

Lecture Notes on Thermal Physics

Laws of Thermodynamics

Last updated on January 15, 2026

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Undergraduate Lecture Notes

Topics Covered:
Ideal gas • Real gas • 0th Law • 1st Law • problem set

Academic Year 2025–2026

IEHE, Bhopal

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Chapter 1

Ideal Gas

1.1 Introduction

An ideal gas has the following properties.

- The molecules of an ideal gas are point masses with negligible volume.
- There are no intermolecular forces between the gas molecules.
- Collisions between molecules and with the walls of the container are perfectly elastic.

1.2 Ideal Gas Laws

The behavior of an ideal gas is described by the following fundamental gas laws.

Boyle's Law

At constant temperature, the pressure of a given mass of gas is inversely proportional to its volume:

$$P \propto \frac{1}{V} \quad (T = \text{constant})$$

or

$$PV = \text{constant} \quad (1.1)$$

Charles's Law

At constant pressure, the volume of a given mass of gas is directly proportional to its absolute temperature:

$$V \propto T \quad (P = \text{constant})$$

or

$$\frac{V}{T} = \text{constant} \quad (1.2)$$

Gay-Lussac's Law

At constant volume, the pressure of a given mass of gas is directly proportional to its absolute temperature:

$$P \propto T \quad (V = \text{constant})$$

or

$$\frac{P}{T} = \text{constant} \quad (1.3)$$

Avogadro's Law

At constant temperature and pressure, the volume of a gas is directly proportional to the number of moles of the gas:

$$V \propto n \quad (T, P = \text{constant})$$

or

$$\frac{V}{n} = \text{constant} \quad (1.4)$$

This law implies that equal volumes of all gases, at the same temperature and pressure, contain the same number of molecules. As a consequence, one mole of any ideal gas occupies a volume of 22.4 L at standard temperature and pressure (STP).

1.3 Ideal Gas Equation

Above mentioned gas laws implies the following proportionality:

$$PV \propto nT \quad (1.5)$$

This gives **macroscopic equation of state** for an ideal gas is

$$PV = nRT \quad (1.6)$$

where R is a proportionality constant. Its called the universal gas constant.

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

Fundamental Constant

The number of constituent particles in one mole of any substance is defined as **Avogadro's Number (N_A)**:

$$N_A = 6.02214076 \times 10^{23} \text{ mol}^{-1}$$

Hence Total number of molecules of the gas of n mole is:

$$N = nN_A \quad (1.7)$$

Ideal gas equation reduces to:

$$PV = \frac{N}{N_A} RT$$

The quantity

$$\frac{R}{N_A} = k_B = 1.380649 \times 10^{-23} \text{ J K}^{-1} \quad (1.8)$$

is defined as the Boltzmann constant.

Thus, the ideal gas equation can be written in its **microscopic form** as

$$PV = Nk_B T \quad (1.9)$$

This form of the ideal gas equation relates macroscopic thermodynamic variables to microscopic molecular properties.

It leads to another form of ideal gas equation:

$$P = \bar{n}k_B T \quad (1.10)$$

where $\bar{n} = \frac{N}{V}$: Number density of the molecules in the system.

1.4 Work Done By an Ideal Gas

To understand the energy transfer in a thermodynamic process, we examine a gas filled inside a cylinder equipped with a movable piston.

Pressure is defined as the force acting per unit area:

$$P = \frac{F}{A} \implies F = P \cdot A \quad (1.11)$$

When an external force \vec{F} is applied to the piston, causing it to move by an infinitesimal displacement $d\vec{l}$, the work done is:

$$\delta W = \vec{F} \cdot d\vec{l} \quad (1.12)$$

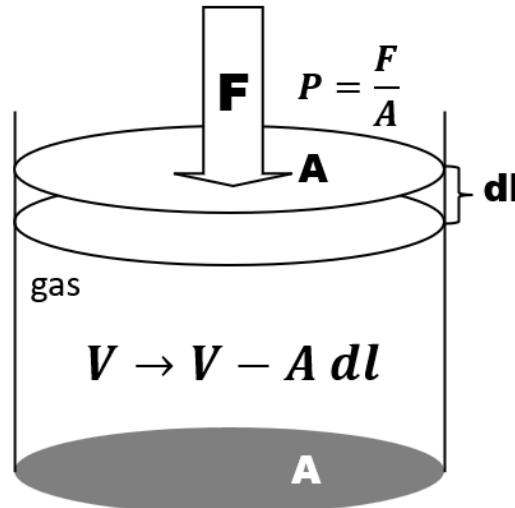


Figure 1.1: Cylinder-piston system: The gas is being compressed by an external force F .

1.4.1 Work Done by the External Agent

Substituting the force relation into the work equation, where the displacement dl occurs over the cross-sectional area A :

$$\delta W = (P \cdot A)dl \quad (1.13)$$

Since the change in volume is $dV = A \cdot dl$, the work done **by the external force on the system** is:

$$\delta W_{ext} = +P dV \quad (1.14)$$

1.4.2 System Perspective (Work Done by the Gas)

From the system's (the gas) point of view, if it is being compressed, the volume is decreasing. In physics, we often define work based on the system's action.

