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The Kinetic Theory of Gases

Module Overview

Acknowledgments

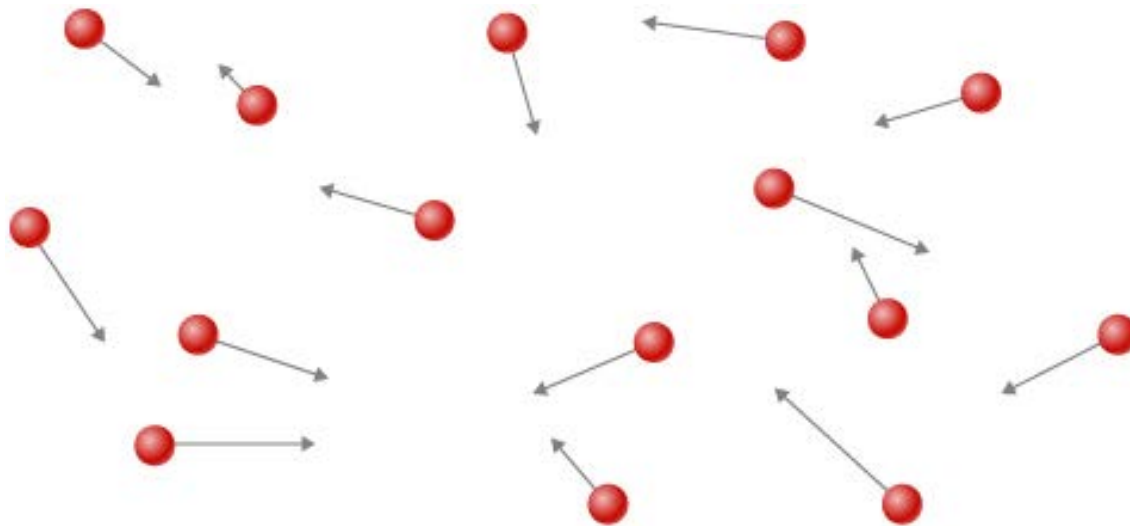
This presentation is based on and includes content derived from the following OER resource:

University Physics Volume 2

An OpenStax book used for this course may be downloaded for free at:
<https://openstax.org/details/books/university-physics-volume-2>

Molecular Model of an Ideal Gas

The molecules in a gas are separated from one another by distances much larger than the molecules themselves. As a result, the forces between them are often negligible unless they collide with one another.



(University Physics Volume 2. OpenStax. Fig. 2.2.)

The Gas Laws

Boyle's law states that the pressure P of a gas is inversely proportional to its volume, V . Charles' law states that the volume of a gas is proportional to its absolute temperature, T . Gay-Lussac's law states that the pressure of a gas is proportional to its temperature.

These laws show that gases at low density and high temperature, called **ideal gases**, obey the **ideal gas law**, $pV = Nk_B T$, where N is the number of molecules and $k_B = 1.38 \times 10^{-23}$ J/K is the **Boltzmann constant**.

For a gas in a closed container, the number of molecules does not change, so changes in the pressure, volume, and temperature at different times are related by $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$.

Moles and Avogadro's Number

The SI unit for amount of substance is the **mole** (mol), the amount of substance with the same number of molecules as exactly 12 grams of carbon-12. The number of molecules in a mole is called **Avogadro's number**, N_A , which is equal to $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$. The number of molecules in a substance N may be written in terms of the number of moles n by the expression $N = N_A n$. Avogadro's number may also be used to convert from the mass of a single molecule m to the mass of a mole of molecules M by the relation $M = N_A m$. If the mass of one mole of a substance is M , then the total mass of the substance m_s is given by $m_s = nM$. The unified atomic mass unit (u) is defined such that the mass of one carbon-12 atom is 12 u. The conversion between unified atomic mass units and grams is Avogadro's number, $6.02 \times 10^{23} \text{ u} = 1 \text{ g}$.

The Ideal Gas Law Restated Using Moles

The ideal gas law may be rewritten as $pV = \frac{N}{N_A} N_A k_B T$. The quantity $\frac{N}{N_A}$ is equal to the number of moles n of the substance, and we define the **universal gas constant**, $R \equiv N_A k_B$, to obtain the ideal gas law in terms of moles, $pV = nRT$. In SI units, $R = 8.31 \frac{\text{J}}{\text{mol}\cdot\text{K}}$.

Note that both sides of the ideal gas law have units of energy. The right side is roughly equal to the total translational energy of the gas, and the left side describes the work that the gas can do.

