Kinetic Theory of Gases

Chapter 33

Kinetic theory of gases envisions gases as a collection of atoms or molecules in motion. Atoms or molecules are considered as particles. This is based on the concept of the particulate nature of matter, regardless of the state of matter.

A particle of a gas could be an atom or a group of atoms (molecule).

The Kinetic Theory relates the 'micro world' to the 'macro world'.

http://www.chemtutor.com/sta.htm

The Kinetic Theory relates the 'micro world' to the 'macro world'.

http://www.chemtutor.com/sta.htm

Postulates

Gas particles are very far apart.

Gas particles in constant random motion.

Gas particles do not exert forces on each other due to their large intermolecular distances.

Pressure in a gas is due to particle collisions (elastic) with the walls of the container from translational motion - the microscopic explanation of pressure.

Collisions with the wall are elastic, therefore, *translational energy* of the particle is conserved with these collisions.

Each collision imparts a linear *momentum* to the wall, which *results the gaseous pressure*. In Newtonian mechanics *force* defined as the change of momentum, here, due to the collision; *pressure* is force per unit area.

In KT, the pressure arising from the collision of a single molecule at the wall is derived and then scaled up to the collection of molecules in the container, to obtain the ideal gas law (IGL);

\[ PV = nRT \]
Gas kinetic theory derives the relationship between root-mean-squared speed and temperature.

The particle motions are random, therefore velocities along all directions are equivalent. Therefore the average velocity (vector) along any dimension/direction will be zero.

Now, the root-mean-squared velocity = root-mean-squared speed; it is nonzero.

A distribution of translational energies; therefore, many velocities would exist for a collection of gaseous particles.

What is the distribution of the particle velocities?

Root mean square velocity, translational energy:

\[
\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle
\]

By definition

\[
\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle
\]

Random motion

Therefore,

\[
\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle
\]

\[
\langle v_x^2 \rangle = \frac{3}{3} \langle v_x^2 \rangle
\]

Using

\[
\langle v_x^2 \rangle = \frac{1}{2} \frac{k_T m}{2}
\]

Remember

\[
m \langle v_x^2 \rangle = k_T T
\]

\[
m \langle v_x^2 \rangle = k_T T
\]

Number density of particles = \( \bar{N} = \frac{n N_A}{V} \)

where \( N_A = \) Avagadro Number

Half of the molecules moving on x axis with a (velocity component in the x direction) within the volume \( v_x \Delta t \) collides with one surface in the x direction.

\[
N_{\text{coll}} = \bar{N} \times (Av_x \Delta t) \left( \frac{1}{2} \right) = \frac{n N_A}{V} (Av_x \Delta t) \left( \frac{1}{2} \right)
\]

\( N_{\text{coll}} \) = number of collisions on the wall of area A in time \( \Delta t \).
Change of momentum on a surface during $\Delta t =$

\[ \Delta p_{\text{total}} = (2m v_x) (N_{\text{coll}}) \]

Force on the surface = Rate of change of momentum =

\[ F = \frac{\Delta p_{\text{total}}}{\Delta t} = \frac{nN_A}{V} Am(v_x^2) \]

Pressure = Force per unit area =

\[ P = \frac{F}{A} = \frac{nN_A}{V} m(v_x^2) \]

Pressure arises because of the molecular motion of gases; microscopic/molecular model of pressure.

The fact that component velocities of all molecules are not the same, necessitates the definition of an average in each direction.

Thus $v_j$ arises because of a probability distribution of $v_j$ values $f(v_j)$ in each direction ($j = x, y, z$)

\[ \Omega(v_x, v_y, v_z) = f(v_x)f(v_y)f(v_z) \]

velocity distribution function

Being a probability function,

\[ \int_{all v_j} f(v_j)dv_j = 1 \]

Derivation of distribution functions $f(v_j)$

\[ \ln \Omega(v_x, v_y, v_z) = \ln f(v_x) + \ln f(v_y) + \ln f(v_z) \]

\[ \ln \Omega(v_x, v_y, v_z) = \ln f(v_x) + \ln f(v_y) + \ln f(v_z) \]

\[ \frac{\partial \ln \Omega(v)}{\partial v_x} = \frac{d \ln f(v_x)}{dv_x} \]

\[ \frac{\partial \ln \Omega(v)}{\partial v_y} = \frac{d \ln f(v_y)}{dv_y} \]

\[ \frac{\partial \ln \Omega(v)}{\partial v_z} = \frac{d \ln f(v_z)}{dv_z} \]