If the system is being worked upon (compressed), it is "doing" negative work because the displacement is opposite to the direction of the internal gas pressure.

Sign Convention for your Notes

- **Compression ($dV < 0$):**

Work done *by the gas* $\delta W = PdV$ is negative ($dW < 0$).

- **Expansion ($dV > 0$):**

Work done *by the gas* $\delta W = PdV$ is positive ($dW > 0$).

1.4.3 Total Work Done

For a finite change in volume from V_1 to V_2 , the total work done by the gas is obtained by integration:

$$W = \int_{V_1}^{V_2} P dV \quad (1.15)$$

This expression is valid for quasi-static thermodynamic processes, where the system remains in equilibrium at every stage.

Isothermal Process

For an isothermal process ($T = \text{constant}$) of an ideal gas ($PV = nRT$),

The work done by the gas is given by

$$W = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \ln \left(\frac{V_2}{V_1} \right) \quad (1.16)$$

Adiabatic Process

In an adiabatic process, (no heat is exchanged with the surroundings $\Delta Q = 0$). The equation of state is

$$PV^\gamma = \text{constant}$$

where $\gamma = \frac{C_P}{C_V}$. The work done is

$$W = \int_{V_1}^{V_2} \frac{K}{V^\gamma} dV = \frac{KV_1^{-\gamma} - KV_2^{-\gamma}}{\gamma - 1} = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1} \quad (1.17)$$

In this process, the work done comes at the expense of internal energy.

Isochoric Process

In an isochoric ($V = \text{constant}$) process,

$$dV = 0$$

Hence, the work done is

$$W = \int P dV = 0$$

No mechanical work is done, and any heat supplied changes only the internal energy.

Isobaric Process

In an isobaric process ($P = \text{constant}$), The work done is

$$W = \int_{V_1}^{V_2} P dV = P(V_2 - V_1) \quad (1.18)$$

Using the ideal gas equation ($PV = nRT$), this can also be written as

$$W = nR(T_2 - T_1) \quad (1.19)$$

Cyclic Process

In a cyclic process, the system returns to its initial state. The work done over one complete cycle is

$$W = \oint P dV$$

and is equal to the area enclosed by the cycle on the P - V diagram.

Free Expansion

In free expansion, the gas expands into a vacuum.

$$P_{\text{external}} = 0$$

Hence, the work done is

$$W = 0$$

No work is done despite the increase in volume.

Problem 1.1

calculate work done by the gas following the polytropic path: $PV^x = C$ where C is a constant.

1.5 Kinetic Theory of Ideal Gases

The Kinetic Theory of Gases provides a microscopic explanation for macroscopic properties like pressure and temperature. It treats a gas as a collection of a large number of molecules in constant, random motion.

Consider an ideal gas consisting of N molecules, each of mass m , enclosed in a cubical container of side L . The volume of the container is $V = L^3$.

Momentum Change per Collision

Suppose a molecule moves with velocity $\vec{v} = (v_x, v_y, v_z)$. When it collides elastically with the wall perpendicular to the x-axis, its velocity component v_x reverses to $-v_x$. The change in momentum (Δp_x) is:

$$\Delta p_x = (-mv_x) - (mv_x) = -2mv_x \quad (1.20)$$

The momentum transferred **to the wall** is $+2mv_x$.

Force exerted per collision on the wall

The time taken for the molecule to travel across the box and back to the same wall is:

$$\Delta t = \frac{2L}{v_x}$$

The rate of change of momentum (force f_x) exerted by one molecule is:

$$f_x = \frac{\Delta p}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L} \quad (1.21)$$

1.5.1 Pressure

The total force F_x exerted by all N molecules is:

$$F_x = \sum_{i=1}^N \frac{mv_{xi}^2}{L} = \frac{m}{L} \sum_{i=1}^N v_{xi}^2 \quad (1.22)$$

Pressure P is Force divided by Area ($A = L^2$):

$$P = \frac{F_x}{L^2} = \frac{m}{L^3} \sum v_{xi}^2 = \frac{m}{V} \sum v_{xi}^2 \quad (1.23)$$

Root Mean Square Velocity

Since the motion is random, the average velocity components are equal in all directions:

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} \langle v^2 \rangle \quad (1.24)$$

Substituting $\sum v_{xi}^2 = N \langle v_x^2 \rangle = \frac{1}{3} N \langle v^2 \rangle$:

$$P = \frac{1}{3} \frac{Nm \langle v^2 \rangle}{V} \quad (1.25)$$

$$PV = \frac{1}{3}mN\langle v^2 \rangle \quad (1.26)$$

Defining the total mass $M = Nm$, density of the gas $\rho = M/V$ and $v_{rms} = \sqrt{\langle v^2 \rangle}$:

$$P = \frac{1}{3}\rho v_{rms}^2 \quad (1.27)$$

1.5.2 Kinetic Energy and Temperature

From the ideal gas law $PV = Nk_B T$ and 1.26:

$$\frac{1}{3}Nm v_{rms}^2 = Nk_B T \quad (1.28)$$

The average translational kinetic energy of a single molecule is:

$$\kappa_{avg} = \langle \frac{1}{2}mv^2 \rangle = \frac{1}{2}m\langle v^2 \rangle = \frac{1}{2}mv_{rms}^2 = \frac{3}{2}k_B T \quad (1.29)$$

Key Insight

Temperature is a direct measure of the average translational kinetic energy of the molecules.

