

Chapter 9

The kinetic-molecular theory

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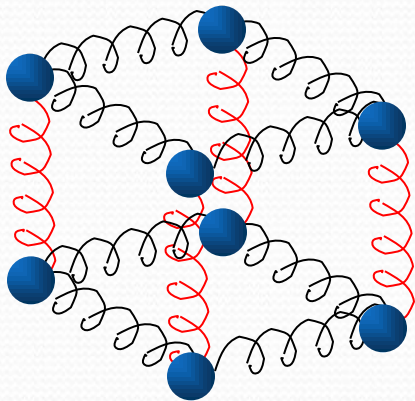


What is heat?

What is temperature?

It was once common belief that heat was an invisible substance. It even had a name--“caloric (热质),” and it was believed that it could be transferred between objects but neither created nor destroyed. To heat up an object this caloric had to flow into it. This, they thought, explained why objects expanded when heated. But this theory could not explain, for example, how heat could emanate (产生) from a cold piece of wood once it is set on fire? Where did the caloric come from? If it had been in the wood in the first place, the wood should have been hot all along.

The caloric theory was abandoned in the 19th century and replaced with the kinetic-molecular theory. This new theory stated that all matter is made up of atoms/molecules. The faster they move, the hotter an object will be.



The hotter something is, the faster its molecules are moving or vibrating, and the higher its temperature. Temperature is proportional to the average kinetic energy of the atoms or molecules that make up a substance.

In this two chapters we will study **Ideal Gas**.

■ Ideal Gas

Assumptions:

- The particles have negligible volume
- They have perfectly elastic collisions
- There are no intermolecular forces
- They are moving in random directions
- The average separation between molecules is large
- Molecules obeys Newton's Law
- Consists of identical molecules

§ 9.1 Equilibrium state

■ The State Parameters of the Gas

□ P (pressure)

SI unit

Pa

$$1 \text{ Pa} = 1 \text{ N/m}^2$$

$$1 \text{ mmHg} = 1.333 \times 10^2 \text{ Pa}$$

$$1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}$$

□ V (volume)

SI unit:

m^3

Other units: $1 \text{ l} = 10^{-3} \text{ m}^3$

$$1 \text{ cm}^3 = 10^{-6} \text{ m}^3$$

□ T (temperature)

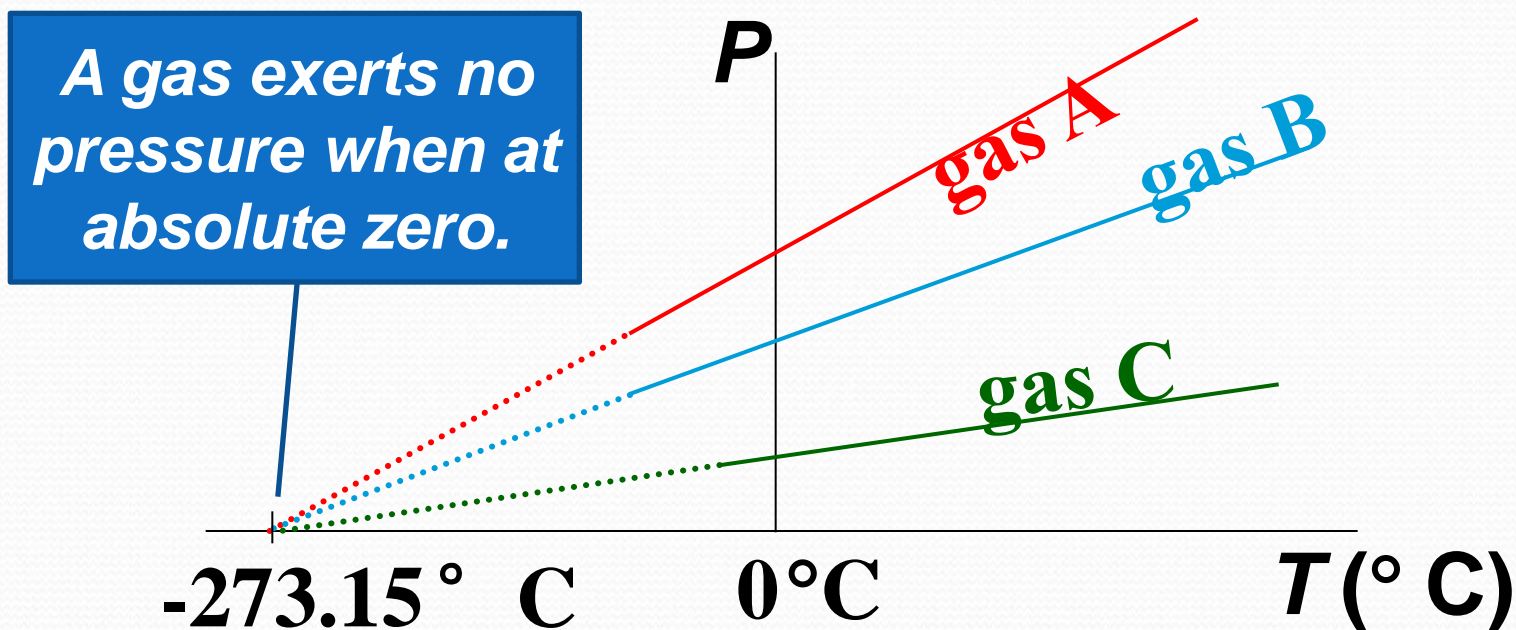
- **Fahrenheit(华氏温标):** water freezes at **32° F**; boils at **212° F**
- **Celsius scale(摄氏温标):** water freezes at **0° C**; boils at **100° C**
- **Kelvin scale(开尔文):** water freezes at **273.15K**; boils at **373.15K**

$$T_c = T_k - 273.15$$

$$T_F = 1.8T_c + 32$$

□ Charles' law(查理定律)

Graphing Pressure vs. Temperature for a variety of gases and extrapolating.