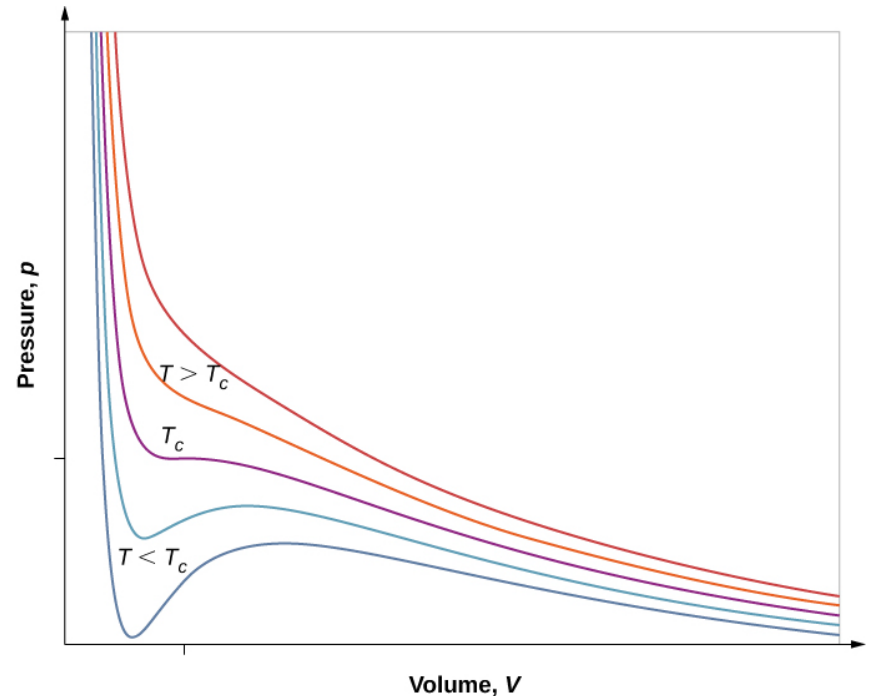
The van der Waals Equation of State

The **van der Waals equation of state** generalizes the ideal gas law by taking into account the attractive forces between molecules and the finite volume of the molecules composing the gas. The attractive forces are added by including an additional pressure term with coefficient a . The volume of the molecules in the gas are subtracted from the total volume in which the molecules may move with a coefficient b , which is roughly the volume of a mole of molecules. Both of the two coefficients must be determined experimentally for each gas.

The equation of state is given by $\left[p + a \left(\frac{n}{V} \right)^2 \right] (V - nb) = nRT$.

pV Diagrams, Part 1

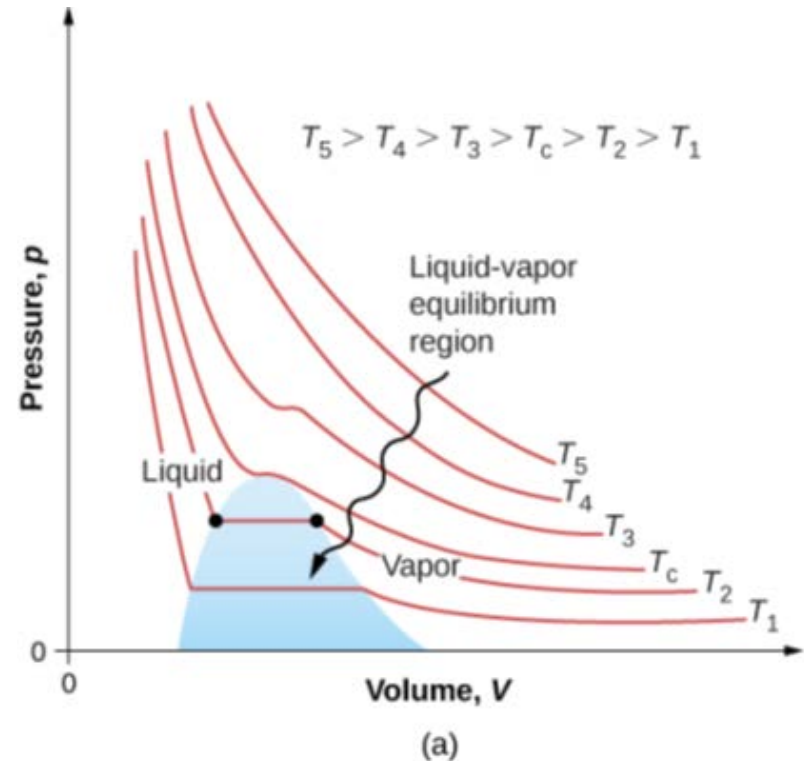
A pV diagram shows how pressure and volume are related at fixed temperatures, called isotherms. For an ideal gas, all the isotherms are hyperbolas. For the van der Waals equation of state, the isotherms at lower temperatures deform, and at a **critical temperature**, T_c , the curve has zero slope at a point. Below T_c , there are regions where increasing the volume would also increase the pressure.