Chain rule

Math supplement
Similarly
\[ \frac{d \ln \Omega(v)}{v d v} = \frac{d \ln f(v)}{v d v} \]

\[ \frac{d \ln \Omega(v)}{v_1 d v_1} = \frac{d \ln f(v_1)}{v_1 d v_1} \]

\[ \frac{d \ln \Omega(v)}{v_2 d v_2} = \frac{d \ln f(v_2)}{v_2 d v_2} \]

\[ \frac{d \ln \Omega(v)}{v_3 d v_3} = \frac{d \ln f(v_3)}{v_3 d v_3} \]

In general
\[ \frac{d \ln f(v_j)}{v_j d v_j} = \frac{df(v_j)}{v_j f(v_j) d v_j} = -\gamma \quad \text{for } j = x, y, z \]

Because derivatives of three independent variables are equal, the derivatives must be constant, say \( \gamma \) \((\gamma > 0)\).

Upon rearrangement and integration,
\[ \int \frac{df(v_j)}{f(v_j)} = -\int \gamma v_j d v_j \]

\[ \ln f(v_j) = -\frac{1}{2} \gamma v_j^2 \]

\[ f(v_j) = A e^{-\gamma v_j^2/2} \]

where \( A \) = integration constant

Note the distribution (probability) function!

Evaluating \( A \):

\[ \int_{-\infty}^{\infty} f(v_j) d v_j = 1 = \int_{-\infty}^{\infty} A e^{-\gamma v_j^2/2} d v_j \]

\[ 1 = 2A \int_{0}^{\infty} e^{-\gamma v_j^2/2} d v_j \]

\[ 1 = A \sqrt{\frac{2 \pi \gamma}{2 \pi \gamma}} \]

\[ \sqrt{\frac{\gamma}{2 \pi}} = A \quad \text{Math supplement} \]

\[ f(v_j) = \left( \frac{\gamma}{2 \pi} \right)^{1/2} e^{-\gamma v_j^2/2} \]

Distribution function: probability of a gas particle having a velocity within a given range, e.g. \( v_x \) and \( v_x + dv_x \).

\[ \langle v_x^2 \rangle = \frac{kT}{m} = \frac{1}{2} \left[ \int_{-\infty}^{\infty} v_x^2 f(v_x) d v_x \right] \quad \text{averaging} \]

\[ = \frac{1}{\sqrt{2 \pi \gamma}} \int_{-\infty}^{\infty} v_x^2 e^{-\gamma v_x^2/2} d v_x \]

\[ = \frac{1}{\sqrt{2 \pi \gamma}} \left[ \frac{2 + \gamma^2}{2 \pi \gamma} \right] \quad \text{use tables} \]

\[ = \frac{1}{\sqrt{2 \pi \gamma}} \left( \frac{2 + \gamma^2}{2 \pi \gamma} \right) \quad \text{Math supplement} \]

\[ = \frac{m}{\gamma} = \frac{kT}{\gamma} \]

Mean/average

\[ \langle v_x^2 \rangle = \frac{kT}{m} = \frac{1}{2} \left( \frac{m}{2 \pi \gamma} \right)^{1/2} \quad \text{where } \gamma = \frac{m}{kT} \]

Substituting for \( \gamma \) in \( f(v_j) \);

\[ f(v_j) = \left( \frac{m}{2 \pi kT} \right)^{1/2} e^{-mv_j^2/2kT} = \left( \frac{M}{2 \pi RT} \right)^{1/2} e^{(-Mr_j^2)/2RT} \]

\[ M = \frac{m}{kT} \]

\[ 2.0 \times 10^3 \text{ molecules/particle} \]

\[ 0.001 \text{ s}^{-1} \]

\[ 0.000 \text{ s}^{-1} \]
Deriving the distribution function for $v$

$$v = \left( v_x^2 + v_y^2 + v_z^2 \right)^{1/2}$$

Changing the 'volume' element (in Cartesian) to variable $v$, spherical coordinates.

replace $dv_x dv_y dv_z$ by $4\pi v^2 dv$

and $v_x^2 + v_y^2 + v_z^2$ by $v^2$

$$F(v) \, dv = \frac{4\pi}{(2\pi kT)^{3/2}} \frac{m^{3/2}}{\sqrt{\pi}} e^{-mv^2/(2kT)} \, dv$$

$$F(v) \, dv = \frac{4\pi}{(2\pi RT)^{3/2}} \frac{M^{3/2}}{\sqrt{\pi}} e^{-Mv^2/(2kT)} \, dv$$

Notice the shape, blue. $v_{ave}$'s of Xe, H$_2$, He? Earth and Jupiter ($\times300$)
Notice the shape, blue.

\[ v_{\text{ave}} \] of Xe, H\(_2\), He?