Absolute zero can never be reached, but there is no limit to how close we can get to it.

$$T(\text{min.})=2.4 \times 10^{-11}\text{k}$$

Steven Chu(朱棣文), Ph.D (born February 28, 1948), is an American physicist and currently the 12th United States Secretary of Energy.

As a scientist, Chu is known for his research in cooling and trapping of atoms with laser light, which won him the Nobel Prize in Physics in 1997.



■ Equilibrium State

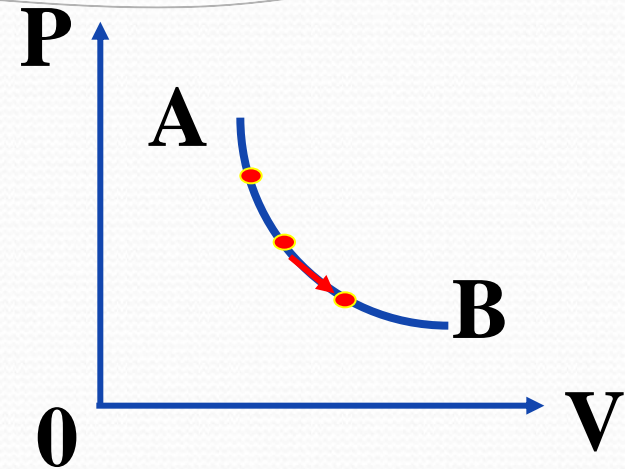
Put a gas with a certain mass into a container with a given volume, after a relatively long time, the pressure **P** of the gas in every part of the container is the same, so is the temperature **T** everywhere. Now the state parameters of the system all have definite values and they **don't change with time**. If the gas isn't affected by the external world, its macroscopical properties do not change with time, such a state is called an **equilibrium state**.

A point

——an equilibrium state

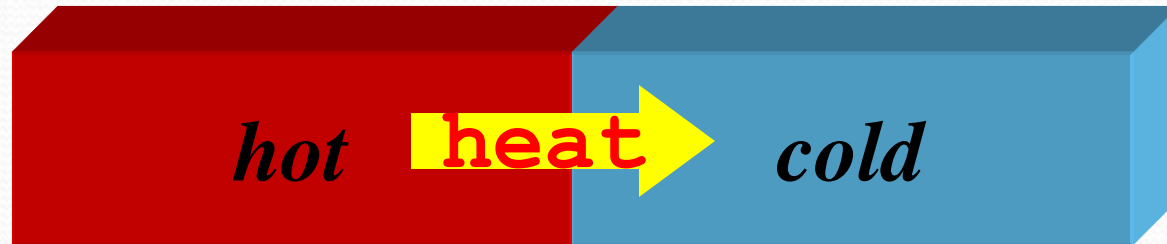
A line(path)

——a quasistatic process

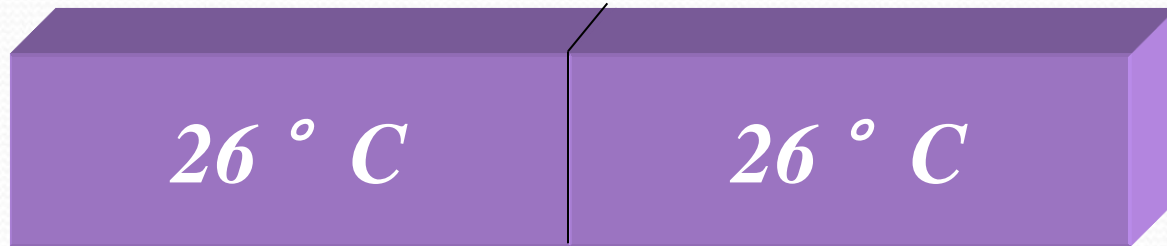


In thermodynamics, a quasistatic process is a thermodynamic process that happens infinitely slowly. No real process is quasistatic, but such processes can be approximated by performing them very slowly. A quasistatic process ensures that the system will go through a sequence of states that are infinitesimally close to equilibrium.

