

The Kinetic-Molecular Theory of Gases (Section 6.7 in Petrucci et. al.)

The **ideal gas law** is an **empirical model** for the behavior of gases based on experimental observations. The **kinetic-molecular theory** is a model that provides **theoretical justification** for the ideal gas law. The model is based on the following assumptions:

- Molecular size is negligible compared with the distance that separates the molecules of a gas.
- Gas molecules are always moving with a distribution of molecular speeds.
- There are no intermolecular forces. The only interaction between molecules is during molecular collisions.
- Collisions of molecules with the wall of a container are elastic; no energy is lost during the collision.

Today we will use these assumptions to derive the kinetic-molecular theory of gases!

Imagine a cube containing gas molecules. We've discussed earlier that pressure arises from the force imposed by molecules colliding with the walls of the box. Based on this idea what variables will affect the pressure?

Based on this idea we predict that pressure will be proportional to the _____, _____, _____, and inversely proportional to the _____. Let's derive an expression for pressure using these four variables!

A few useful formulas from physics that we will need:

$$v = \qquad \text{impulse} =$$

$$P = \qquad \text{momentum} = p =$$

Consider a single molecule in a cube with side length L traveling with a velocity, v , that is only in the x direction. As the molecule travels across the length of the cube it will eventually hit the wall and reverse its direction.

For an elastic collision momentum is conserved, so this change in momentum must be transferred to the wall.

We can calculate the time between collisions as follows:

Therefore the momentum transferred to the wall per second (or the force exerted) by this single molecule is:

From force we can determine the pressure:

We don't have one molecule, we have many molecules so let's modify the equation to include N molecules:

And molecules don't just travel in the x direction; they also travel in the y and the z direction.

Kinetic-molecular theory of gas: $P =$

or $PV =$

This equation is a mathematical statement of Boyle's Law ($PV = \text{constant}$) if the molecular speed depends only on temperature. For now let's assume that it does (we'll go into this in detail later) and derive a relationship between temperature and the mean-square speed.

From the ideal gas law: $PV = nRT$

Therefore,

Since

$$\frac{N}{n} =$$

Also, note that $mN_A = M$

Therefore the mean-square molecular speed is directly proportional to temperature:

The root-mean-square speed is:

We can use the root-mean-square speed to derive an expression for the average kinetic energy of a mole of a gas:

The kinetic energy of the molecules of an ideal gas depends only on its temperature. Therefore, we can think of temperature as a measurement of the average kinetic energy of gas molecules.

Distribution of Molecular Speeds

The speeds of ideal gas molecules obey the Maxwell-Boltzmann speed distribution:

$$f(u) = 4\pi \left(\frac{M}{2\pi k_B T}\right)^{3/2} u^2 e^{-\left(\frac{Mu^2}{2k_B T}\right)}$$

Also written as

$$f(u) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} u^2 e^{-\left(\frac{mu^2}{2k_B T}\right)}$$

Where the Boltzmann constant is given as:

$$k_B = \frac{R}{N_A} = \frac{8.3145 \text{ J}/(\text{mol} \cdot \text{K})}{6.022 \times 10^{23}/\text{mol}} = 1.38066 \times 10^{-23} \text{ J/K}$$

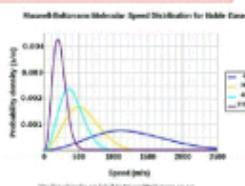
Distribution of Molecular Speeds

The area under the curve from u to $u + \Delta u$ corresponds to the fraction of molecules that have a speed between u and $u + \Delta u$.

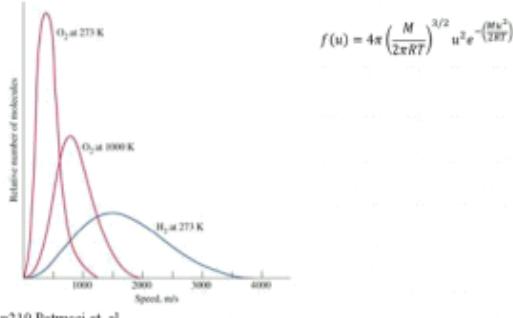
$$\int_u^{u+\Delta u} f(u) du = \text{fraction of molecules with speed between } u \text{ and } u + \Delta u$$

The total area under the curve is 1.

$$\int_0^{\infty} f(u) du = 1.0$$



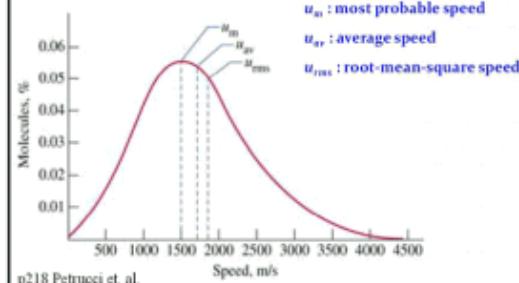
Effect of Temperature and Mass



p219 Petrucci et. al.

Distribution of Molecular Speeds

Hydrogen gas at 0 °C



p218 Petrucci et. al.

Average Velocities

1) Most probable speed

Find the maximum value of the distribution function by setting the derivative equal to zero.

$$u_{\text{mp}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2k_B T}{m}}$$

2) Average speed

Find the expected value of the distribution function by evaluating: $\int_0^{\infty} u f(u) du$.

$$u_{\text{av}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8k_B T}{\pi m}}$$

3) Root-mean-square speed

Evaluate the integral $\int_0^{\infty} u^2 f(u) du$ and take the square root.

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3k_B T}{m}}$$

*use $R = 8.3145 \text{ J}/(\text{mol} \cdot \text{K})$ to obtain speeds in units of m/s