1.6 Principle of Equipartition of Energy

✓ Statement of the Principle

For a dynamical system in thermal equilibrium at temperature T , the total energy is distributed equally among all its active degrees of freedom. The average energy associated with each individual degree of freedom is equal to $\frac{1}{2}k_B T$.

1.6.1 Consistency with Kinetic Theory

In our previous discussion on the kinetic theory of gases, we derived the equation of state for one mole of an ideal gas as $pV = RT$. From this, we established that the average translational kinetic energy of a molecule is:

$$\bar{\kappa} = \frac{3}{2}k_B T \quad (1.30)$$

Since a monoatomic gas is considered to have only translational motion in three-dimensional space ($f = 3$), this result is perfectly consistent with the Equipartition Principle, which assigns $\frac{1}{2}k_B T$ to each of the three translational axes (x, y, z).

1.6.2 Analysis of Degrees of Freedom (f)

- **Monoatomic Gas:** As confirmed by kinetic theory, these gases possess only translational degrees of freedom ($f = 3$).

$$u_{av} = 3 \times \left(\frac{1}{2} k_B T \right) = \frac{3}{2} k_B T \quad (1.31)$$

- **Diatom Gas:** At standard temperatures, a diatomic molecule acts as a rigid rotator. It possesses 3 translational and 2 rotational degrees of freedom (rotation about the axis joining the two atoms is neglected as the moment of inertia is negligible), giving $f = 5$.

$$u_{av} = 5 \times \left(\frac{1}{2} k_B T \right) = \frac{5}{2} k_B T \quad (1.32)$$

unless Vibrational modes are activated.

- **Polyatomic Gas:** For more complex molecules, the situation includes:

- **3 Translational modes.**
- **3 Rotational modes** (or 2 if the molecule is linear).
- **Vibrational modes:** Unlike translation or rotation, each vibrational mode contributes **two** degrees of freedom (one for kinetic energy and one for potential energy). Therefore, each active vibration contributes $1k_B T$ to the total energy.

The "Frozen" Degrees of Freedom

It is important to note that vibrational modes (and sometimes rotational ones at very low temperatures) must be "activated" by reaching a specific temperature threshold. If the thermal energy is too low, these modes remain "frozen" and do not contribute to the heat capacity of the gas.

Excercise

Given a non-linear triatomic molecule (like H_2O) where vibrations are neglected, calculate the total internal energy for 1 mole of the gas.

We will continue our discussion on various degree of freedom and associated energy with it in chapter ??

1.7 Maxwellian Distribution of an Ideal Gas

In a system of an ideal gas in thermal equilibrium at temperature T , the molecules move in random directions with varying speeds. The Maxwell-Boltzmann distribution describes the probability of a molecule having a specific velocity.

In simple language: if we randomly choose a molecule in a gas and look at its velocity, the probability of finding its velocity in the infinitesimal volume d^3v (centered at $\vec{v} = v_x, v_y, v_z$) is given by $f(\vec{v})d^3v$.

Similarly, If we ask the question of what is the probability of finding only the x -component of the velocity to be v_x within a range dv_x , that probability will be $f(v_x)dv_x$.

Because the gas is isotropic, the motions in the x , y , and z directions are independent, meaning:

$$f(\vec{v})d^3v = f(v_x)f(v_y)f(v_z)dv_xdv_ydv_z \quad (1.33)$$

The Maxwell-Boltzmann distribution

Maxwell and Boltzmann figured out that any function of energy for an individual molecule in thermal equilibrium can be described by a specific distribution.

Discrete Form: The number of molecules n_i in a state with energy ϵ_i is proportional to the Boltzmann factor:

$$n_i \propto e^{-\frac{\epsilon_i}{k_B T}} \quad (1.34)$$

$$n_i = \frac{N}{Z}e^{-\frac{\epsilon_i}{k_B T}} \quad (1.35)$$

where $N = \sum n_i$ and $Z = \sum e^{-\epsilon_i/k_B T}$ is the partition function.

Continuous Form: For a continuous range of energies, the probability density (making sure $\int f(\epsilon)d\epsilon = 1$) is:

$$\frac{N_\epsilon d\epsilon}{N} = f(\epsilon)d\epsilon = Ae^{-\frac{\epsilon}{k_B T}}d\epsilon \quad (1.36)$$

where A is a normalization constant.