■ Thermal Equilibrium

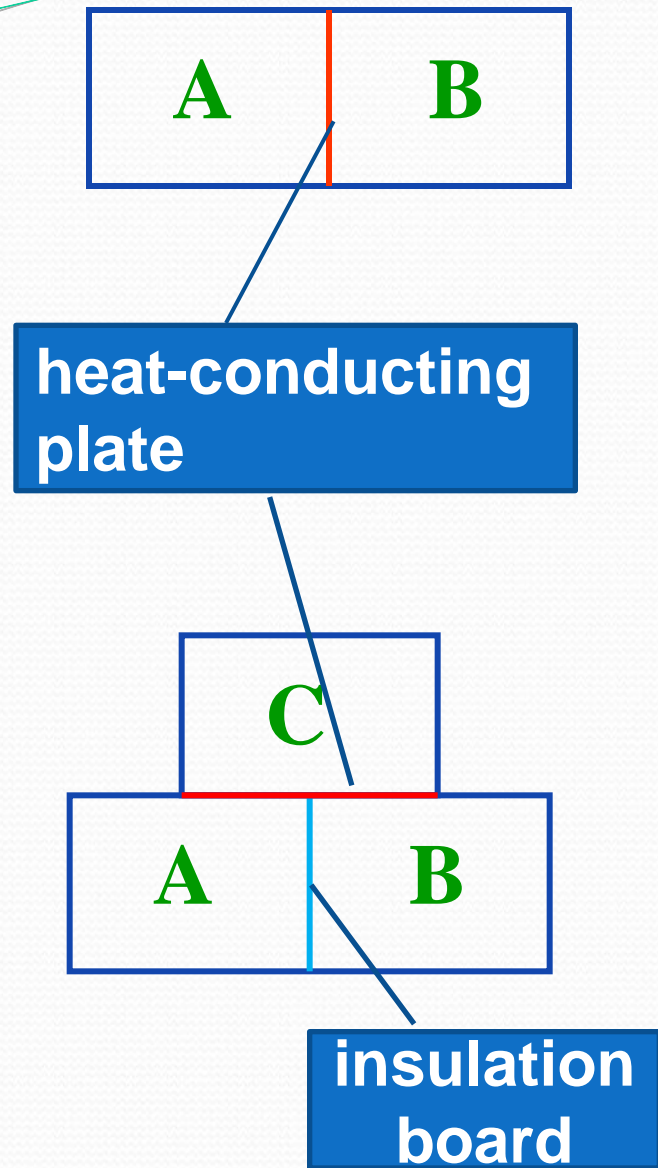


Two bodies are said to be at thermal equilibrium if they are at the same temperature. This means there is no net exchange of thermal energy between the two bodies. The top pair of objects are in contact, but since they are at different temps, they are not in thermal equilibrium, and energy is flowing from the hot side to the cold side.



No net heat flow

The two purple objects are at the same temperature and, therefore are in thermal equilibrium. There is no net flow of heat energy here.



Under an equilibrium state

$$T_A = T_B$$

If object A is in thermal equilibrium with object B, and if object B is in thermal equilibrium with object C, then objects A and C are also in equilibrium. This is sort of a “transitive property of heat.”

$$T_A = T_C = T_B$$

——Zeroth law of thermodynamics

§ 9.2 The Ideal Gas Law

$$PV = \mu RT = \frac{M}{M_{mol}} RT \quad \text{In K}$$

μ : the number of moles of the ideal gas

$$\mu = \frac{N}{N_A}$$

Total number
of molecules

Avogadro's number: the number of atoms, molecules, etc, in a mole of a substance:

$$N_A = 6.02 \times 10^{23} / \text{mol}.$$

R: the Gas Constant(普适气体常量):

$$R = 8.31 \text{ J/mol} \cdot \text{K}$$

According to the ideal gas state equation

$$\begin{aligned} P &= \frac{1}{V} \frac{M}{M_{mol}} RT \\ &= \frac{1}{V} \frac{mN}{m} \cdot \frac{R}{N_A} T \\ &= nkT \end{aligned}$$

n ——— number density of molecules
k = $1.38 \times 10^{-23} \text{ J/K}$
——— Boltzmann constant

Example 9.1 Consider a given mass of an ideal gas. Please draw curves representing isobaric(等压) process, isochoric(等体) process, and isothermal(等温) processes on (a) a p - V diagram, (b) a p - T diagram, and (c) a V - T diagram.

Solution:

According to the ideal gas state equation

$$PV = \mu RT$$

Isothermal process

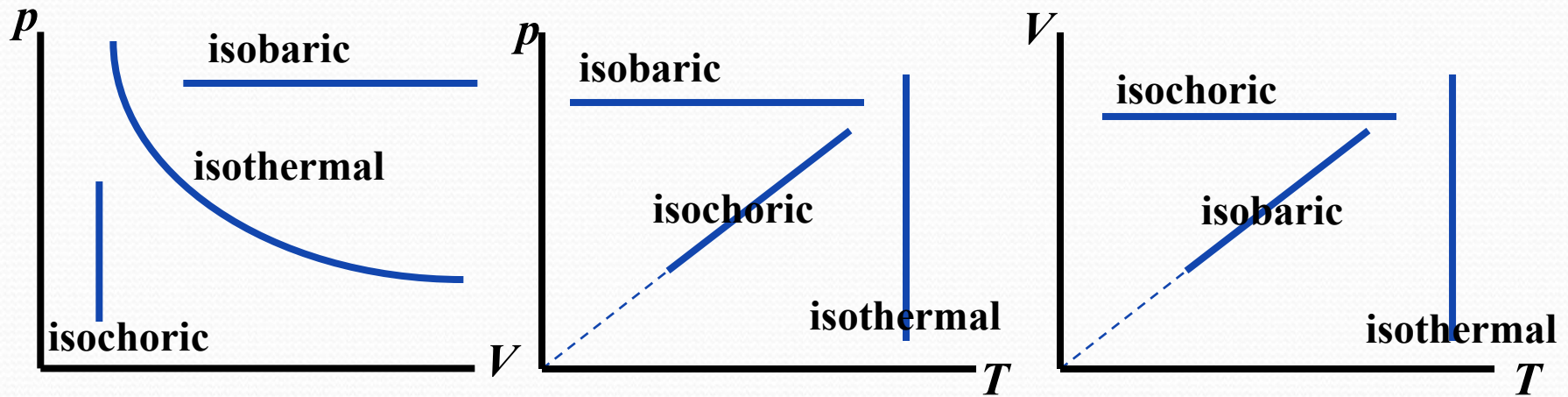
$$PV = \frac{M}{M_{mol}} RT$$

Isochoric process

$$\frac{P}{T} = \frac{M}{M_{mol}} \frac{R}{V}$$

Isobaric process

$$\frac{V}{T} = \frac{M}{M_{mol}} \frac{R}{P}$$



§ 9.3 Expression for Pressure

Pressure: Results from collisions of molecules on the surface

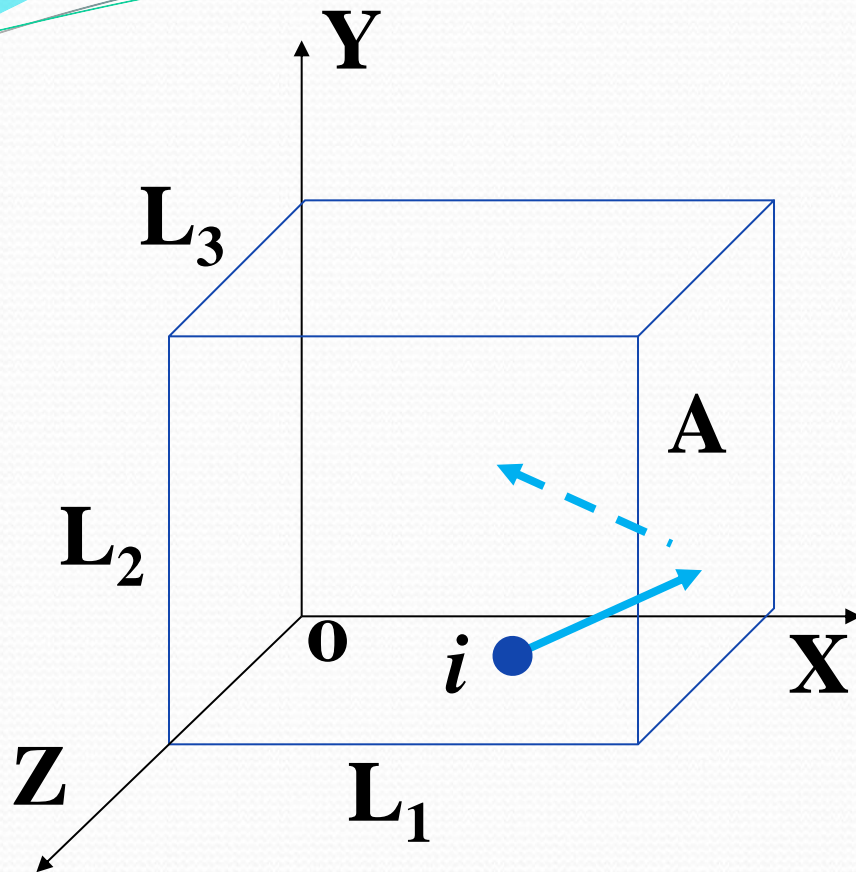
Pressure: $P = \frac{F}{A}$

Force
Area

Force: $F = \frac{dp}{dt}$

Rate of change of momentum
given to the surface

**Momentum given by each collision
times the number of collisions in time dt**



Only molecules moving toward the surface hit the surface. Assuming the surface is normal to the x axis, half the molecules of speed v_x move toward the surface.

Only those close enough to the surface hit it in time dt , those within the distance $v_x dt$

The number of collisions hitting an area A in time dt is

$$\frac{1}{2} \left(\frac{N}{V} \right) \cdot A \cdot v_x \cdot dt$$

The momentum given by each collision to the surface is

$$2mv_x$$

Momentum in time dt :

$$dp = (2mv_x) \cdot \frac{1}{2} \cdot \left(\frac{N}{V} \right) \cdot A \cdot v_x dt$$

Force:

$$F = \frac{dp}{dt} = (2mv_x) \cdot \frac{1}{2} \cdot \left(\frac{N}{V} \right) \cdot A \cdot v_x$$

Pressure:

$$P = \frac{F}{A} = \frac{N}{V} m v_x^2$$

Not all molecules have the same speed

\Rightarrow average $\overline{v_x^2}$

$$P = \frac{N}{V} m \overline{v_x^2}$$

$$v_x^2 = \frac{1}{3} v^2 = \frac{1}{3} (v_x^2 + v_y^2 + v_z^2)$$

$$\overline{v_x^2} = \frac{1}{3} \overline{v^2} = \frac{1}{3} v_{rms}^2$$

v_{rms} is the root-mean-square speed

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}}{3}}$$

Pressure:
$$P = \frac{1}{3} \frac{N}{V} m \overline{v^2} = \frac{2}{3} \left(\frac{N}{V} \right) \left(\frac{1}{2} m \overline{v^2} \right)$$

Average Translational Kinetic Energy:

$$\overline{\mathcal{E}_t} = \frac{1}{2} m \overline{v^2} = \frac{1}{2} m v_{rms}^2$$

Pressure:

$$P = \frac{2}{3} \cdot \frac{N}{V} \cdot \overline{\mathcal{E}_t} = \frac{2}{3} n \overline{\mathcal{E}_t}$$

§ 9.4 The Microscopic Interpretation of Temperature

$$\left\{ \begin{array}{l} P = nkT \\ P = \frac{2}{3} n \overline{\varepsilon_t} \end{array} \right. \longrightarrow \overline{\varepsilon_t} = \frac{3}{2} kT$$

- Temperature expresses the degree of the thermal motion of large quantities of molecules.
- Just like pressure, the temperature is a macroscopic physical quantity, but also it is a statistical quantity.

$$\left\{ \begin{array}{l} \overline{\varepsilon_t} = \frac{1}{2} m \overline{v^2} \\ \overline{\varepsilon_t} = \frac{3}{2} kT \end{array} \right. \rightarrow v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M_{mol}}}$$

Example 9.2 (a) Compute the root-mean-square speed of a nitrogen molecule(氮气分子) at **20.0 °C**. At what temperatures will the root-mean-square speed be (b) half that value and (c) twice that value?

