Kinetic Theory of Gases

- Everything up to this point has been empirical
  - There is clearly a great deal of truth in the equations
  - However, there is no physical picture
- To gain insight, one must develop and validate models
- We look at a molecular (kinetic theory of gases) model to begin that process.
- We begin that process today
HCl and NH₃ gases at the same temperature and pressure are introduced at opposite ends of a glass tube. A ring of solid NH₄Cl forms where the two gases meet inside the tube.

\[
\text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4\text{Cl}
\]

Where will the ring form?

A. At the center
B. Closer to the HCl end
C. Closer to the NH₃ end
Three Postulates of Kinetic Theory of Gases

1. Gas composed of hard spherical particles that are small relative to the mean distances between them.

2. Particles are in constant motion and have kinetic energy.

3. Neither attractive nor repulsive forces exist between the particles except on contact (collision).
ConcepTest #2

Which of the following gases deviates most from the postulates of kinetic molecular theory? (i.e., deviates most from ideal gas behavior)

A. He
B. H₂
C. N₂
D. NH₃
E. CH₄
Kinetic-Molecular Theory

Consistent with Ideal Gas Law, Dalton’s Law, Graham’s Law and many other observations
Consider a molecule colliding elastically with a wall.
Relationship between Force and Change of Momentum

Momentum, \( p = mv \)
\[ F = ma = m \frac{dv}{dt} = d(mv)dt = dp/dt \]

What is change of velocity on each collision?
\[ \Delta v = v_{\text{final}} - v_{\text{initial}} = v_x - (-v_x) = 2v_x \]

What is change of momentum on each collision?
\[ \Delta p = 2v_x m \]
Collision rate for one molecule with a wall

Box with dimensions x by y by z

Number of collisions in time $\Delta t = \frac{v_x \Delta t}{2x}$

Number of collisions per unit time $= \frac{v_x}{2x}$
Force (momentum change) per Unit Time for One Particle

\[ F = ma = \frac{d\mathbf{p}}{dt} = (\text{Change of Momentum per Collision}) \times (\text{Number of Collisions per Unit Time}) \]

\[ \frac{d\mathbf{p}}{dt} = F_x = (2v_x m)(v_x/2x) \]

\[ = \frac{mv_x^2}{x} \]

This is the force exerted on the wall by one particle.
Pressure is Force per Unit Area

\[ P_x = \frac{F_w}{A} = \frac{F_x}{yz} \]

\[ F_x = (2v_x, m) \left( \frac{v_x}{2x} \right) = \frac{mv_x^2}{x} \]

\[ P_x = \frac{mv_x^2}{xyz} \]

\[ P_x = \frac{mv_x^2}{V} \]
What changes are required when N molecules and a distribution of velocities are considered?

\[ P_x = \frac{mv_x^2}{V} \]

Multiply by N
Replace \( v_x^2 \) with \( \langle v_x^2 \rangle \)

\[ P_x = P_y = P_z = P \text{ implies} \]

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

and

\[ P_x = m\langle v_x^2 \rangle / V \rightarrow P = Nm\langle v^2 \rangle / 3V \]
Fundamental Equation from Simple Kinetic Theory of Gases

\[ PV = Nm\langle v^2 \rangle / 3 \]

Parallels the ideal gas law:

\[ PV = nRT \]

\[ nRT = \frac{Nm\langle v^2 \rangle}{3} \]

\[ \langle v^2 \rangle = \frac{3RT}{M} \]

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

with \( M \) (molar mass) = \( mN / n \)
At a given temperature, which of the following gases has the smallest $v_{rms}$?

A. He
B. $\text{H}_2$
C. $\text{N}_2$
D. $\text{NH}_3$
E. $\text{CH}_4$
Connection between Kinetic Energy & Temperature

Average Kinetic Energy per Molecule

\[ \langle \varepsilon \rangle = \frac{1}{2} m \langle v^2 \rangle \]

Substitute this expression into the pressure equation to obtain the relationship between kinetic energy and \( T \):

\[ E_k = \frac{3}{2} RT \text{ (per mole)} \quad \text{or} \]

\[ \langle \varepsilon_k \rangle = \frac{3}{2} k_B T \text{ (per molecule)} \]
Flask A contains 8 g H₂, and Flask B contains 8 g He. The flasks have the **same volume and temperature**. Compare the gas density (g/cm³), the kinetic energy per mole, and the total kinetic energy of the gases in the two flasks.

