Kinetic-molecular theory of gases

CH102 Spring 2014
Boston University

**Goal:** Relate $T$ to speed of gas particles

**Pathway:** Get microscopic expression for $PV$

**Key idea:** Force is exchange of momentum $p$ with wall per unit time.

**Note:** Here upper-case $P$ is used for pressure and lower-case $p$ is used for momentum.

---

Force due to $j^{th}$ particle of mass $m$ and speed $u_j$

\[ \Delta p = 2\ m\ u_j \] (elastic collision)

\[ \Delta t = 2\ L/u_j \] (travel to opposite wall and back)

\[ F = \Delta p/\Delta t = m\ u_j^2/L \]

Pressure due to $j^{th}$ particle of mass $m$ and speed $u_j$

\[ P_j = F/\text{area} = F/L^2 = m\ u_j^2/L^3 \]

That is $P_j = m\ u_j^2/V$

---

Pressure due to $j^{th}$ particle of mass $m$ and speed $u_j$

\[ P_j = m\ u_j^2/V \]

Different particles have different speeds

In terms of the average speed $u$, and adding up contributions of all of the particles in the gas, the **total pressure** $P$ in terms of the number of moles $n$ and the molar mass $M$ is

\[ P = n\ M\ u^2/(3\ V) \]

since the number of particles $N$ times their mass $m$ can be expressed as

\[ N\ m = n\ N_a\ m = n\ M \]
Calculation of molecular speeds

We have discovered that a single particle $k$ exerts a pressure

$$p_k = \frac{m}{V} u_k^2$$

The total pressure $p$ is that due to collisions with the container wall of all the $N$ particles in the container.

What pressure would be generated by $N$ particles?

$N$ particles exert a pressure

$$p = \left(\frac{m}{V}\right) N u_{avg}^2$$

in terms of the average squared speed

$$u_{avg}^2 = \frac{(u_1^2 + u_2^2 + u_3^2 + \ldots + u_N^2)}{N}$$

How can we express this pressure in terms if the molar mass $M$ of the particles?

$N$ particles exert a pressure

$$p = \left(\frac{nM}{V}\right) u_{avg}^2$$

in terms of the average squared speed

$$u_{avg}^2 = \frac{(u_1^2 + u_2^2 + u_3^2 + \ldots + u_N^2)}{N}$$

the molar mass

$$M = m N_A$$

and the moles of gas particles

$$n = \frac{N}{N_A}$$
Calculation of molecular speeds

The expression

\[ p = \left( \frac{nM}{V} \right) u_{avg}^2 \]

assumes the particles are moving back and forth along a single direction, say \( x \), and so the average of the squared speed is actually \( u_{x,avg}^2 \).

\[ p = \left( \frac{nM}{V} \right) u_{x,avg}^2 \]

What do we expect to be true about the average squared speeds along \( y \) and \( z \), \( u_{y,avg}^2 \) and \( u_{z,avg}^2 \)?

if we ignore gravity and currents in the gas?

---

Calculation of molecular speeds

If we ignore gravity and currents in the gas the average of the squared speeds in each direction is the same

\[ u_{x,avg}^2 = u_{y,avg}^2 = u_{z,avg}^2 \]

Using the Pythagorean theorem, how can we express each of these average squared directional speeds in terms if the average squared speed \( u_{avg}^2 \) of the gas particles?

\[ u_{x,avg}^2 + u_{y,avg}^2 + u_{z,avg}^2 = u_{avg}^2 \]

Since the average squared directional speeds are all the same, they are each equal to one third of the average squared speed,

\[ u_{x,avg}^2 = u_{y,avg}^2 = u_{z,avg}^2 = \frac{1}{3} u_{avg}^2 \]

How can we express the pressure of the gas,

\[ p = \left( \frac{nM}{V} \right) u_{x,avg}^2 \]

in terms of \( u_{avg}^2 \)?
Calculation of molecular speeds

Since
\[ u^2_{x,\text{avg}} = u^2_{y,\text{avg}} = u^2_{z,\text{avg}} = \frac{1}{3} u^2_{\text{avg}} \]
the pressure of the gas can be expressed as
\[ p = (n \frac{M}{V}) u^2_{x,\text{avg}} = (n \frac{M}{V}) \frac{1}{3} u^2_{\text{avg}} \]

How can we use the ideal gas law to get an expression for the average squared speed in terms of temperature?

Root mean square speed

The root mean square speed of a gas is the square root of the mean (average) speed \( u_{\text{rms}} \)
\[ u_{\text{rms}} = \sqrt{u^2_{\text{avg}}} = \sqrt[3]{3 \frac{R}{M} T} \]

In terms of the average molar kinetic energy, \( E_{k,\text{avg}} = \frac{M}{2} \), the total pressure is
\[ P = \frac{2}{3} n E_{k,\text{avg}} / V \]
But from the ideal gas law
\[ P = n \frac{R}{V} T \]
Combining these two expressions, we find that \( T \) is a measure of the average molar kinetic energy,
\[ E_{k,\text{avg}} = \frac{3}{2} R T \]
Kinetic-molecular theory of gases

$T$ is a measure of the average molar kinetic energy,

$$E_{k,\text{avg}} = \frac{3}{2} RT$$

Since $Mu^2/2$, the squared rms speed is ...

$$u^2 = \frac{3 RT}{M}$$