L_N^2 + 2\vec{L}_1 \cdot \vec{L}_2 + 2\vec{L}_1 \cdot \vec{L}_3 + ... + 2\vec{L}_{N-1} \cdot \vec{L}_N \qquad (40)$$

In the *averaging* process, all the dot products have an average value over time of zero, whereas the squared terms are equal to $L^2$.

$$\langle R_N^2 \rangle = NL^2 \qquad (41)$$

Connecting this with the properties of a gas. $L^2 = \lambda^2$, after $N$ steps the time is $t = \tau N$

$$\langle r^2 \rangle = \frac{t}{\tau}\lambda^2 \qquad (42)$$

It is typical in random walk problems that the displacement *squared* is linear in time or that the displacement is proportional to the square root of the time.