<table>
<thead>
<tr>
<th>Density</th>
<th>( E_k / n )</th>
<th>Total KE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. ( A &gt; B )</td>
<td>( A &gt; B )</td>
<td>( A &gt; B )</td>
</tr>
<tr>
<td>B. ( A &gt; B )</td>
<td>( A = B )</td>
<td>( A &gt; B )</td>
</tr>
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<td>C. ( A = B )</td>
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Collisions Between Molecules

Molecule A travels with velocity $v_A$ in a container of B molecules.

Collision will occur each time the distance between the center of molecule A and molecule B is $\leq d_{AB}$

where $d_{AB} = (d_A + d_B)/2$

$d_A = \text{molecule A diameter}$

$d_B = \text{molecule B diameter}$

$d_{AB} = \text{collision diameter for AB collisions}$
The collision frequency $Z_A$ for one $A$ molecule with $N_B B$ is

$$Z_A = \pi d_{AB}^2 \langle v_A \rangle N_B / V, \ s^{-1}$$
Going from one A molecule to \( N_A \) A molecules/cm\(^3\)

When we have a density \( N_A/V \) of A molecules, we express the total rate of A-B collisions as

\[
Z_{AB} = \frac{\pi d_{AB}^2 v_A N_A N_B}{V^2} \text{s}^{-1} \text{cm}^3
\]

\( Z_{AB} \) is the Collision Density

We have still ignored the fact that the B molecules are moving. Thus we need to replace \( v_A \) with the average relative speed between A and B, \( \langle v_{rel} \rangle \).

So

\[
\langle v_{rel} \rangle = \left( \langle v_A \rangle^2 + \langle v_B \rangle^2 \right)^{\frac{1}{2}}
\]
Getting the correct relative collision speeds

Using this information we go back to correct the expression for the number of collisions per sec of one molecule of A with B molecules with density $N_B/V$.

$$Z_A = \frac{\pi d_{AB}^2 \left( \left\langle v_A \right\rangle^2 + \left\langle v_B \right\rangle^2 \right)^{\frac{1}{2}}}{V} N_B$$

and the A-B collision density for $N_A/V$ molecules with $N_B/V$ is

$$Z_{AB} = \frac{\pi d_{AB}^2 \left( \left\langle v_A \right\rangle^2 + \left\langle v_B \right\rangle^2 \right)^{\frac{1}{2}}}{V^2} N_A N_B$$
Consider collisions only between A molecules.

We found $Z_A = \frac{\pi d_{AB}^2 \langle v_A \rangle N_B}{V} \quad s^{-1}$ for a single A molecule with B molecules.

If the B molecules become A's and are allowed to move, then $\langle v_A \rangle \rightarrow \left( \langle v_A \rangle^2 + \langle v_A \rangle^2 \right)^{\frac{1}{2}} = \sqrt{2} \langle v_A \rangle$ and $d_{AB}^2$ becomes $d_A^2$.

So for a one component gas,

Collision frequency $Z_A = \frac{\sqrt{2} \pi d_A^2 \langle v_A \rangle N_A}{V} \quad s^{-1}$

and the collision density $Z_{AA} = \frac{\sqrt{2} \pi d_A^2 \langle v_A \rangle N_A^2}{2V^2} \quad m^{-3} s^{-1}$
Consider a gas of $A$ molecules with average speed $\langle v_A \rangle$ and number density $n_A = N_A/V$. One can show (but we will not) that the flux, $F$, of molecules passing in one direction through a plane of unit area is given by

$$F = \frac{n_A \langle v_A \rangle}{4} \text{ molecules cm}^{-2} \text{s}^{-1}$$

This is a very useful relation to remember, but here we wish to focus on the average velocity, and see if we can understand the basis for the molecular speed distribution that seems ubiquitous.

There is a key, universal, fundamental concept:

Mother Nature does not play favorites, but rather selects in an unbiased manner from the allowed outcomes.
Mother Nature’s choices

One example of this is that a gas will uniformly fill a box that is free of any external forces. If there are external forces (such as gravity), the gas assumes an exponential distribution of the form

\[ N(z) = e^{\frac{mgz}{mgz_o}} \]

where \( mgz_o \) is a sort of average gravitational potential and \( z_o \) is a “scale height” of the gas.

We see this characteristic form of an energy relation virtually everywhere: rates of reaction, energy distributions of gas particles . . . How does it arise?
Possible arrangements of particles with fixed total energy

While the real systems of interest typically have \(~N_A\) particles, we illustrate the concept on an embarrassingly small, but simple, system.

Consider a system comprised of 4 particles. Any particle can have only discrete energies: \(E = 0, 1, 2, 3, 4 \ldots\) (quantized). Let the total energy of the system be 3.

What is the average energy per particle, \(\langle E \rangle\)?