(University Physics Volume 2. OpenStax. Fig. 2.7.)

pV Diagrams, Part 2

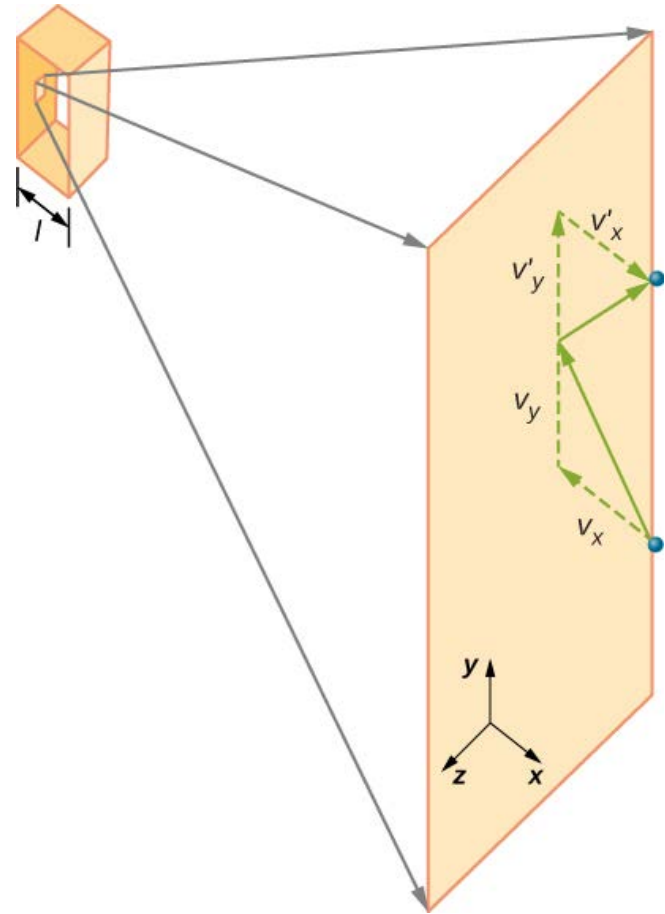
The positive-sloped regions are understood to describe a phase transition. Above the critical temperature, no phase transition occurs. For example, a **supercritical** gas is a gas with the density of a liquid but that does not condense because it has a temperature above the critical temperature.



(University Physics Volume 2. OpenStax. Fig. 2.8.)

Pressure, Temperature, and RMS Speed, Part 1

The **kinetic theory of gases** relates the macroscopic properties of a gas to its molecular behavior. We assume there is a large number N of molecules, each with mass m , and that the particles obey Newton's laws and move constantly in random directions. The pressure on the walls of a container is due to molecular collisions.



(University Physics Volume 2. OpenStax. Fig. 2.10.)

Pressure, Temperature, and RMS Speed, Part 2

The pressure and volume of a gas are related to the average speed \bar{v} of the molecules by $pV = \frac{1}{3}Nm\bar{v}^2$. The average kinetic energy of a molecule is determined by the temperature of the gas, $\bar{K} = \frac{3}{2}k_{\text{B}}T$. The internal energy of a gas of noninteracting molecules is the sum of the kinetic energies of the N molecules in the gas, $E_{\text{int}} = \frac{3}{2}Nk_{\text{B}}T$, or $E_{\text{int}} = \frac{3}{2}nRT$. The **root-mean-square (rms) speed** of a molecule is an estimate of its speed, which is related to its mass m and temperature by $v_{\text{rms}} = \sqrt{\frac{3k_{\text{B}}T}{m}}$, or $v_{\text{rms}} = \sqrt{\frac{3RT}{M}}$, where M is the molar mass.

Vapor Pressure, Partial Pressure, and Dalton's Law

The **partial pressure** of a gas is the pressure it would create if it occupied the total volume available. When gases are mixed, they come to thermal equilibrium, have the same average kinetic energy, and obey the ideal gas law separately. This leads to **Dalton's law of partial pressures**, which states that the total pressure of a mixture of gases is the sum of the partial pressures of the component gases.

Vapor pressure is the partial pressure of a vapor at which it is in equilibrium with its liquid phase. The partial pressure of a vapor in air, such as water vapor, cannot exceed its vapor pressure or the vapor will begin to condense. The temperature at which condensation occurs for a sample of air is called the dew point.

