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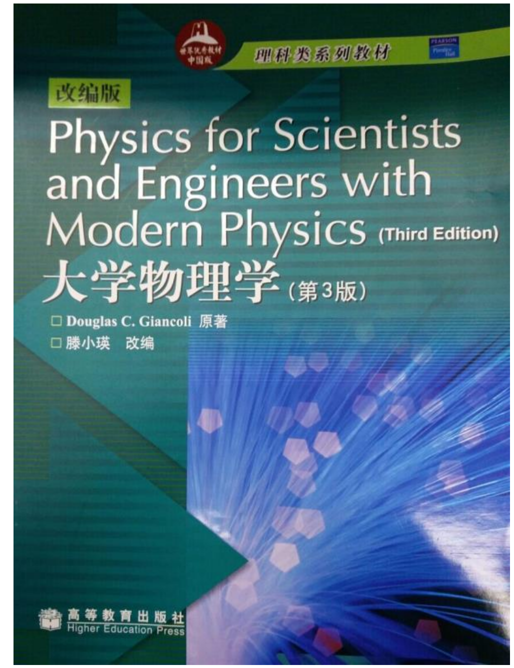

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Chapter 15&16
Kinetic Theory of Gases

1. The Ideal Gas Law

2. Pressure and Temperature of Ideal Gas

3. Distribution of Molecular Speeds

4. Mean Free Path

Introduction

Thermal Physics

Statistical Mechanics

(Kinetic Theory of Gases)

It describes how <u>macroscopic observations</u> (such as pressure and temperature) are related to <u>microscopic parameters</u> that <u>fluctuate around an average</u>.

Thermodynamics

It is a branch of physics that deals with heat, work, and temperature, and their relation to energy, and physical properties of matter.

(Laws of Thermodynamics)

Equation of State: A relation between the **pressure**, the **volume**, the **temperature**, and the mass of a gas.

$$f(P,V,T) = 0$$

For a given quantity of gas at **higher** T and **lower** P, it is found experimentally that

When T = C, PV = C	Boyle's law
When P = C, V/T = C	Charles's law
When V = C, P/T = C	Gay-Lussac's law

$$PV \propto T$$

15-1 The Ideal Gas Law (P377)

At low enough densities, all real gases tend to obey the relation:

$$\boxed{PV = nRT}$$ **(ideal gas law)**

n **represents the number of moles and** ***R*** **is the universal gas constant that has the same value for all gases**

$$R = 8.31\ \mathrm{J/(mol\cdot K)}$$

Another form of ideal gas law is: $\boxed{PV = NkT}$

k **is called Boltzmann constant, which is defined as**

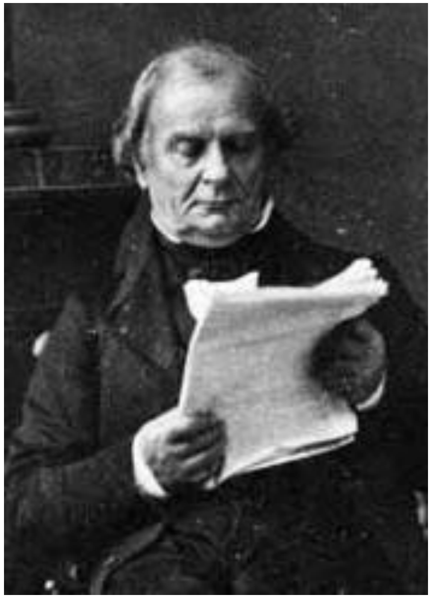
$$k = \frac{R}{N_A} = 1.38\times 10^{-23}\ \mathrm{J/K}$$

N **is total number of molecules.**

$$\boxed{PV = nRT}$$

(ideal gas law)

It was first stated by Benoît Paul Émile Clapeyron in 1834



French engineer and physicist Benoît Clapeyron (克拉珀龙) (1799-1864)

Honors

- One of the founders of thermodynamics
- Member of the French Academy of Sciences
- One of the 72 names inscribed on the Eiffel Tower

A gas whose macroscopic properties are governed by $PV = nRT$ ($PV = NkT$) is called ideal gas.

All *real gases* approach the ideal state at low enough densities——that is, under the conditions in which their molecules are far enough apart that they do not interact with one another.