Based on the Boltzmann factor $e^{-\epsilon/k_B T}$, where $E = \frac{1}{2}mv^2$, the distribution for a single component is:

$$f(v_x)dv_x = A \exp\left(-\frac{mv_x^2}{2k_B T}\right)dv_x \quad (1.37)$$

Normalization Constant

Since $f(v_x)$ is a probability density, it must satisfy the normalization condition

$$\int_{-\infty}^{\infty} f(v_x) dv_x = 1. \quad (1.38)$$

Substituting the expression for $f(v_x)$,

$$A \int_{-\infty}^{\infty} e^{-\frac{mv_x^2}{2k_B T}} dv_x = 1. \quad (1.39)$$

Using the standard Gaussian integral

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}, \quad (1.40)$$

we obtain

$$\int_{-\infty}^{\infty} e^{-\frac{mv_x^2}{2k_B T}} dv_x = \sqrt{\frac{2\pi k_B T}{m}}. \quad (1.41)$$

which yields

$$A = \sqrt{\frac{m}{2\pi k_B T}}. \quad (1.42)$$

1.7.1 Velocity distribution

Substituting the value of A , the Maxwell distribution for one velocity component becomes

$$f(v_x)dv_x = \left(\frac{m}{2\pi k_B T} \right)^{1/2} \exp \left(-\frac{mv_x^2}{2k_B T} \right) dv_x \quad (1.43)$$

Multiplying the three independent components together, we get the velocity vector distribution:

$$f(v_x, v_y, v_z)d^3v = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp \left(-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2k_B T} \right) dv_x dv_y dv_z \quad (1.44)$$

Since the energy of a molecule is purely kinetic, $\epsilon = \frac{1}{2}mv^2 = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$, the probability of finding a molecule with a specific velocity vector is:

$$f(\vec{v})d^3\vec{v} = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp \left(-\frac{mv^2}{2k_B T} \right) d^3\vec{v} \quad (1.45)$$

To find the Speed Distribution, we look at the magnitude v . We integrate over all possible directions in velocity space (spherical coordinates), where the volume element d^3v becomes $4\pi v^2 dv$:

$$F(v)dv = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 \exp \left(-\frac{mv^2}{2k_B T} \right) dv \quad (1.46)$$

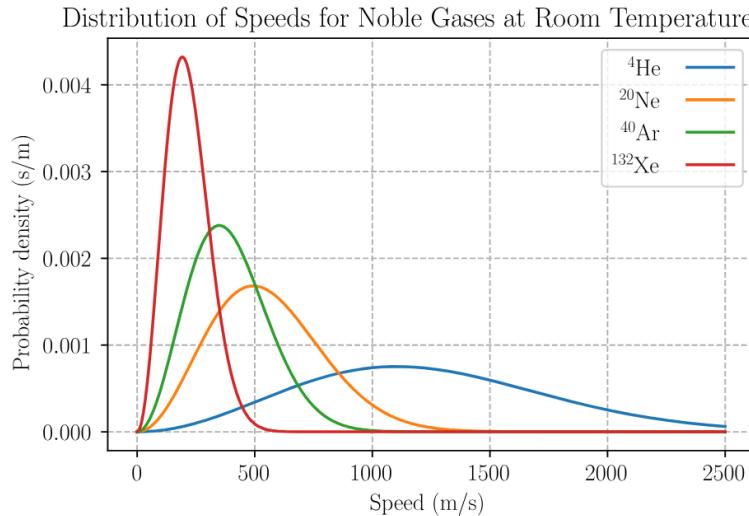


Figure 1.2: Velocity distributions of inert gases

Most Probable Speed (v_{mp})

This is found by setting $\frac{dF(v)}{dv} = 0$:

$$\frac{d}{dv} \left[v^2 \exp \left(-\frac{mv^2}{2k_B T} \right) \right] = 0 \quad (1.47)$$

yields:

$$\boxed{v_{mp} = \sqrt{\frac{2k_B T}{m}}} \quad (1.48)$$

Average Speed (v_{avg})

The average is the first moment of the distribution:

$$\langle v \rangle = \int_0^\infty v F(v) dv = \sqrt{\frac{8k_B T}{\pi m}} \quad (1.49)$$

$$\boxed{\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}}} \quad (1.50)$$

Root Mean Square Speed (v_{rms})

The mean square speed is the second moment:

$$\langle v^2 \rangle = \int_0^\infty v^2 F(v) dv = \frac{3k_B T}{m} \quad (1.51)$$

$$\boxed{v_{rms} = \sqrt{\frac{3k_B T}{m}}} \quad (1.52)$$

The relationship between these speeds is:

$$\boxed{v_{mp} < v_{avg} < v_{rms}} \quad (1.53)$$

1.7.2 Momentum

Using $p = mv$, the distribution of momentum magnitude is:

$$F(p) dp = 4\pi \left(\frac{1}{2\pi m k_B T} \right)^{3/2} p^2 \exp \left(-\frac{p^2}{2m k_B T} \right) dp \quad (1.54)$$

1.7.3 Energy Distribution

The kinetic energy of a gas molecule is given by

$$\epsilon = \frac{1}{2}mv^2. \quad (1.55)$$

Using the Maxwell velocity distribution and transforming from velocity space to energy space, the distribution of translational energy is obtained as

$$F(\epsilon) d\epsilon = \frac{2}{\sqrt{\pi}} \frac{1}{(kT)^{3/2}} \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon. \quad (1.56)$$

Average energy

This distribution shows that molecular energies are not equal but are spread over a range of values, with the mean energy given by

$$\langle \epsilon \rangle = \frac{3}{2}kT. \quad (1.57)$$

Using $\epsilon = \frac{1}{2}mv^2$, we transform the variable to energy:

$$F(\epsilon)d\epsilon = \frac{2\sqrt{\epsilon}}{\sqrt{\pi}(k_B T)^{3/2}} \exp\left(-\frac{\epsilon}{k_B T}\right) d\epsilon \quad (1.58)$$

1.8 Transport phenomenon

1.8.1 Mean free path

The *mean free path* (λ) is defined as the average distance traveled by a gas molecule between two successive collisions. To derive this, we model gas molecules as hard spheres of diameter d .