Mean Free Path and Mean Free Time

In a gas, the **mean free path** λ is the average distance a molecule travels between collisions. The **mean free time** τ is the time between collisions.

Assuming all molecules are spheres with radius r , the mean free path of a molecule, in terms of the container volume V and the number of molecules N , is $\lambda = \frac{V}{4\sqrt{2}\pi r^2 N}$. In terms of the gas pressure and temperature, $\lambda = \frac{k_B T}{4\sqrt{2}\pi r^2 p}$.

The mean free time is the mean free path divided by the rms speed of the gas, $\tau = \frac{k_B T}{4\sqrt{2}\pi r^2 p v_{\text{rms}}}$.

Heat Capacity of a Gas at Constant Volume

The molar heat capacity at constant volume C_V is defined by $C_V = \frac{1}{n} \frac{Q}{\Delta T}$ with V held constant. The molar heat capacity relates the heat added or removed from a gas to its change in temperature by $Q = nC_V\Delta T$.

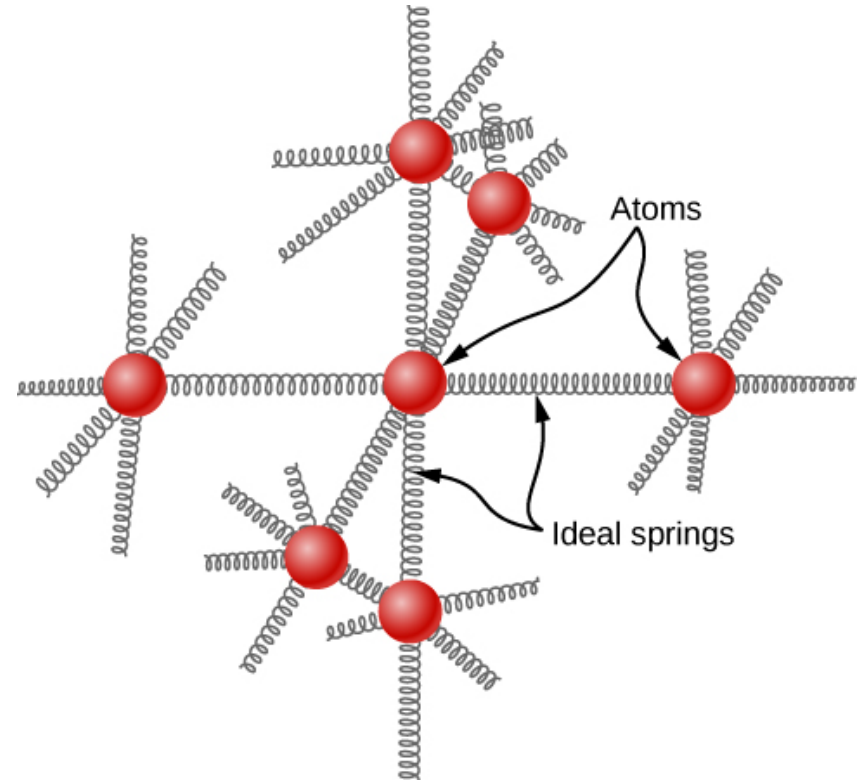
At fixed volume, the only change in internal energy is due to heat, $\Delta E_{\text{int}} = Q$. Because change in internal energy is caused by a change in temperature, and for a monatomic gas $\Delta E_{\text{int}} = 3nR\Delta T/2$, we can rewrite the molar heat capacity at constant volume simply as $C_V = \frac{3}{2}R$.

Degrees of Freedom

A **degree of freedom** is an independent possible motion of a molecule. For example, there are three degrees of freedom corresponding to translation in each of the three spatial dimensions, and polyatomic molecules have additional degrees of freedom from their ability to rotate and vibrate. The 3 in the equations $C_V = \frac{3}{2}R$ and $\bar{K} = \frac{3}{2}k_B T$ are due to the fact that each of the three translational degrees of freedom contributes a factor of $\frac{1}{2}$ to the coefficient. The **equipartition theorem** states that for a system with d degrees of freedom, its energy and molar heat capacity are given by $\bar{K} = \frac{d}{2}k_B T$ and (for an ideal gas) $C_V = \frac{d}{2}R$.

Molar Heat Capacity of Solid Elements

A spring model of solids gives rise to six degrees of freedom, one kinetic and one potential for each of the three possible directions. The Law of Dulong and Petit formalizes this by stating that the molar specific heat of a metal should be $3R$. This model works well for most elements at room temperature, but fails for some very light and very heavy elements, and for all elements at very low temperatures.