The microscopic model of ideal gas:

(a) Density of gas is small, so the size of molecules is smaller than their mean distance;

(b) The interactions between molecules can be neglected except collisions;

(c) Any collision between molecules is elastic.

15-2 Pressure and Temperature of Ideal Gas

(P384)

This section is typical method of microscopic research which is called kinetic theory of gases.

Kinetic theory is based on an atomic model of matter. The basic assumption of kinetic theory is that the measurable properties of gases combined actions of countless numbers of atoms and molecules.

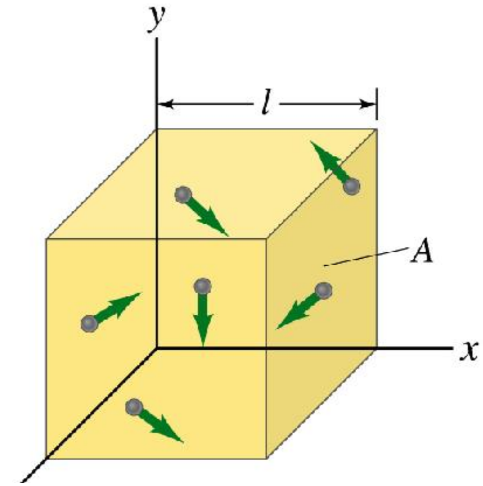
The characteristic size of an atom is about 10^{-10} m.

The density of molecules is 3×10^{19} cm^{-3}.

World population is 7×10^{9}.

Pressure formula of ideal gas:

What is the connection between the pressure P exerted by the gas on the walls and the speeds of the molecules?



Statistical Hypotheses (统计假设):

(a) At equilibrium, the distribution of molecules on the position is uniform, which means that the density of number of molecules is the same everywhere,

$$n' = \frac{dN}{dV} = \frac{N}{V}$$

与 $n = \dfrac{N}{N_A}$ 相区别

(b) At equilibrium, velocity of each molecule has the same probability to point to any directions. That is, the distribution of velocity of molecules is uniform in direction, which leads to the mean-square speeds of all components of velocity are same

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$$

where $$\overline{v_x^2} = \frac{v_{1x}^2 + v_{2x}^2 + \cdots + v_{Nx}^2}{N}$$

Since $v^2 = v_x^2 + v_y^2 + v_z^2$, **or** $\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$

we have $$\boxed{\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3}\overline{v^2}}$$

Due to the elastic collisions of molecules, the change of momentum of a molecule in *x* direction is

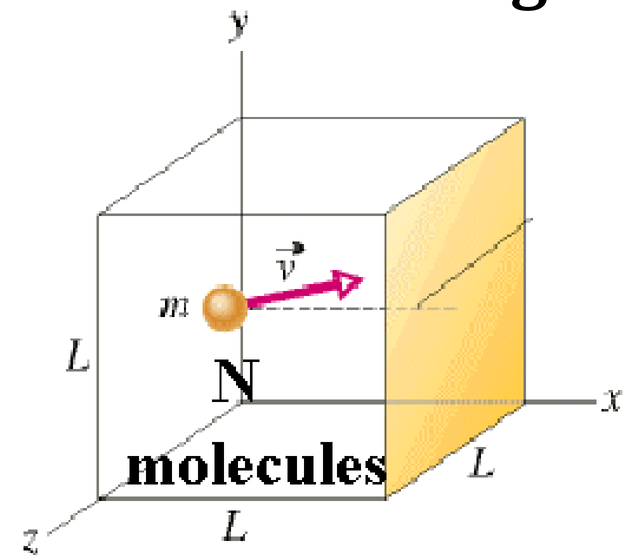
$$-mv_{ix} - mv_{ix} = -2mv_{ix}$$

The average rate at which momentum is delivered to the shaded wall by this single molecule is

$$F_i = \frac{\Delta(mv_i)}{\Delta t} = \frac{2mv_{ix}}{2L/v_{ix}} = \frac{mv_{ix}^2}{L} \quad \text{(due to one molecule)}$$

The total force due to all molecules *N* in the box acting on the area $A=L^2$ is

$$F = \frac{m}{L}\sum_i v_{ix}^2 = \frac{m}{L} N \frac{\overline{v^2}}{3}$$



The macroscopic pressure of molecules acting on wall:

$$P = \frac{F}{A} = \frac{m}{L^3} N \frac{\overline{v^2}}{3}$$

So, $$\boxed{P = \frac{1}{3}\frac{N m \overline{v^2}}{V} = \frac{1}{3} n' m v^2_{rms}}$$ Eq.(16-2) of P386