Earth and Jupiter \((\times 300)\)

At lower angular velocities slower moving molecules go through the second slit.

Detector signal proportional to the number of particles reaching the detector.

**Most probable velocity** \(v_{\text{mp}}\):

\[
F(v) \, dv = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \nu^2 e^{-m\nu^2/2kT} \, dv
\]

Most probable velocity \(v_{\text{mp}}\): differentiate \(F(v)\), set to zero.

\[
2v_{\text{mp}} - \frac{mv_{\text{mp}}^2}{kT} = 0
\]

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

**Mean (average) velocity:**

\[
v_{\text{ave}} = \langle v \rangle = \int_0^\infty \nu F(\nu) \, d\nu
\]

\[
= \int_0^\infty \nu \left( 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \nu^2 e^{-m\nu^2/2kT} \right) \, d\nu
\]

\[
= 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \int_0^\infty \nu^2 e^{-m\nu^2/2kT} \, d\nu
\]

\[
= 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \left( \frac{2kT}{m} \right)^{1/2}
\]

\[
v_{\text{ave}} = \left( \frac{8kT}{\pi m} \right)^{1/2} = \left( \frac{8RT}{\pi M} \right)^{1/2}
\]

**Root mean square velocity:**

Using: \(\langle v^2 \rangle = \frac{kT}{m}\) \hspace{1cm} (Assumption slide 4)

and \[
\sqrt{\langle v^2 \rangle} = \sqrt{3 \langle v^2 \rangle} = v_{\text{rms}}
\]

\[
v_{\text{rms}} = \left( \langle v^2 \rangle \right)^{1/2} = \left( \frac{3kT}{m} \right)^{1/2} = \left( \frac{3RT}{M} \right)^{1/2}
\]
Particle collision rates: (Hard sphere model)

Particles interact when spheres attempt to occupy the same region of the phase. (consider one moving particle – orange, label 1; all other particles stationary are red – label 2

\[ \sigma = \pi (r_1 + r_2)^2 \]

\[ \sigma = \text{collisional cross-section.} \]

Because the collisional ‘partners are moving too’ in reality, an “effective speed”, \( <v_{12}> \), of orange particle will be considered in the model to emulate the collisions the orange particle encounters;

\[ \langle v_{12} \rangle = (\langle v_1 \rangle^2 + \langle v_2 \rangle^2)^{1/2} \]
Because the collisional partners are moving, an effective speed \( v_{12} \) used to model the system:

\[
\langle v_{12} \rangle = \left( \langle v_1 \rangle^2 + \langle v_2 \rangle^2 \right)^{1/2} = \left( \frac{8kT}{\pi m_1} + \frac{8kT}{\pi m_2} \right)^{1/2} \\
= \frac{8kT}{\pi} \left( \frac{1}{m_1} + \frac{1}{m_2} \right)^{1/2} \\
= \left( \frac{8kT}{\pi \mu} \right)^{1/2} \\
\mu = \frac{m_1 m_2}{m_1 + m_2} \text{; reduced mass}
\]

Collisional partner (red) density = \( \frac{N_2}{V} \)

Volume covered by orange in \( dt = V_{cyl} \)

\( V_{cy} = \sigma v_{12} dt \)

Collisions by it in time \( dt = V_{coli} \left( \frac{N_2}{V} \right) \)

Particle collisional frequency of it = \( z_{12} \)

\[ z_{12} = \frac{N_2 (V_{coli})}{V \left( \sigma v_{12} dt \right)} = \frac{N_2}{V} \left( \frac{\sigma v_{12} dt}{\sigma} \right) = \frac{N_2}{V} \left( \frac{8kT}{\pi \mu} \right)^{1/2} \]

For a sample of one type of gas:

\[ z_{11} = \frac{N_1}{V} \sqrt{\frac{2}{\pi m_1}} \left( \frac{8kT}{\pi m_1} \right)^{1/2} = \frac{P_1 N_A}{RT} \left( \frac{8kT}{\pi M_1} \right)^{1/2} \]

Total collisional frequency, two types of gases \( Z_{12} \):

\[ Z_{12} = Z_{11} \]

\[ Z_{11} = \frac{N_1}{V} z_{11} = \frac{1}{\sqrt{2}} \left( \frac{N_1}{V} \right)^{1/2} \left( \frac{8kT}{\pi m_1} \right)^{1/2} = \frac{1}{\sqrt{2}} \left( \frac{P_1 N_A}{RT} \right)^{1/2} \left( \frac{8kT}{\pi M_1} \right)^{1/2} \]