(University Physics Volume 2, OpenStax, Fig. 2.14.)

The Maxwell-Boltzmann Distribution

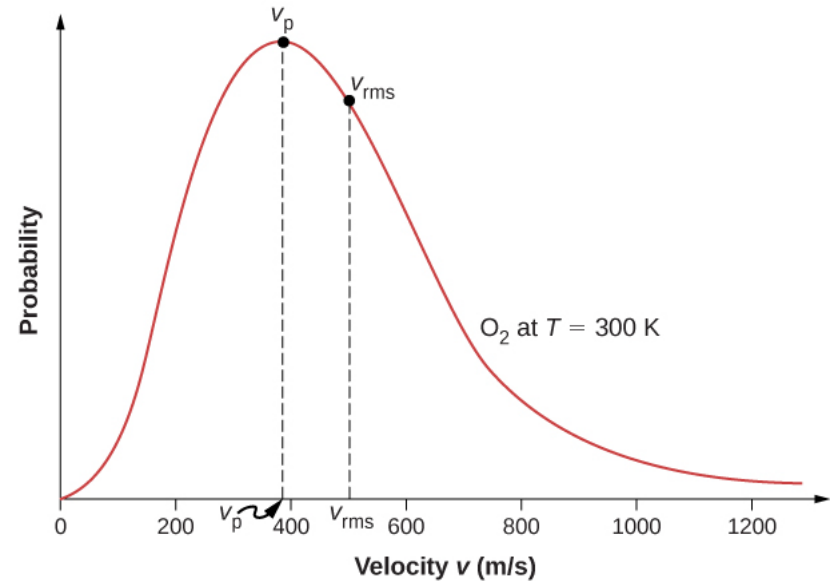
The distribution of molecular speeds of a gas is called the **Maxwell-Boltzmann distribution**. It is given by the equation,

$$f(v) = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T}.$$

This probability distribution can be used to compute the average speed by

$$\text{integrating } \bar{v} = \int_0^{\infty} v f(v) dv = \sqrt{\frac{8 RT}{\pi M}}.$$

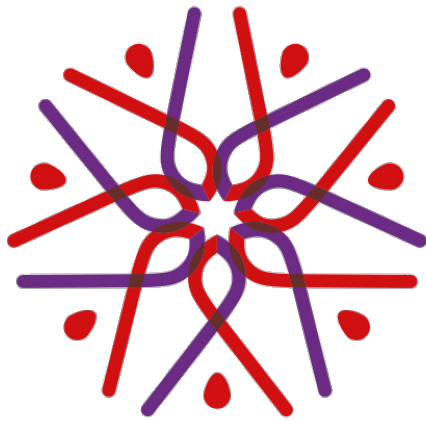
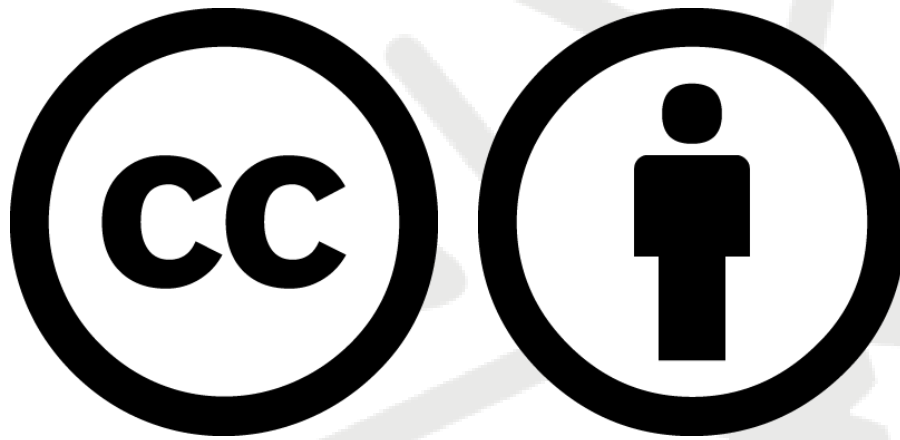
The **peak speed**, v_p , is $v_p = \sqrt{\frac{2RT}{M}}$.



(University Physics Volume 2. OpenStax. Fig. 2.15.)

How to Study this Module

- Read the syllabus or schedule of assignments regularly.
- Understand key terms; look up and define all unfamiliar words and terms.
- Take notes on your readings, assigned media, and lectures.
- As appropriate, work all questions and/or problems assigned and as many additional questions and/or problems as possible.
- Discuss topics with classmates.
- Frequently review your notes. Make flow charts and outlines from your notes to help you study for assessments.
- Complete all course assessments.



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