It gives the relation how the pressure of the gas (macroscopic quantity) depends on the speed of the molecules (microscopic quantity).

$$\boxed{P = \frac{2}{3} n' \left(\frac{1}{2} m v^2_{\mathrm{rms}}\right) = \frac{2}{3} n' \overline{K}}$$ —— **pressure formula**

Average translational kinetic energy of molecules:

分子平均平动动能(P386)

$$\bar{K} = (\frac{1}{2}mv^2)_{avg} = \frac{1}{2}mv_{rms}^2$$

Comparing $P = \frac{2}{3}n'\bar{K}$ with ideal gas equation $P = n'kT$, we have the average translational kinetic energy formula of a single atomic molecule of an ideal gas is

$$\boxed{\bar{K} = \frac{3}{2}kT}$$

root-mean-square speed （方均根速律）

$$\boxed{v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}}}$$

Explanations:

(1) The macroscopic quantities, such as pressure and temperature, of an ideal gas are microscopically statistical average quantities of motion of molecules（气体的压强、温度均是微观量的统计平均量）

(2) The temperature of a gas is the measurement for $\bar{K}$ (气体的温度是气体分子平均平动动能的量度, 宏观量T的微观意义:物体内部分子无规则热运动的剧烈程度)

Examples:

1. What is the average translational kinetic energy of molecules in an ideal gas at 37 °C?

Solution:

We use $\bar{K} = \frac{3}{2}kT$ **and change 37°C to 310K:**

$$\bar{K} = \frac{3}{2}kT = \frac{3}{2}(1.38 \times 10^{-23}\ \mathrm{J/K})(310\ \mathrm{K})$$

$$= 6.42 \times 10^{-21}\ \mathrm{J}$$

2. A gas is at 20 °C. To what temperature must it be raised to double the rms speed of its molecules?

Solution:

$$V_{rms} = \sqrt{\frac{3kT}{m}} \qquad V_{rms1} = \sqrt{\frac{3k \times 293}{m}}$$

$$V_{rms2} = 2V_{rms1} = \sqrt{\frac{3k \times 293 \times 4}{m}} = \sqrt{\frac{3k \times 1172}{m}}$$

$$T_2 = 1172 - 273 = 899\ °\text{C}$$

Summary

$$\boxed{PV = nRT} \quad \text{or} \quad \boxed{P = n'kT}$$

ideal gas law

$$\boxed{P = \frac{1}{3}\frac{Nm\overline{v^2}}{V} = \frac{2}{3}n'\overline{K}}$$

pressure formula

$$\boxed{\overline{K} = \frac{3}{2}kT}$$

average translational kinetic energy formula

$$\boxed{v_{\mathrm{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}}}$$

root-mean-square speed

The total translational kinetic energy of N molecules of gas is simply N times the average energy per molecule.

$$K_{total} = N\bar{K} = \frac{3}{2}NkT = \frac{3}{2}nRT$$

Examples:

A helium balloons has a volume of 0.3 m^3 and contains 2 mol of helium gas at 20 °C. Assuming the helium behaves like an ideal gas. What is the total translational kinetic energy of the gas molecules?

$$K_{total} = \frac{3}{2}nRT = \frac{3}{2}(2\ \text{mol})(8.31\ \text{J/mol·K})(293\ \text{K})$$

$$= 7.3 \times 10^3\ \text{J}$$

15-3 Distribution of Molecular Speeds (P388)

The speed of individual molecule is random; The speeds of immense molecules must obey some rules of distribution.

