# Kinetic-molecular theory of gases

CH102 Spring 2014
Boston University



## Kinetic-molecular theory of gases

Goal: Relate $T$ to speed of gas particles

Pathway: Get microscopic expression for $P V$

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.





## Kinetic-molecular theory of gases

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

$$\Delta p = 2\ m\ u_j \text{ (elastic collision)}$$

$$\Delta t = 2\ L/u_j \text{ (travel to opposite wall and back)}$$

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

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 $\mathbf{P_j = m\ u_j^2/V}$





## Kinetic-molecular theory of gases

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

$$N\ m = n\ N_o\ m = n\ M$$



## Calculation of molecular speeds

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

$$p_k = m\, u_k^2/V$$

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

What pressure would be generated by ***N* particles**?

BOSTON UNIVERSITY 5



## Calculation of molecular speeds

$N$ particles exert a pressure

$$p = (m/V)\,(u_1^2 + u_2^2 + u_3^2 + \ldots + u_N^2)$$

How can we express this pressure in terms if the **average** of the **squared speed** of the particles?

BOSTON UNIVERSITY 6



## Calculation of molecular speeds

$N$ particles exert a pressure

$$p = (m/V)\, N\, u^2_{\text{avg}}$$

in terms of the average squared speed

$$u^2_{\text{avg}} = (u_1^2 + u_2^2 + u_3^2 + \ldots u_N^2)/N$$

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

BOSTON UNIVERSITY 7



## Calculation of molecular speeds

$N$ particles exert a pressure

$$p = (n\, M/V)\, u^2_{\text{avg}}$$

in terms of the average squared speed

$$u^2_{\text{avg}} = (u_1^2 + u_2^2 + u_3^2 + \ldots u_N^2)/N$$

the molar mass

$$M = m\, N_A$$

and the moles of gas particles

$$n = N/N_A$$

BOSTON UNIVERSITY 8

## Calculation of molecular speeds

The expression

$$p = (n\,M/V)\,u_{avg}^2$$

assumes the particles are moving back and forth along a **single direction, say x**, and so the average of the squared speed is actually $u^2_{x,avg}$,

$$p = (n\,M/V)\,u^2_{x,avg}$$

What do we expect to be true about the average squared speeds along *y* and *z*,

$$u^2_{y,avg} \text{ and } u^2_{z,avg}\ ?$$

if we **ignore gravity and currents** in the gas?

BOSTON UNIVERSITY



## Calculation of molecular speeds

The expression

$$p = (n\,M/V)\,u_{avg}^2$$

assumes the particles are moving back and forth along a **single direction, say x**, and so the average of the squared speed is actually $u^2_{x,avg}$,

$$p = (n\,M/V)\,u^2_{x,avg}$$

What do we expect to be true about the average squared speeds along *y* and *z*,

$$u^2_{y,avg} \text{ and } u^2_{z,avg}\ ?$$

if we **ignore gravity and currents** in the gas?

BOSTON UNIVERSITY



## 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**

$$u^2_{x,avg} = u^2_{y,avg} = u^2_{z,avg}$$

Using the **Pythagorean theorem**, how can we express each of these average squared **directional** speeds in terms if the average squared speed $u^2_{avg}$ of the gas particles?

BOSTON UNIVERSITY



## Calculation of molecular speeds

By the Pythagorean theorem,

$$u^2_{x,avg} + u^2_{y,avg} + u^2_{z,avg} = u^2_{avg}$$

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

$$u^2_{x,avg} = u^2_{y,avg} = u^2_{z,avg} = ⅓\,u^2_{avg}$$

How can we express the pressure of the gas,

$$p = (n\,M/V)\,u^2_{x,avg}$$

**in terms of $u^2_{avg}$**?

BOSTON UNIVERSITY



## Calculation of molecular speeds

Since

$$u^2_{x,\text{avg}} = u^2_{y,\text{avg}} = u^2_{z,\text{avg}} = ⅓\, u^2_{\text{avg}}$$

the pressure of the gas can be expressed as

$$p = (n\,M/V)\, u^2_{x,\text{avg}} = (n\,M/V)\, ⅓\, u^2_{\text{avg}}$$

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

BOSTON UNIVERSITY



## Calculation of molecular speeds

Since the total pressure satisfies the **microscopic** expression

$$p = (n\,M/V)\, ⅓\, u^2_{\text{avg}}$$

but also the **macroscopic** expression

$$p = n\,R\,T/V$$

the temperature of the gas obey the relation

$$\boldsymbol{u^2_{\text{avg}} = 3\,R\,T/M}$$

This expression is the fundamental **connection** between microscopic **motion** and the macroscopic concept **temperature**.

BOSTON UNIVERSITY



## Root mean square speed

The root mean square speed of a gas is the square root of the mean (average) speed $u^2_{\text{avg}}$,

$$\boldsymbol{u_{\text{rms}} = \sqrt{u^2_{\text{avg}}} = \sqrt{3\,R\,T/M}}$$

BOSTON UNIVERSITY



## Kinetic-molecular theory of gases

In terms of the **average molar kinetic energy, $E_{\text{k,avg}} = M\,u^2/2$** , the total pressure is

$$P = (2/3)\, n\, E_{\text{k,avg}}/V$$

But from the ideal gas law

$$P = n\,R\,T/V$$

Combining these two expressions, we find that $T$ is a measure of the average molar kinetic energy,

$$\boldsymbol{E_{\text{k,avg}} = (3/2)\,R\,T}$$

BOSTON UNIVERSITY



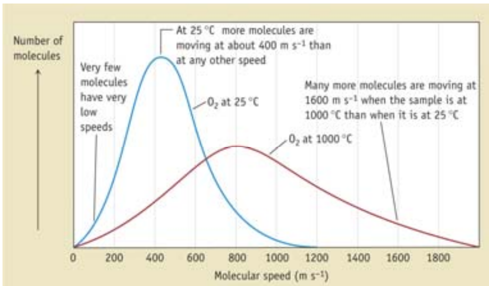
# Kinetic-molecular theory of gases

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

$$E_{k,avg} = (3/2)\, R\, T$$

Since $M\, u^2/2$ , the squared rms speed is …

$$u^2 = 3\, R\, T/M$$




BOSTON UNIVERSITY

17