A. 3
B. 4
C. 0.75
D. 12
E. Not enough information given
Consider a system comprised of 4 particles. Any particle can have only discrete energies: \( E = 0, 1, 2, 3, 4 \ldots \) (quantized). Let the total energy of the system be three.

I have chosen two different distributions of energies, with both satisfying energy conservation. What is the average energy per particle, \( \langle E \rangle \)?

A. 3  
B. 4  
C. 0.75  
D. 12  
E. Not enough information given
Possible arrangements of particles with fixed total energy

Consider a system comprised of 4 particles. Any particle can have only discrete energies: $E = 0, 1, 2, 3, 4 \ldots$ (quantized). Let the total energy of the system be three.

With all possible arrangements enumerated, we make the \textit{ergodic} assumption, namely that the system visits all of the available configurations with equal probability.

What is the average occupancy of each energy level?

<table>
<thead>
<tr>
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<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
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<td>3</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
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<tr>
<td>II.</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>III.</td>
<td>1</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Totals/4</td>
<td>1.5</td>
<td>1</td>
<td>0.25</td>
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Plot $n(E)$ vs. $E$
Possible arrangements of particles with fixed total energy

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Energy randomization leads to an exponential distribution of occupied energy levels at constant total energy

\[ f(E) = 3e^{-\frac{E}{0.75}} \]
The probability that a system with fixed total energy has particular energy, $E$, is now given by

$$P(E) \propto \exp \left[ -\frac{E}{k_B T} \right]$$

Probability that molecule has velocity along the $x$-axis between $v_x$ and $v_x + dv_x$

$$dP_x = B \exp \left[ -\frac{mv_x^2}{2k_B T} \right]$$

Similar expressions for velocities along the $y$-axis and $z$-axis
The probability that the molecular velocity is between \( v_x \) & \( v_x+dv_x \), \( v_y \) & \( v_y+dv_y \), and \( v_z \) & \( v_z+dv_z \) is given by

\[
dP_x dP_y dP_z = B^3 \exp\left[-\frac{mv_x^2}{2k_BT}\right] \times \exp\left[-\frac{mv_y^2}{2k_BT}\right] \times \exp\left[-\frac{mv_z^2}{2k_BT}\right] \, dv_x \, dv_y \, dv_z
\]

This expression simplifies using \( u^2 = u_x^2+u_y^2+u_z^2 \)

\[
dP_x dP_y dP_z = B^3 e^{-\frac{mv^2}{2k_BT}} \, dv_x \, dv_y \, dv_z
\]

But we must convert to spherical polar coordinates to get the volume element in \( v \)!
Spherical Polar Co-ordinates

Volume = \(4\pi u^2 du\)

Volume = \(du_x du_y du_z\)
Maxwell distribution of molecular speeds

Volume element \((dv_x \, dv_y \, dv_z)\) transformation from cartesian to spherical polar coordinates:
\[
\begin{align*}
  x &= r \sin \theta \cos \phi, \\
  y &= r \sin \theta \sin \phi \\
  z &= r \cos \theta
\end{align*}
\]
Volume element transform:
\[dv_x \, dv_y \, dv_z \rightarrow 4\pi v^2 dv\]

\[
dP = 4\pi B^3 v^2 e^{-\frac{mv^2}{2kB T}} \, dv
\]

For a normalized distribution, \(\int_0^{\infty} P(v) \, dv = 1\) We use this constraint to set \(B\), giving

\[
P(v) \, dv = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-\frac{mv^2}{2kB T}} \, dv = 4\pi \left(\frac{M}{2\pi R T}\right)^{3/2} v^2 e^{-\frac{Mv^2}{2RT}} \, dv
\]
Characteristics of $P(v)$

$$P(v) dv = 4\pi \left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} v^2 e^{-\frac{Mv^2}{2RT}} dv$$

- Low temperature or high molecular mass
- Intermediate temperature or molecular mass
- High temperature or low molecular mass
Characteristics of $P(v)$

$$P(v) \, dv = 4\pi \left( \frac{M}{2\pi R T} \right)^{\frac{3}{2}} v^2 e^{-\frac{M v^2}{2RT}} \, dv$$

$c^* = (2RT/M)^{1/2}$

$\bar{c} = (8RT/\pi M)^{1/2}$

$c = (3RT/M)^{1/2}$

$f(v) = 4\pi (M/2\pi R T)^{1/2}$

$1/e$
Maxwell speed distributions are shown for three situations.

(I) If the curves represent 3 different gases at the same T, which curve shows the gas of greatest molar mass?

(II) If the curves represent the same gas at 3 different T, which curve shows the highest T?

A. blue; blue  C. red; blue
B. blue; red    D. red; red
Helium velocity distribution as $f(T)$