1. The Maxwell Distribution

In 1859, Scottish physicist James Clerk Maxwell showed the speed distribution of gas molecules in equilibrium:

$$\boxed{f(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}}}$$

Maxwell distribution of speeds

or

$$\boxed{f(v) = 4\pi\left(\frac{M_{mol}}{2\pi RT}\right)^{3/2} v^2 e^{-\frac{M_{mol}v^2}{2RT}}}$$

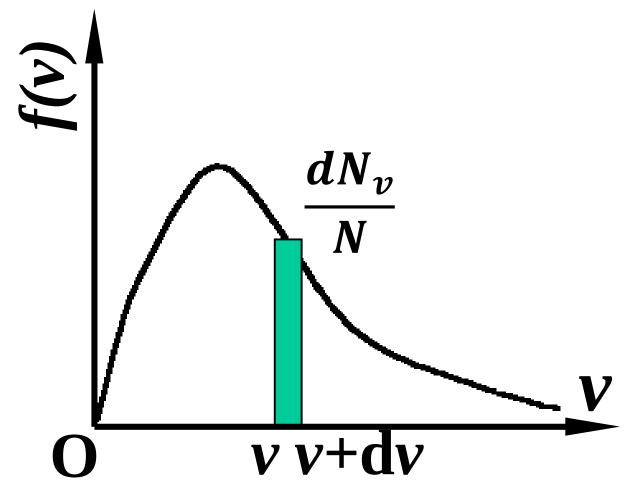
$$f(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}}$$

Physical meaning:

(1) $f(v) = \dfrac{dN_v}{N dv}$ 速率 v 附近单位速率区间内分子数占总分子数的比例。

(2) $f(v)dv = \dfrac{dN_v}{N}$

(3) $\dfrac{\Delta N}{N} = \displaystyle\int_{v_1}^{v_2} f(v)dv$



— **the fraction of molecules with speeds in an interval of v_1 to v_2**

($v_1 \sim v_2$ 速率区间内分子数占总分子数的比例)

2. Two properties of $f(v)$

(1) One of fundamental properties of any probability function is the normalization (归一化):

$$\int_0^{\infty} f(v)dv = \int_0^{\infty} 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}} dv = 1$$

$$\int_0^{N} \frac{\mathrm{d}N}{N} = \int_0^{\infty} f(v)\,\mathrm{d}v \equiv 1$$ —— **condition of normalization**

(2) Based on the rule of statistics, if probability function is $f(x)$, for any measurable function $\xi(x)$, the average of its measurement is:

$$\overline{\xi(x)} = \int_{-\infty}^{\infty} \xi(x) f(x)\mathrm{d}x$$

3. Three kinds of special speeds

(1) The average speed $\bar{v}$

$$\bar{v} = \int_0^\infty v f(v)\mathrm{d}v$$

$$= \int_0^\infty 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^3 \mathrm{e}^{-mv^2/2kT}\,\mathrm{d}v = \sqrt{\frac{8kT}{\pi m}}$$

$$\boxed{\bar{v} = \sqrt{\frac{8kT}{\pi m}} = 1.60\sqrt{\frac{kT}{m}}}$$

average speed

It is used to find the average distance of molecules.

(2) The root-mean-square speed v_{rms}

By the similar way, the root-mean-square speed is:

$$\sqrt{\overline{v^2}} = \left(\int_0^\infty v^2 f(v)dv\right)^{\frac{1}{2}}$$

so $$\boxed{v_{rms} = \sqrt{\frac{3kT}{m}} = 1.73\sqrt{\frac{kT}{m}}}$$ **(which agrees with the Eq. got earlier)**

v_{rms} can be used to calculate *average translational kinetic energy*.

(3) The most probable speed（最概然速率）v_p

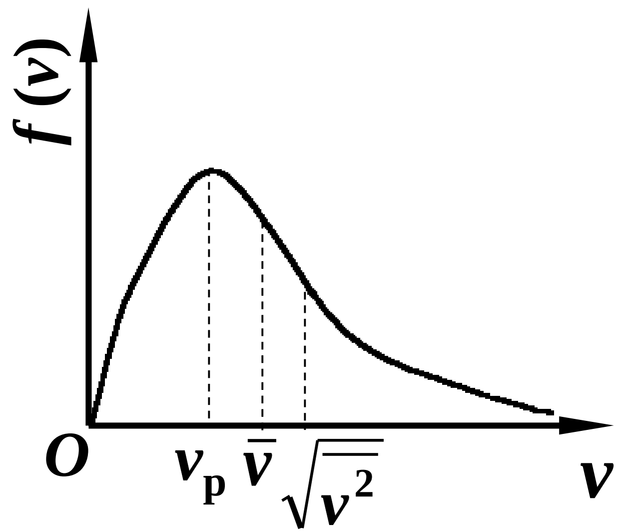
What does it mean? —— It has the largest probability