Solution (a)

$$v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.31 \text{ J/mol} \cdot \text{K})(293 \text{ K})}{28.0 \times 10^{-3} \text{ kg/mol}}} = 511 \text{ m/s}$$

(b) Since $v_{rms} \propto \sqrt{T}$ $\frac{v_{rms}'^2}{v_{rms}^2} = \frac{T'}{T}$

for $0.5v_{rms}$ $T' = 0.5^2 T = 73.3 \text{ K} = -200^\circ \text{C}$

for $2v_{rms}$ $T'' = 2^2 T = 1.17 \times 10^3 \text{ K} = 899^\circ \text{C}$

Example 9.3 In a container with a volume of $V=10\text{L}$, there is the ideal gas of the mass $M=100\text{g}$. If the root-mean-square speed is $v_{rms} = 200\text{m/s}$, what is the pressure? (unit in mmHg)

Solution

Method 1

$$\begin{aligned} P &= \frac{2}{3} n \overline{\varepsilon_t} = \frac{2}{3} \cdot \frac{N}{V} \cdot \frac{1}{2} m \overline{v^2} = \frac{M}{3V} \overline{v^2} \\ &= \frac{100 \times 10^{-3}}{3 \times 10 \times 10^{-3}} \times (200)^2 \times \frac{1}{1.333 \times 10^2} \\ &= 1.0 \times 10^3 (\text{mmHg}) \end{aligned}$$

Method 2

$$P = nkT = n \frac{m}{3} \overline{v^2} = \frac{\rho}{3} \overline{v^2} = \frac{M}{3V} \overline{v^2} = \dots$$

Method 3

$$P = \frac{M}{VM_{mol}} RT = \frac{M}{3V} \overline{v^2} = \dots$$

§ 9.5 Equipartition of Energy(能量均分)

- When the gas is at equilibrium state there is no preferred direction of the direction of motion of the gas molecules, the probability of the molecular motion in all directions are equal .
- The theorem of equipartition of energy states that molecules in thermal equilibrium have the same average energy $kT/2$ associated with each independent degree of freedom of their motion.

——The Equipartition Theorem of Energy

■ Degrees of freedom (自由度)

- The degree of freedom can be defined as the minimum number of independent coordinates which can specify the position of the system completely.
- We also define that the number of independent velocity square terms in the energy expression of the molecule as degrees of freedom, denoted by symbol i .

□ **monatomic molecule**(单原子分子)

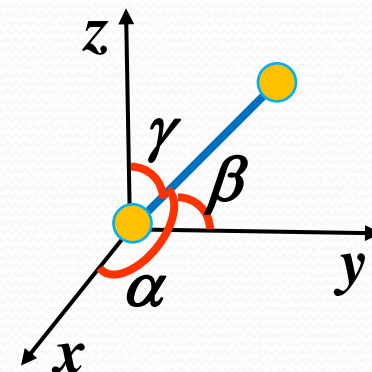


$$i = 3$$

□ **rigid diatomic molecule** (刚性双原子分子)

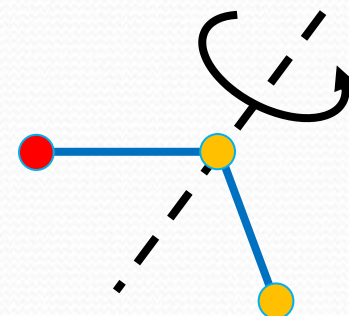
$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1$$

$$i = 5$$



□ **rigid polyatomic molecule** (刚性多原子分子)

$$i = 6$$



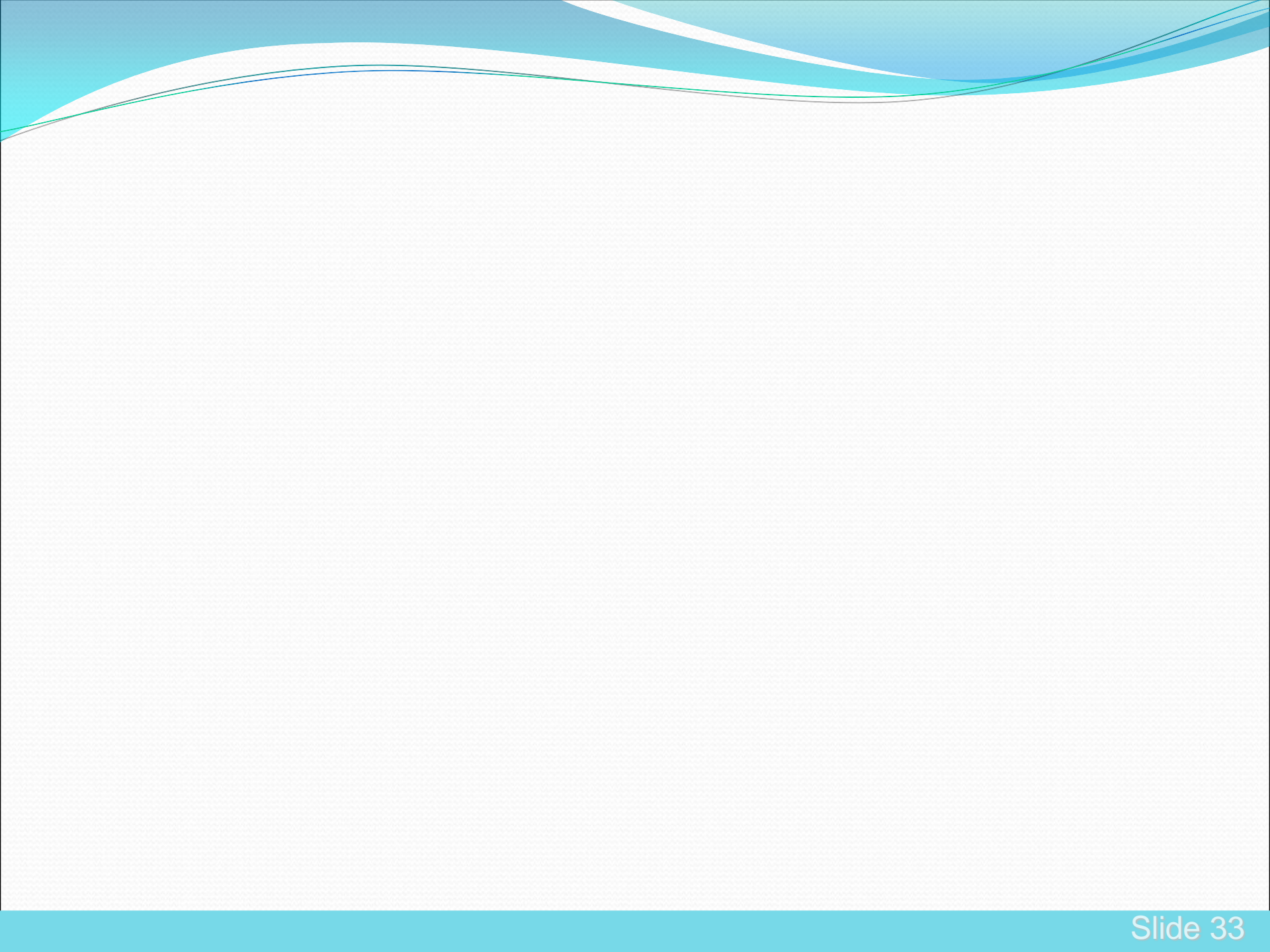
- Rigid molecules have translational kinetic energy and rotational kinetic energy(转动动能).
- non-rigid molecules have translational kinetic energy, rotational kinetic energy and vibrational kinetic energy(振动动能).

