


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.



2

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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 **$P_j = m u_j^2 / V$**



3

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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

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


4

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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**?

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Calculation of molecular speeds

N particles exert a pressure

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

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

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Calculation of molecular speeds

N particles exert a pressure

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

in terms of the average squared speed

$$u_{\text{avg}}^2 = (u_1^2 + u_2^2 + u_3^2 + \dots + u_N^2) / N$$

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

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Calculation of molecular speeds

N particles exert a pressure

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

in terms of the average squared speed

$$u_{\text{avg}}^2 = (u_1^2 + u_2^2 + u_3^2 + \dots + u_N^2) / N$$

the molar mass

$$M = m N_A$$

and the moles of gas particles

$$n = N / N_A$$

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Calculation of molecular speeds

The expression

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

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

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

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

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

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

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Calculation of molecular speeds

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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**

$$u_{x,\text{avg}}^2 = u_{y,\text{avg}}^2 = u_{z,\text{avg}}^2$$

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

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Calculation of molecular speeds

By the Pythagorean theorem,

$$u_{x,\text{avg}}^2 + u_{y,\text{avg}}^2 + u_{z,\text{avg}}^2 = u_{\text{avg}}^2$$

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

$$u_{x,\text{avg}}^2 = u_{y,\text{avg}}^2 = u_{z,\text{avg}}^2 = \frac{1}{3} u_{\text{avg}}^2$$

How can we express the pressure of the gas,

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

in terms of u_{avg}^2 ?

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Calculation of molecular speeds

Since

$$u_{x,\text{avg}}^2 = u_{y,\text{avg}}^2 = u_{z,\text{avg}}^2 = \frac{1}{3} u_{\text{avg}}^2$$

the pressure of the gas can be expressed as

$$p = (n M/V) u_{x,\text{avg}}^2 = (n M/V) \frac{1}{3} u_{\text{avg}}^2$$

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

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Calculation of molecular speeds

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

$$p = (n M/V) \frac{1}{3} u_{\text{avg}}^2$$

but also the **macroscopic** expression

$$p = n R T/V$$

the temperature of the gas obey the relation

$$u_{\text{avg}}^2 = 3 R T/M$$

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

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Root mean square speed

The root mean square speed of a gas is the square root of the mean (average) speed u_{avg}^2 ,

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

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

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

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,

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

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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 ...

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

The graph shows the number of molecules versus molecular speed (m s⁻¹) for oxygen gas (O₂) at two different temperatures. The x-axis ranges from 0 to 1800 m s⁻¹ with major ticks every 200 units. The y-axis is labeled 'Number of molecules'. Two curves are shown: a blue curve for O₂ at 25 °C and a red curve for O₂ at 1000 °C. The blue curve is narrower and taller, peaking at approximately 400 m s⁻¹. The red curve is broader and shorter, peaking at approximately 1600 m s⁻¹. Annotations include: 'Very few molecules have very low speeds' pointing to the start of the blue curve; 'At 25 °C, more molecules are moving at about 400 m s⁻¹ than at any other speed' pointing to the peak of the blue curve; and 'Many more molecules are moving at 1600 m s⁻¹ when the sample is at 1000 °C than when it is at 25 °C' pointing to the peak of the red curve. A 'BOSTON UNIVERSITY' logo is in the bottom left corner of the slide.

17