Collision Rate

Consider a single molecule moving with speed v through a background of identical molecules with number density n (molecules per unit volume). A collision occurs whenever the centers of two molecules come within a distance d of each other.

During a short time interval dt , the molecule sweeps out a cylindrical volume:

$$dV = \sigma v dt = \pi d^2 v dt \quad (1.59)$$

where $\sigma = \pi d^2$ is the effective collision cross-section. The number of molecules dN within this volume (and thus the number of collisions) is:

$$dN = n(\pi d^2 v dt) \quad (1.60)$$

The collision frequency f is the number of collisions per unit time:

$$f = \frac{dN}{dt} = n\pi d^2 v \quad (1.61)$$

Mean Free Path

The average time between collisions, known as the *mean free time* (τ), is the reciprocal of the frequency:

$$\tau = \frac{1}{n\pi d^2 v} \quad (1.62)$$

The mean free path λ is the distance covered during this time:

$$\lambda = v\tau = \frac{1}{n\pi d^2} \quad (1.63)$$

Correction for Relative Motion

The initial derivation assumes "target" molecules are stationary. In reality, all molecules are moving randomly. To account for this, we must use the average relative velocity v_{rel} .

For any two molecules with velocities \vec{v}_1 and \vec{v}_2 , the relative velocity is $\vec{v}_{rel} = \vec{v}_1 - \vec{v}_2$. Squaring this gives:

$$v_{rel}^2 = v_1^2 + v_2^2 - 2\vec{v}_1 \cdot \vec{v}_2 \quad (1.64)$$

Taking the average over the distribution:

1. Due to random motion, the dot product term $2\vec{v}_1 \cdot \vec{v}_2$ averages to zero.
2. Since the molecules are identical, $\langle v_1^2 \rangle = \langle v_2^2 \rangle = \langle v^2 \rangle$.

Thus, $\langle v_{rel}^2 \rangle = 2\langle v^2 \rangle$, which implies $v_{rel} = \sqrt{2}v$. Substituting this into our collision frequency calculation yields the corrected mean free path:

$$\lambda = \frac{1}{\sqrt{2}n\pi d^2} \quad (1.65)$$

Dependence on Temperature and Pressure

Using the ideal gas law $P = nk_B T$, we substitute $n = \frac{P}{k_B T}$:

$$\lambda = \frac{k_B T}{\sqrt{2}\pi d^2 P} \quad (1.66)$$

- Typical values of the mean free path in gases at atmospheric pressure are of the order of 10^{-7} m.

Microscopic motion to Macroscopic transport

The mean free path provides the crucial link between the microscopic motion of molecules and the macroscopic transport properties of gases.

Transport Phenomena in Gases

When a gas is not in equilibrium—due to differences in temperature, velocity, or concentration—random molecular motion acts to equalize these gradients. This process is known as *transport phenomena*. Molecules "transport" physical quantities as they move through their mean free path (λ).

Table 1.1: Primary Transport Phenomena

Phenomenon	Quantity Transported	Driving Gradient	Coefficient
Viscosity	Momentum (mv)	Velocity (du/dz)	Viscosity (η)
Thermal Conduction	Heat Energy	Temperature (dT/dz)	Conductivity (K)
Diffusion	Mass/Molecules	Concentration (dn/dz)	Diffusion (D)

1.8.2 Viscosity: The Transport of Momentum

Viscosity is the internal friction of a gas, resulting from the transfer of momentum from high-velocity layers to low-velocity layers.

Consider a gas flowing in the x -direction with a velocity gradient du/dz along the z -axis. Consider an imaginary plane P at height z where the flow velocity is u .

- Molecules reaching P from **above** ($z + \lambda$) carry momentum: $m(u + \lambda \frac{du}{dz})$.
- Molecules reaching P from **below** ($z - \lambda$) carry momentum: $m(u - \lambda \frac{du}{dz})$.

Let n be the number density and \bar{v} be the average thermal speed. Statistically, the number of molecules crossing the plane P per unit area per unit time from one side (assuming movement in six directions) is $\frac{1}{6}n\bar{v}$.

The downward momentum flux p_{\downarrow} is:

$$p_{\downarrow} = \frac{1}{6}nm\bar{v} \left(u + \lambda \frac{du}{dz} \right) \quad (1.67)$$

The upward momentum flux p_{\uparrow} is:

$$p_{\uparrow} = \frac{1}{6}nm\bar{v} \left(u - \lambda \frac{du}{dz} \right) \quad (1.68)$$

The net momentum transfer per unit area per unit time (shear stress τ) is the difference:

$$\tau = p_{\downarrow} - p_{\uparrow} = \frac{1}{6}nm\bar{v} \left(2\lambda \frac{du}{dz} \right) = \frac{1}{3}nm\bar{v}\lambda \frac{du}{dz} \quad (1.69)$$

By Newton's Law of Viscosity, $\tau = \eta \frac{du}{dz}$. Comparing the expressions, we find:

$$\boxed{\eta = \frac{1}{3}nm\bar{v}\lambda} \quad (1.70)$$

Properties of Gas Viscosity

1. **Pressure Independence:** Since $\lambda = \frac{1}{\sqrt{2\pi d^2 n}}$, substituting this into η cancels n . Thus, η is independent of pressure for an ideal gas.
2. **Temperature Dependence:** Since $\bar{v} \propto \sqrt{T}$, the viscosity increases with temperature: $\eta \propto \sqrt{T}$.