For H_2 molecule

$T < 50 \text{ k}$, $i=3$ (translation)

$50 \text{ k} < T < 600 \text{ k}$, $i=5$ (translation + rotation)

$T > 600 \text{ k}$, $i=6$ (translation
+rotation + vibration)



Example 9.4 What is the average translational kinetic energy of nitrogen molecules at 1600K, (a) in joules and (b) in electron-volts? (c) What are the average rotational kinetic energy and average kinetic energy of the same molecules ?

Solution

$$\begin{aligned} \text{(a)} \quad \bar{\varepsilon}_t &= \frac{3}{2} k_B T = \frac{3}{2} \times 1.38 \times 10^{-23} \times 1600 \\ &= 3.31 \times 10^{-20} \text{ J} \end{aligned}$$

$$\text{(b)} \quad 1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$$

$$\bar{\varepsilon}_t = \frac{3.31 \times 10^{-20} \text{ J}}{1.60 \times 10^{-19} \text{ J/eV}} = 0.21 \text{ eV}$$

$$\begin{aligned} \text{(c)} \quad \bar{\varepsilon}_r &= \frac{2}{2} k_B T = 1.38 \times 10^{-23} \times 1600 \\ &= 2.21 \times 10^{-20} \text{ J} \end{aligned}$$

$$\begin{aligned} \bar{\varepsilon}_k &= \frac{5}{2} k_B T = \frac{5}{2} \times 1.38 \times 10^{-23} \times 1600 \\ &= 5.52 \times 10^{-20} \text{ J} \end{aligned}$$

■ The Internal Energy of the Ideal Gas

The interactions between molecules are negligible, the gas has no potential energy. The internal energy of the ideal gas is the sum of the kinetic energies of the molecules.

The internal energy of an ideal gas with mass M (the degree of freedom of the gas is i and the mole mass is M_{mol}) is

$$E_k = N \cdot \overline{\varepsilon_k} = \frac{M}{M_{mol}} N_A \cdot \frac{i}{2} kT = \frac{M}{M_{mol}} \cdot \frac{i}{2} RT$$

Example 9.5 P, V and T are all same of two bottles of hydrogen(氢) and helium(氦) gas. What is the ratio of E_{H_2} / E_{He}

Solution

$$\therefore E = \frac{M}{M_{mol}} \cdot \frac{i}{2} RT = \frac{i}{2} PV$$

$$\therefore \frac{E_{H_2}}{E_{He}} = \frac{i_{H_2}}{i_{He}} = \frac{5}{3}$$

Example 9.6 The increment of the internal energy of a quantity of ideal gas is **41.6J** when the temperature of the gas rises **1K**. What is the mass of the ideal gas?

Solution $E = \frac{M}{M_{mol}} \cdot \frac{i}{2} RT$

$$\rightarrow \Delta E = \frac{M}{M_{mol}} \cdot \frac{i}{2} R \Delta T$$

$$\begin{aligned} \rightarrow M &= \frac{2M_{mol}\Delta E}{iR\Delta T} = \frac{2 \times 2.0 \times 10^{-3} \times 41.6}{5 \times 8.31 \times 1} \\ &= 4.0 \times 10^{-3} \text{ (kg)} \end{aligned}$$

§ 9.6 Distribution of Molecular Speeds

Based on the characteristic of the molecular thermal motion of gases at equilibrium states, Maxwell applied the method of probability(概率) and derived the speed distribution law of gas molecules at equilibrium.

