

The Kinetic Theory of Gas



Agenda Today

- Ideal gas
- Pressure and temperature (micro interpretation)
- Internal energy of idea gas
- Distribution law of molecular speed for ideal gas
- mean free path

The ideal-gas law (理想气体状态方程)

$$PV = \frac{m}{M} RT$$

M: molar mass (摩尔质量)

R: universal gas constant (普适气体常数)

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

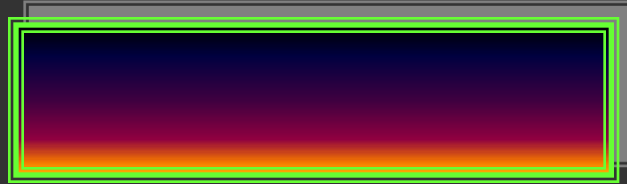
Avogadro's number:

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

The number of moles

$$\frac{m}{M} = \frac{N}{N_A}$$

Other forms of idea-gas Law



K : Boltzmann's constant

$$1.38 \times 10^{-23} \text{ J/K}$$

$$\rho = \frac{M}{RT} P$$

The molecular interpretation of temperature: the kinetic theory of gases

1 the gas consists of a large number of molecules that make elastic collisions with each other and with the walls of the container

2 the molecules are separated, on the average, by the distances that are very large compared with their diameters

3 the molecules did not exert force on each other except when they collide

4 there is no preferred position for a molecule and no preferred direction for velocity, when there is no external force

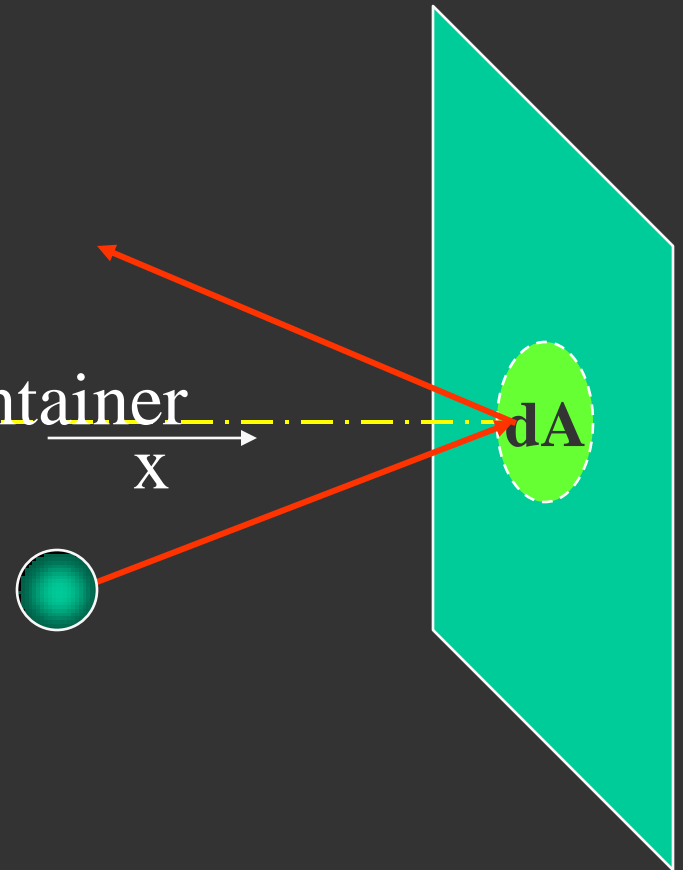
Suppose the gas is held in a cube container, one molecule moves ceaselessly