(分布在速率v_p—v_p+dv速率间隔的分子数占总分子数的概率最大)
which can be got from df (v_p) / dv = 0:

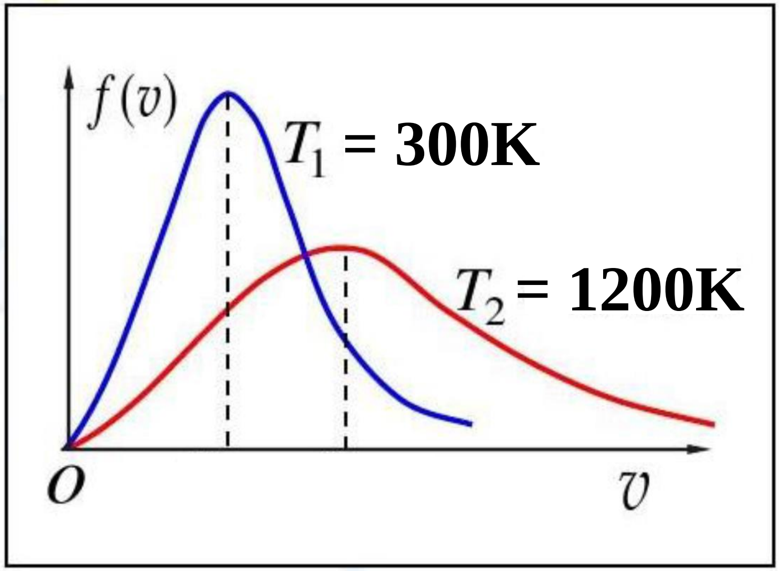
$$\boxed{v_p = \sqrt{\frac{2kT}{m}} = 1.41\sqrt{\frac{kT}{m}}}$$

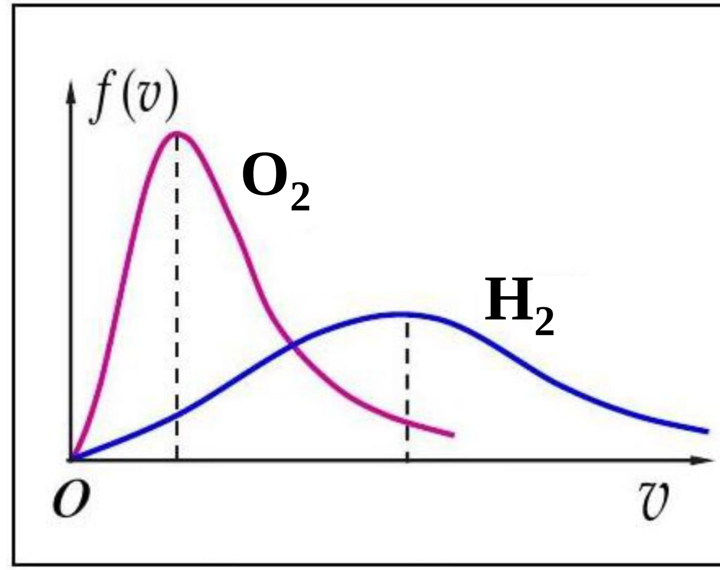
$$\bar{v} = 1.60\sqrt{\frac{kT}{m}}$$

$$v_{rms} = \sqrt{\overline{v^2}} = 1.73\sqrt{\frac{kT}{m}}$$



$$v_p < \bar{v} < \sqrt{\overline{v^2}}$$





300 K vs 1200 K

The same gas

O_2 vs H_2

The same temperature

Notes:

Conditions of Maxwell distribution of speeds:

(1) Thermal equilibrium;

(2) A huge number of molecules, and a great deal of collisions among them.