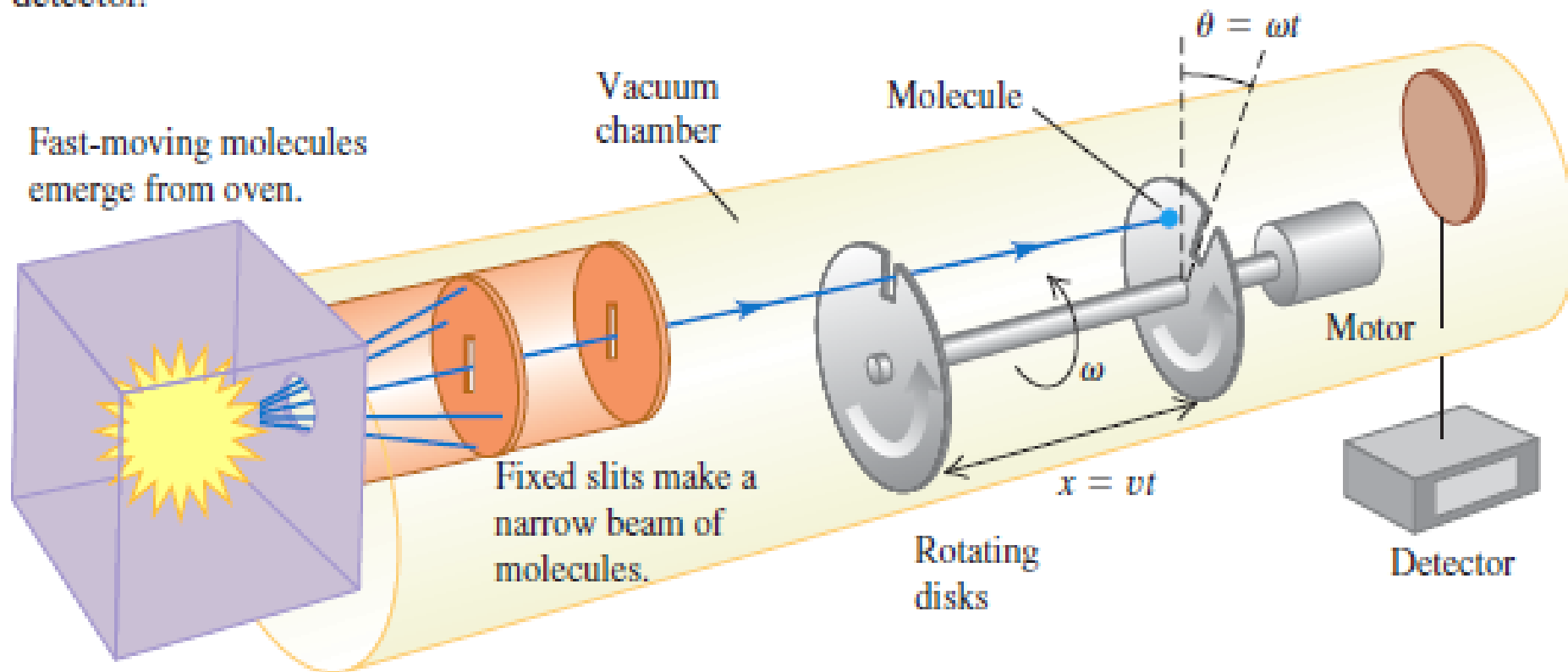
$$f(v) = \frac{dN_v}{Ndv}$$

——the distribution function of speeds

N: Total number of molecules

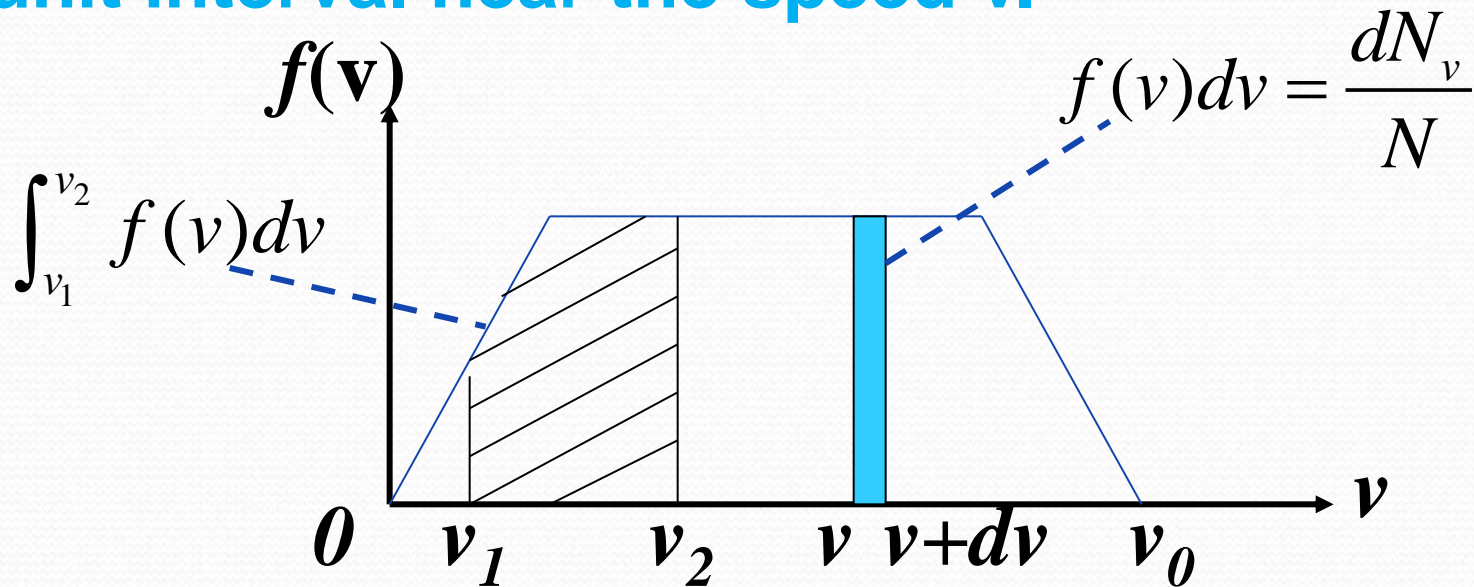
dN_v: Number of molecules in the speed interval
v ~ v + dv

18.22 A molecule with a speed v passes through the slit in the first rotating disk. When the molecule reaches the second rotating disk, the disks have rotated through the offset angle θ . If $v = \omega x / \theta$, the molecule passes through the slit in the second rotating disk and reaches the detector.



The physical significance of the distribution function of speeds

The ratio of the number of molecules dN with speeds in the unit interval near speed v and the total number of molecules N , or the probability of a molecule having a speed in the unit interval near the speed v .