Accounts for double counting

<p>| TABLE 33.1 Collisional Parameters for Various Gases |</p>
<table>
<thead>
<tr>
<th>Species</th>
<th>( r ) (nm)</th>
<th>( \sigma ) (nm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.13</td>
<td>0.21</td>
</tr>
<tr>
<td>Ne</td>
<td>0.14</td>
<td>0.24</td>
</tr>
<tr>
<td>Ar</td>
<td>0.17</td>
<td>0.36</td>
</tr>
<tr>
<td>Kr</td>
<td>0.20</td>
<td>0.52</td>
</tr>
<tr>
<td>N₂</td>
<td>0.19</td>
<td>0.43</td>
</tr>
<tr>
<td>O₂</td>
<td>0.18</td>
<td>0.40</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.20</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Mean Free Path:

Average distance a particle would travel between two successive collisions two types of molecules, say 1 and 2.

\[ \lambda = \frac{\nu_{ave} dt}{(z_{11} + z_{12}) dt} = \frac{\nu_{ave}}{(z_{11} + z_{12})} \]

For one type of molecules,

\[ \lambda = \frac{\nu_{ave}}{z_{11}} = \frac{\nu_{ave}}{\left( \frac{N_1}{V} \right)^{1/2} \sqrt{2 \sigma \nu_{ave}}} = \left( \frac{RT}{P_1 N_A} \right) \left( \frac{1}{\sqrt{2 \sigma}} \right) \]

Effusion:

Effusion is the process in which a gas escapes through a small aperture. This occurs if the diameter of the aperture is considerably smaller than the mean free path of the molecules (effusion rate = number of molecules that pass through the opening (aperture) per second). Once the particle passes through it generally wont come back because of the low partial pressure on the other side.

Pressure of the gas and size of the aperture is such the molecules do not undergo collisions near or when passing through the opening.
Effusion rate decreases with time because of the reduction in gas pressure inside the container due to effusion/diffusion.

\[
\frac{dP}{dt} = \frac{d}{dt} \left( \frac{NkT}{V} \right) = \frac{kT}{V} \frac{dN}{dt}
\]

And rate of loss of molecules

\[
\frac{dN}{dt} = -ZcA = \frac{-PA}{(2\pi m kT)^{1/2}}
\]

Collisional Flux \( Z_c \):

\[ Z_c = \text{number of collisions per unit time per unit area, by one type of molecule; definition.} \]

\[ Z_c = \frac{dN_c}{dt} = \frac{1}{4} \bar{N}v_{ave} \]

\[ v_{ave} = \left( \frac{8kT}{\pi m} \right)^{1/2} \]

Note: \( \bar{N} = \frac{N}{V} = \frac{nN_A}{V} = \frac{P}{kT} \) using IGL

Upon substitution for \( v_{ave} \), \( \bar{N} \) and simplification;

\[ Z_c = \frac{P}{(2\pi m kT)^{1/2}} = \frac{PN_A}{(2\pi MRT)^{1/2}} \]

Integration yields;

\[ P = P_0 \exp \left[ -\frac{Am}{V} \left( \frac{kT}{2\pi m} \right)^{1/2} \right] \]

\[ f(v_j) = \left( \frac{m}{2\pi kT} \right)^{1/2} e^{-mv_j^2/2kT} = \left( \frac{M}{2\pi RT} \right)^{1/2} e^{-Mv_j^2/2RT} \]
\[ f(-v_{i0} \leq v_i \leq v_{i0}) = \frac{1}{\sqrt{\pi}} \int_{-v_{i0}}^{v_{i0}} e^{-\xi^2} d\xi \]

\[ \text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_{0}^{z} e^{-t^2} dt = f(-z \leq v_i \leq z) \]

\[ \xi^2 = \frac{mv_i^2}{2kT} \quad \text{at} \quad v_i = v_{i0} = \sqrt{2kT/m} \]

\[ \xi^2 = \frac{mv_{i0}^2}{2kT} = 1 \quad \xi = 1 \]

\[ \text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_{0}^{z} e^{-t^2} dt \]

\[ \text{erf}(1) = \frac{2}{\sqrt{\pi}} \int_{0}^{1} e^{-t^2} dt = 0.8427 \]

Covers \( v_i \leq \sqrt{2kT/m} \)

Probability \( v_i > \sqrt{2kT/m} \)