Example:

1. A 0.5 mol sample of hydrogen gas is at 300K. Find the average speed, the rms speed, and the most probable speed of the hydrogen molecules.

$$\sqrt{\frac{kT}{m}} = \sqrt{\frac{RT}{M_{mol}}}$$

Solution:

$$\bar{v} = 1.60\sqrt{\frac{RT}{M_{mol}}} = 1.60\sqrt{\frac{8.31 \times 300}{2 \times 10^{-3}}}\ \mathrm{m/s} = 1786\ \mathrm{m/s}$$

$$v_{rms} = 1.73\sqrt{\frac{RT}{M_{mol}}} = 1.73\sqrt{\frac{8.31 \times 300}{2 \times 10^{-3}}}\ \mathrm{m/s} = 1931\ \mathrm{m/s}$$

$$v_p = 1.41\sqrt{\frac{RT}{M_{mol}}} = 1.41\sqrt{\frac{8.31 \times 300}{2 \times 10^{-3}}}\ \mathrm{m/s} = 1574\ \mathrm{m/s}$$

2. Nine particles have speeds of 5.0, 8.0, 12.0, 12.0, 12.0, 14.0, 14.0, 17.0, and 20.0 m/s.

(a) Find the particles' average speed.

$$\bar{v} = \frac{(5.0 + 8.0 + 12.0 \times 3 + 14.0 \times 2 + 17.0 + 20.0)}{9}\ \mathrm{m/s}$$

$$= 12.7\ \mathrm{m/s}$$

(b) What is the rms speed of the particles?

$$\overline{v^2} = \frac{(5.0^2 + 8.0^2 + 12.0^2 \times 3 + 14.0^2 \times 2 + 17.0^2 + 20.0^2)}{9}$$

$$= 178\ \mathrm{m^2/s^2}$$

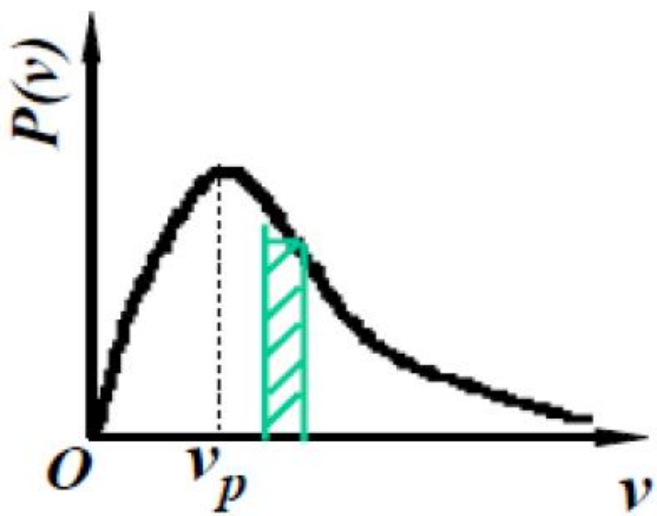
$$v_{rms} = \sqrt{\overline{v^2}} = 13.3\ \mathrm{m/s}$$

(c) What is the most probable speed of the particles?

Three of the particles have a speed of 12.0 m/s, two have a speed of 14.0 m/s, and the remaining four have different speeds. Hence, the most probable speed v_p is 12.0 m/s.

3. (1)What is the meaning of shadow area in the curve?

(2) Expressing the average speed of gases within the speed region (0, v_p) in terms of $P(v)$



Solution:

(2) $$\bar{v} = \frac{\int_0^{v_p} v\, dN_v}{\int_0^{v_p} dN_v} = \frac{\int_0^{v_p} v\, NP(v)dv}{\int_0^{v_p} NP(v)dv}$$