In 1859 Maxwell was the first to theoretically derive the mathematical form of the distribution of speeds of gas molecules at an equilibrium state.

$$f(v) = Av^2 e^{-Bv^2} \text{——Maxwellian } f(v)$$

$$A = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2}, \quad B = \frac{m}{2kT}$$

$\left\{ \begin{array}{l} \mathbf{m} \text{—— the mass of the molecule} \\ \mathbf{k} \text{—— Boltzmann constant} \\ \mathbf{T} \text{—— temperature} \end{array} \right.$

$$\int_0^\infty f(v) dv = 1 \quad \text{——normalization condition}$$

Example 9.7 The following diagram shows the curves of the Maxwell speed distribution at T_1 and T_2 . If $m_1 = m_2$, T_2 and T_1 which is higher? If $T_2 = T_1$, m_1 and m_2 , which is larger?

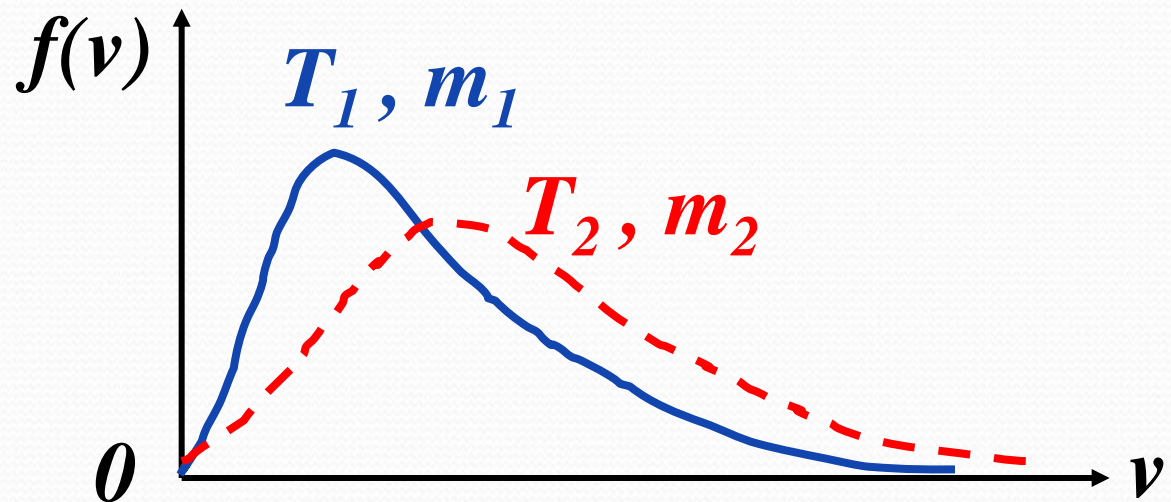
Solution

If $m_1 = m_2$

$T_2 > T_1$

If $T_1 = T_2$,

$m_2 < m_1$



Example 9.8 Explain the physical significance of the following expression:

$$(a) f(v)dv, \quad (b) Nf(v)dv, \quad (c) \int_{v_1}^{v_2} f(v)dv, \quad (d) \int_{v_1}^{v_2} Nf(v)dv$$

Solution

$(a) f(v)dv$ Represents the ratio of the number of molecules dN in the speed interval $v \sim v+dv$ and the total number of molecules N at an equilibrium state.

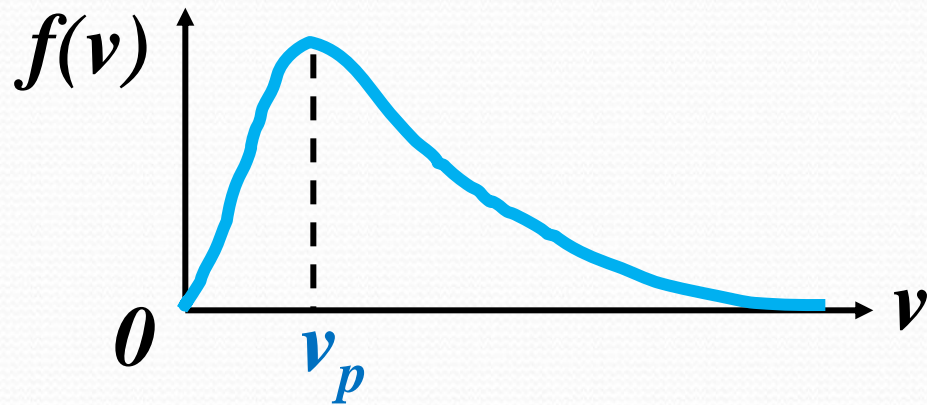
$(b) Nf(v)dv$ Represents the number of molecules dN in the speed interval $v \sim v+dv$ at an equilibrium state.

$(c) \int_{v_1}^{v_2} f(v) dv$ Represents the ratio of the number of molecules between $v_1 \sim v_2$ and the total number of molecules N at an equilibrium state.

$(d) \int_{v_1}^{v_2} Nf(v) dv$ Represents the number of molecules between $v_1 \sim v_2$ at an equilibrium state

■ three-characteristic speed (三个特征速率)

□ The most probable speed (最概然速率/最可几速率)



This gives the value of the speed where the curve has its peak.

$$\left. \frac{df(v)}{dv} \right|_{v_p} = 0$$



$$v_p = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M_{\text{mol}}}}$$

□ **The average speed** (平均速率)

$$\bar{v} = \frac{\int_0^{\infty} v dN}{N} = \int_0^{\infty} v f(v) dv \quad \left(\int_0^{\infty} v^3 e^{-Bv^2} dv = \frac{1}{2B^2} \right)$$
$$= \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M_{\text{mol}}}}$$

□ **The root-mean square speed**

$$\overline{v^2} = \frac{\int_0^{\infty} v^2 dN}{N} = \int_0^{\infty} v^2 f(v) dv \quad \left(\int_0^{\infty} v^4 e^{-Bv^2} dv = \frac{3}{8} \sqrt{\frac{\pi}{B^5}} \right)$$
$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M_{\text{mol}}}}$$

NOTE

For the same ideal gas

$$v_p < \bar{v} < \sqrt{v^2} \propto \sqrt{\frac{T}{m}}$$

See you next time!