1.8.3 Thermal Conduction: Transport of Energy

Thermal conduction is the process by which kinetic energy is transported from a high-temperature region to a low-temperature region.

Let ϵ be the average kinetic energy of a molecule. In a temperature gradient dT/dz , the energy of a molecule is $\epsilon = c_v T$, where c_v is the molecular heat capacity.

The energy carried by molecules crossing a plane z from the hotter side ($z + \lambda$) and colder side ($z - \lambda$) results in a net heat flux q :

$$q = \frac{1}{6}n\bar{v} \left(\epsilon - \lambda \frac{d\epsilon}{dz} \right) - \frac{1}{6}n\bar{v} \left(\epsilon + \lambda \frac{d\epsilon}{dz} \right) \quad (1.71)$$

$$q = -\frac{1}{3}n\bar{v}\lambda \frac{d\epsilon}{dz} \quad (1.72)$$

Since $\frac{d\epsilon}{dz} = \frac{d\epsilon}{dT} \frac{dT}{dz} = C_v \frac{dT}{dz}$:

$$q = -\left(\frac{1}{3}n\bar{v}\lambda C_v\right) \frac{dT}{dz} \quad (1.73)$$

Comparing this to Fourier's law $q = -K \frac{dT}{dz}$, we find the thermal conductivity:

$$K = \frac{1}{3}n\bar{v}\lambda C_v \quad (1.74)$$

properties of Thermal conductivity

- **Pressure Independence:** In both η and K , the term $n\lambda$ appears. Since $\lambda \propto 1/n$, the density cancels out, making both coefficients independent of pressure.
- **Relationship:**

$$\frac{K}{\eta} = \frac{C_v}{m} = s_v \quad (1.75)$$

$$K = \eta m C_v \quad (1.76)$$

It shows that, gases with high viscosity are typically also good thermal conductors.

1.8.4 Self-Diffusion: Transport of Mass

Self-diffusion refers to the transport of molecules within a gas due to a concentration gradient dn/dz .

Let n be the number density of a specific type of molecule (or labeled molecules). The number of molecules crossing a plane P per unit area per unit time is $\frac{1}{6}\bar{v}n$.

In the presence of a gradient, the net flux J is the difference between those moving up from a region of density $(n - \lambda \frac{dn}{dz})$ and those moving down from $(n + \lambda \frac{dn}{dz})$:

$$J = \frac{1}{6}\bar{v} \left(n - \lambda \frac{dn}{dz} \right) - \frac{1}{6}\bar{v} \left(n + \lambda \frac{dn}{dz} \right) \quad (1.77)$$

$$J = -\frac{1}{3}\bar{v}\lambda \frac{dn}{dz} \quad (1.78)$$

Comparing this to Fick's Law, $J = -D \frac{dn}{dz}$, we find the diffusion coefficient:

$$D = \frac{1}{3}\bar{v}\lambda \quad (1.79)$$

This relationship implies that as a gas becomes less dense, its molecules diffuse more rapidly.

Chapter 2

Real Gases

2.1 Andrews' Experiment on CO_2

In an attempt to liquefy CO_2 at different temperatures, Thomas Andrews conducted experiments in 1869. He applied pressure while keeping Temperature fixed, and observe how volume changes with pressure.

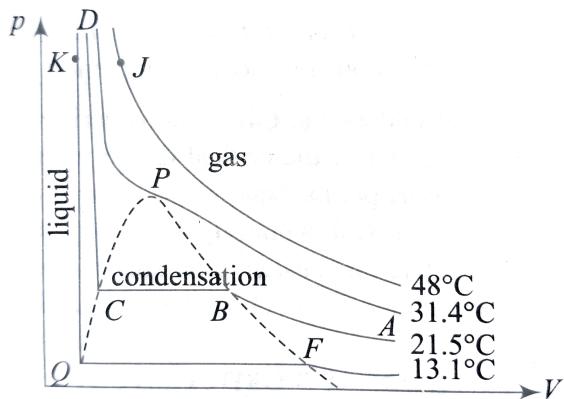


Figure 2.1: Caption

key observations:

- At high temperatures, the isotherms resemble those predicted by the ideal gas law ($PV = \text{Constant}$, Rectangular Hyperbola).
- At lower temperatures, the isotherms exhibit a horizontal portion CB, where pressure remains constant over a range of volumes. (sudden shrink in gas volume, Condensation of gas into liquid), This horizontal region CB corresponds to the coexistence of liquid and gaseous phases.
- As the temperature increases, the horizontal portion of the isotherm shortens and finally disappears at a particular temperature (Point P) called the **critical temperature** $T_c = 31.4/K$.