i.e. $$\bar{v} = \frac{\int_0^{v_p} v\, P(v)dv}{\int_0^{v_p} P(v)dv}$$

Summary

(1) $f(v)=\dfrac{\mathrm{d}N_v}{N\mathrm{d}v}$

速率 v 附近单位速率区间内分子数占总分子数的比例。

(2) $f(v)\mathrm{d}v=\dfrac{\mathrm{d}N_v}{N}$

速率 v 附近 $\mathrm{d}v$ 速率区间内分子数占总分子数的比例。

(3) $\dfrac{\Delta N}{N}=\int_{v_1}^{v_2} f(v)\mathrm{d}v$

$v_1 \sim v_2$ 速率区间内分子数占总分子数的比例。

$$v_p=1.41\sqrt{\frac{kT}{m}}=1.41\sqrt{\frac{RT}{M_{mol}}}$$

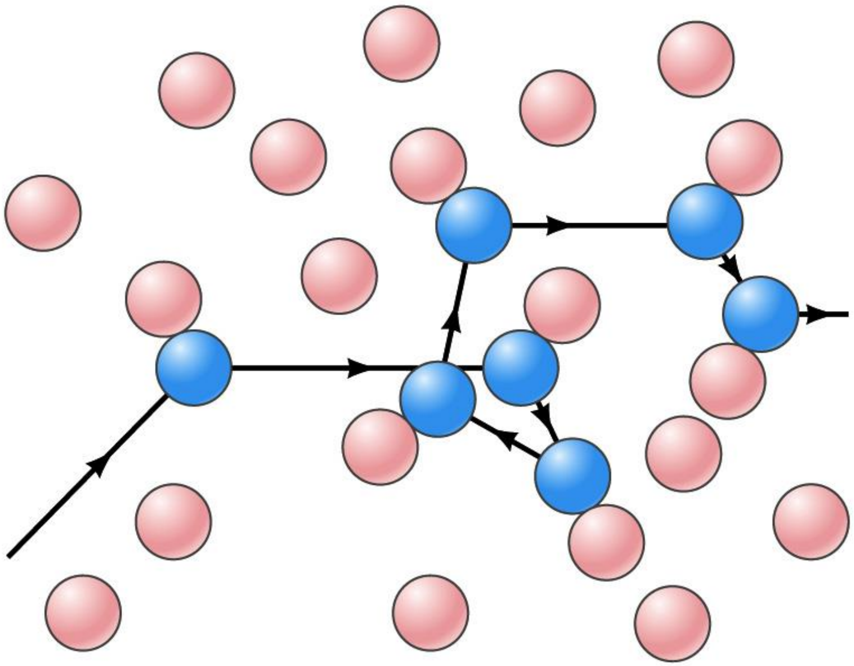
$$\bar{v}=1.60\sqrt{\frac{kT}{m}}=1.60\sqrt{\frac{RT}{M_{mol}}}$$

$$v_{rms}=1.73\sqrt{\frac{kT}{m}}=1.73\sqrt{\frac{RT}{M_{mol}}}$$

15-4 Mean Free Path (P396)

If we were to follow the path of a particular molecule, we would expect to see it follows a zigzag path as shown in the Figure below.

An important parameter for a given situation is the mean free path, which is defined as the average distance a molecule travels between collisions.

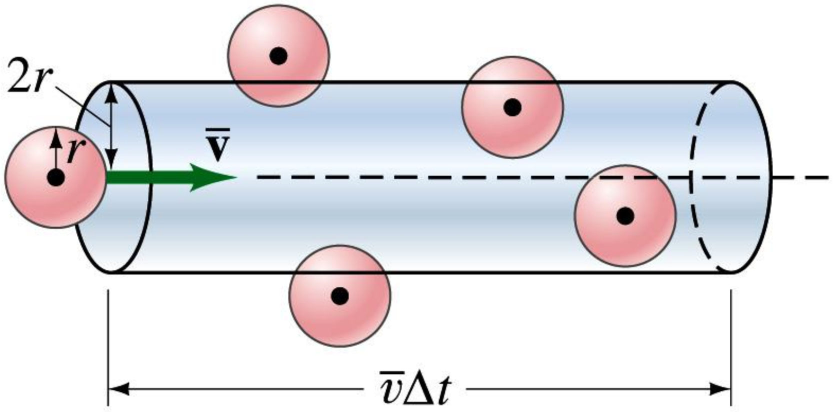


Suppose our gas is made up of molecules which are hard spheres of radius *r*. (有效半径为*r*的刚性球)

The number of molecules whose center lies within the cylinder, or the number of collisions should be

$$n' V_{\text{cylin}} = \frac{N}{V} \cdot \pi (2r)^2 \bar{v} \Delta t$$

We define the mean free path l_M as the average distance between collisions.



The mean free path l_M equals to the distance traveled $(\bar{v}\Delta t)$ in a time Δt divided by the number of collisions made in time Δt .

$$l_M = \frac{\bar{v}\Delta t}{(N/V)\pi(2r)^2\bar{v}\Delta t} = \frac{1}{4\pi r^2 (N/V)}$$

Considering other molecules are actually moving, so the number of collisions in a time Δt must depend on the relative speed of colliding molecules.