¶ At the critical point P:

The pressure and volume at this point are known as the **critical pressure** P_c and **critical volume** V_c , respectively.

- **Critical Temperature (T_c):** The temperature above which a gas cannot be liquefied by pressure alone.
- **Critical Pressure (p_c):** The pressure required for liquefaction at T_c .
- **Critical Volume (V_c):** The volume occupied by 1 mole at p_c and T_c .

- At 13.4°C , CO_2 begins to liquefy at approximately 50 atm (Point P). During liquefaction, pressure remains constant (Line BC) until the gas is entirely liquid. The steep curve CD and QK shows that liquids are highly incompressible.
- The critical point (T_c, P_c, V_c) is a point of inflection (where curve goes concave to convex).

The critical point corresponds to a point of inflection on the critical isotherm:

$$\left(\frac{\partial P}{\partial V}\right)_T = 0, \quad (2.1)$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0. \quad (2.2)$$

2.2 Van der Waals Gas Equation

The ideal gas equation of state assumes that gas molecules occupy negligible volume and exert no forces on one another.

In real gases, both assumptions fail. van der Waals introduced corrections to account for the finite size of molecules and intermolecular attractions.

2.2.1 Correction for Finite Molecular Volume

Real gas molecules have a finite size and therefore exclude a certain volume from being available for molecular motion. Let's calculate the volume not available to a molecule in Total Volume V ,

When two hard spherical molecules of radius r approach each other, the center of one molecule cannot come within a distance $2r$ of the center of the other. Hence, the unavailable volume around each molecule is a sphere of radius $2r$.

The non-available volume at per two molecule location is therefore

$$v'_{\text{non-available}} = \frac{4}{3}\pi(2r)^3 = 8\left(\frac{4}{3}\pi r^3\right). \quad (2.3)$$

Since this non-available volume is shared equally between two molecules, the effective non-available volume per molecule becomes

$$v_{\text{non-available}} = \frac{v'_{\text{non-available}}}{2} = 4 \left(\frac{4}{3} \pi r^3 \right). \quad (2.4)$$

If there are n mole (gas of N molecules, $N = nN_A$) of molecule are in total Volume V , than non-available Volume to a molecule will be

$$V_{\text{non-available}} = 4nN_A \left(\frac{4}{3} \pi r^3 \right) \quad (2.5)$$

In the ideal gas scene, gas in volume V (number of moles = n) has a volume of V available for molecular motion. Here, the volume available for molecular motion will be reduced by $V_{\text{non-available}}$. where

$$V_{\text{available}} = V - V_{\text{non-available}}. \quad (2.6)$$

Accordingly, the volume V in the ideal gas equation must be replaced by $V - 4nN_A \left(\frac{4}{3} \pi r^3 \right)$. Ideal gas equation now reduced to

$$PV_{\text{available}} = nRT \quad (2.7)$$

$$P \left[V - 4nN_A \left(\frac{4}{3} \pi r^3 \right) \right] = nRT \quad (2.8)$$

or we can introduce a parameter b such that

$$P(V - nb) = nRT \quad (2.9)$$

where b is the volume not available for a molecule for motion in Volume V , that contains 1 mole of gas.

$$b = 4N_A \left(\frac{4}{3} \pi r^3 \right) = \frac{1}{n} V_{\text{non-available}}$$

(2.10)

2.2.2 Correction for Intermolecular Attraction

In a real gas, attractive forces act between molecules. A molecule approaching the container wall experiences an inward pull due to neighboring molecules, resulting in a reduction of momentum transferred to the wall. Consequently, the observed pressure P is less than the pressure P_{ideal} that would be exerted in the absence of intermolecular attractions.

The magnitude of this pressure reduction depends on the number of interacting molecular pairs density. In Gas of N molecules, one molecule can make pair with $(N - 1)$ other molecules. hence total of N molecules can make $N(N - 1)/2 \propto N^2$ pairs.

number of interacting pairs per unit volume

$$\text{pair density} \propto \frac{N^2}{V^2} \quad (2.11)$$

Since pressure is determined by local molecular interactions near the container wall and intermolecular attraction is a pairwise effect, the reduction in pressure is proportional to the local density of interacting molecular pairs, which varies as the square of molecular density

$$\Delta P \propto \frac{N^2}{V^2} \quad (2.12)$$

$$P_{ideal} - P = \frac{an^2}{V^2} \quad (2.13)$$

where a is a constant characteristic of the strength of intermolecular attraction.

P_{ideal} is given by Eq. 2.9

$$P_{ideal} = \frac{nRT}{(V - nb)} \quad (2.14)$$

By equation 2.14 and 2.14 :

$$\boxed{\left(P + \frac{n^2a}{V^2} \right) (V - nb) = nRT.} \quad (2.15)$$

- The constant a measures the strength of intermolecular attraction. and Hence Larger values of a correspond to gases that are more easily liquefied.
- The constant b represents the effective molecular volume.



Johannes Diderik van der Waals

His equation of state was the first to bridge the gap between gases and liquids, establishing the principle of the "continuity of states".

Limitations of van der Waals Equation

Despite its success, the van der Waals equation has limitations:

- It fails to accurately predict behavior near the critical point.
- Quantitative agreement with experiments is limited.
- It does not account for molecular shape or quantum effects.

Nevertheless, it represents a major improvement over the ideal gas model.

② Assignment Work

- (a) Determine the SI units for the van der Waals constants a and b based on the equation 2.15.
- (b) Calculate Critical constants using Eq. 2.1 and 2.2 for Van der waals Equation of state.

Answer:

$$V_c = 3b, \quad (2.16)$$

$$P_c = \frac{a}{27b^2}, \quad (2.17)$$

$$T_c = \frac{8a}{27Rb}. \quad (2.18)$$

- (c) Determine the work performed by a gas following a van der Waals equation during isothermal expansion.
- (d) Using Molar Volume $V_m = \frac{V}{n}$, Find the Value of Compressibility factor $Z = \frac{PV_m}{RT}$ for the vdW Equation of state and expand in terms of Negative power of V_m .
- (e) Solve $\frac{\delta Z}{\delta \rho}|_{\rho=0, T=T_B} = 0$ where $\rho = V_m^{-1}$: molar density for vdW equation of state. where T_B is known as Boyle Temperature.

answer:

$$T_B = \frac{a}{Rb} \quad (2.19)$$

- (f) for dilute gas ($\rho \xrightarrow[\text{dilute gas}]{\text{high } V_m} 0$), proof that vdW Equation of state reduces to:

$$PV = nRT_B \quad (2.20)$$

- (g) Try all the above calculations for other Equation of states given in the Appendix A

2.3 Virial Equation of State

👤 Kamerling Onnes

The same guy famous for discovering superconductivity, Also studied the behaviour of real gases. He proposed an idea of write real gas equation as virial equation.

A more general description of real gases is provided by the virial equation of state:

$$\frac{PV_m}{RT} = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \dots \quad (2.21)$$

where $B(T)$, $C(T)$, etc., are temperature-dependent virial coefficients. These coefficient

represents contributions from two-body, three-body and higher-order intermolecular interactions.

since, Molar density $\rho = \frac{V}{n} = V_m^{-1}$,
Equation 2.21 takes the following form:

$$\frac{P}{\rho RT} = 1 + B(T)\rho^2 + C(T)\rho^3 + \dots \quad (2.22)$$

- The second coefficient B is particularly important; it represents pairwise molecular interactions.
- The **Boyle Temperature** is defined as the temperature at which $B = 0$, where the gas obeys Boyle's law over a wide range of pressure.

Appendix A

Equation of states

A.1 Berthelot Equation of State

$$P = \frac{RT}{V_m - b} - \frac{a}{TV_m^2} \quad (\text{A.1})$$

Parameters:

- a : attraction parameter
- b : co-volume parameter

A.2 Clausius Equation of State

$$P = \frac{RT}{V_m - b} - \frac{a}{T(V_m + c)^2} \quad (\text{A.2})$$

Parameters:

- a : attraction constant
- b : excluded volume
- c : correction parameter accounting for molecular structure

A.3 Virial Equation of State

$$\frac{PV_m}{RT} = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \frac{D(T)}{V_m^3} + \dots \quad (\text{A.3})$$

Parameters:

- $B(T)$: second virial coefficient (pair interactions)
- $C(T)$: third virial coefficient (three-body interactions)
- $D(T)$: higher-order interaction coefficients

$$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}V_m(V_m + b)} \quad (\text{A.4})$$

Parameters:

- a : attraction parameter
- b : co-volume parameter

A.5 Soave–Redlich–Kwong (SRK) Equation

$$P = \frac{RT}{V_m - b} - \frac{a\alpha(T)}{V_m(V_m + b)} \quad (\text{A.5})$$

Parameters:

- a : attraction constant
- b : co-volume
- $\alpha(T)$: temperature-dependent correction factor

A.6 Peng–Robinson Equation of State

$$P = \frac{RT}{V_m - b} - \frac{a\alpha(T)}{V_m(V_m + b) + b(V_m - b)} \quad (\text{A.6})$$

Parameters:

- a : attraction parameter
- b : co-volume
- $\alpha(T)$: temperature correction function

A.7 Hard-Sphere Equation of State

$$Z = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad (\text{A.7})$$

Parameters:

- Z : compressibility factor
- η : packing fraction

A.8 Benedict–Webb–Rubin (BWR) Equation

$$P = RT\rho + (B_0RT - A_0)\rho^2 + (bRT - a)\rho^3 + a\alpha\rho^6 \quad (\text{A.8})$$

Parameters:

- A_0, B_0, a, b, α : empirical constants obtained from experiment

A.9 Degenerate Fermi Gas Equation of State

$$P = K\rho^{5/3} \quad (\text{A.9})$$

Parameters:

- K : constant depending on particle mass and Planck's constant

A.10 Bose Gas Equation of State

$$P = \frac{kT}{\lambda^3} g_{5/2}(z) \quad (\text{A.10})$$

Parameters:

- k : Boltzmann constant
- λ : thermal de Broglie wavelength
- $g_{5/2}(z)$: Bose-Einstein function
- z : fugacity

A.11 Radiation Equation of State

$$P = \frac{1}{3}aT^4 \quad (\text{A.11})$$

Parameters:

- a : radiation constant

Bibliography