A careful calculation shows that for a Maxwell distribution of speeds: $v_{rel} = \sqrt{2}\bar{v}$

Hence the mean free path is

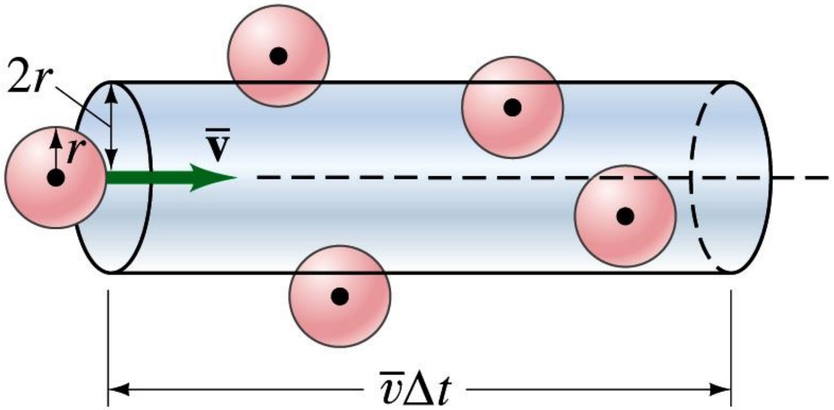
$$\boxed{l_M = \frac{1}{4\pi\sqrt{2}r^2(N/V)}}$$

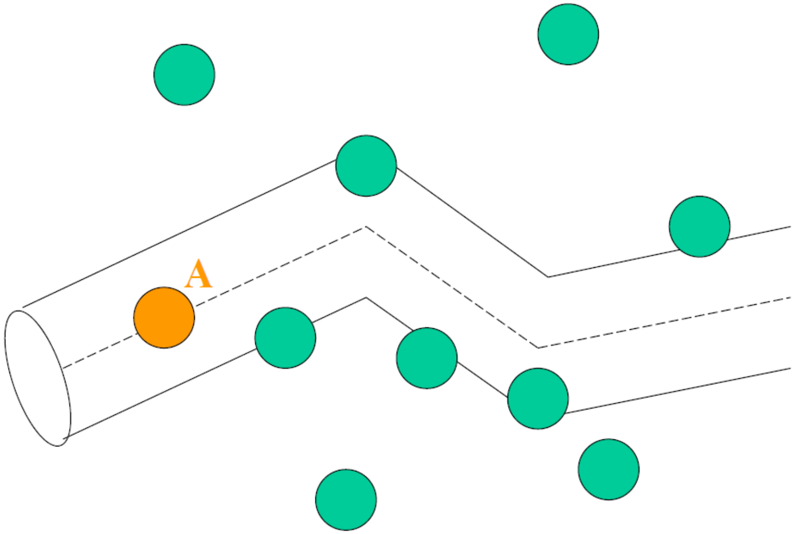
(Mean/Average) collision frequency

— the colliding times for a molecule per unit time:

$$\boxed{\bar{Z} = \frac{\bar{v}}{l_M} = 4\pi\sqrt{2}r^2\bar{v}n'}$$

$$n' V_{\text{cylin}} = \frac{N}{V} \cdot \pi (2r)^2 \bar{v} \Delta t$$





The distribution of molecules on the position is uniform.

$$n' = \frac{\mathrm{d}N}{\mathrm{d}V} = \frac{N}{V}$$

Example:

Estimate the mean free path of hydrogen molecules and the average collision frequency at STP (0 °C, 1 atm). The diameter of H_2 is 2×10^{-10} m.

Solution:

$$\bar{v} = 1.6\sqrt{\frac{RT}{\mu}} = 1.6\sqrt{\frac{8.31 \times 273}{2 \times 10^{-3}}} = 1.70 \times 10^{3}\ \mathrm{m/s}$$

$$\because \quad n' = \frac{p}{kT} = \frac{1.013 \times 10^{5}}{1.38 \times 10^{-23} \times 273} = 2.69 \times 10^{25}\, m^{-3}$$

$$l_M = \frac{1}{\sqrt{2}\pi d^{2} n'} = 2.10 \times 10^{-7}\, m$$

$$\bar{z} = \frac{\bar{v}}{l_M} = 8.10 \times 10^{9}\, s^{-1}$$

Homework for Chap. 16

Problems:

P400-402 1, 2, 5, 8, 12, 14, 33, 39, 47

33. T = 273K
39. Diameter of N_2: $d = 3 \times 10^{-10}$m