The increase of molecule's momentum

$$-\mu v_{ix} - \mu v_{ix} = -2\mu v_{ix}$$

The impulse on the wall of the container

$$2\mu v_{ix}$$



The number of collision
the molecule has with
the wall in dt

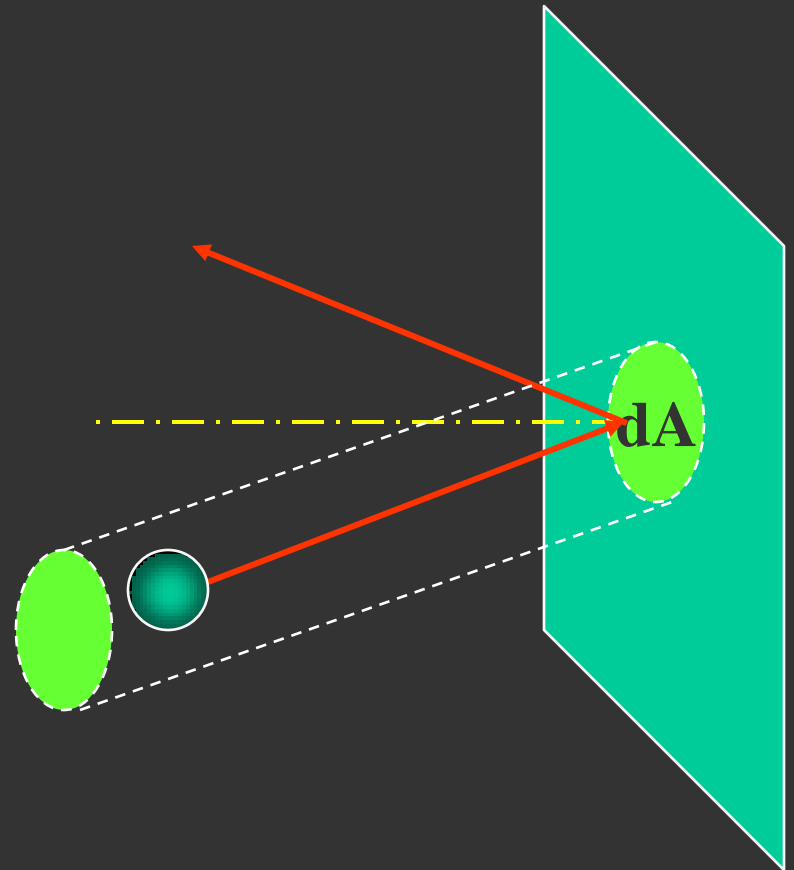
$$\frac{1}{2l_x} v_{ix} dt$$

The impulse of all the
molecule:

$$dI = \sum \frac{\mu v_{ix}^2}{l_x} dt$$

force

$$dF = \frac{dI}{dt} = \sum \frac{\mu v_{ix}^2}{l_x}$$



pressure:
$$P = \frac{dF}{A} = \sum \frac{\mu v_{ix}^2}{Al_x} = \mu \frac{N \overline{v_{ix}^2}}{V}$$

since
$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3} \overline{v^2}$$

$$P = \mu n \overline{v_x^2} = \frac{1}{3} \mu n \overline{v^2}$$

$$\therefore \bar{\varepsilon} = \frac{1}{2} \mu \overline{v^2}$$

$$P = \frac{2}{3} n \bar{\varepsilon}$$

$$\therefore P = nkT = \frac{2}{3} n \bar{\varepsilon}$$

$$\bar{\varepsilon} = \frac{3}{2} kT$$

$$\therefore \bar{\varepsilon} = \frac{1}{2} \mu \overline{v^2} = \frac{3}{2} kT$$

Root mean square speed (方均根速率) $\sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{\mu}}$

$$\therefore \frac{k}{\mu} = \frac{kN_A}{\mu N_A} = \frac{R}{M}$$

Rms speed:

$$\sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{\mu}} = \sqrt{\frac{3RT}{M}}$$

Degree of freedom 自由度

For monatomic molecule $i=3$

diatomic molecule $i=5$

molecule with atom more the three $i=6$

The equipartition theorem (能量按自由度均分原理)

The contribution of each degree of freedom to the average energy of molecule is $kT/2$

The average energy for a molecule

$$\bar{\epsilon}_k = \frac{i}{2} kT$$

For monatomic molecule $i=3$

diatomic molecule $i=5$

molecule with atom more the three $i=6$

The internal energy of ideal-gas:理想气体内能

The kinetic energy of all the molecules in the gas

$$E = \frac{m}{M} E_{mol} = \frac{m}{M} \frac{i}{2} RT$$

Where m is the mass of the gas

M is the molar mass of the gas

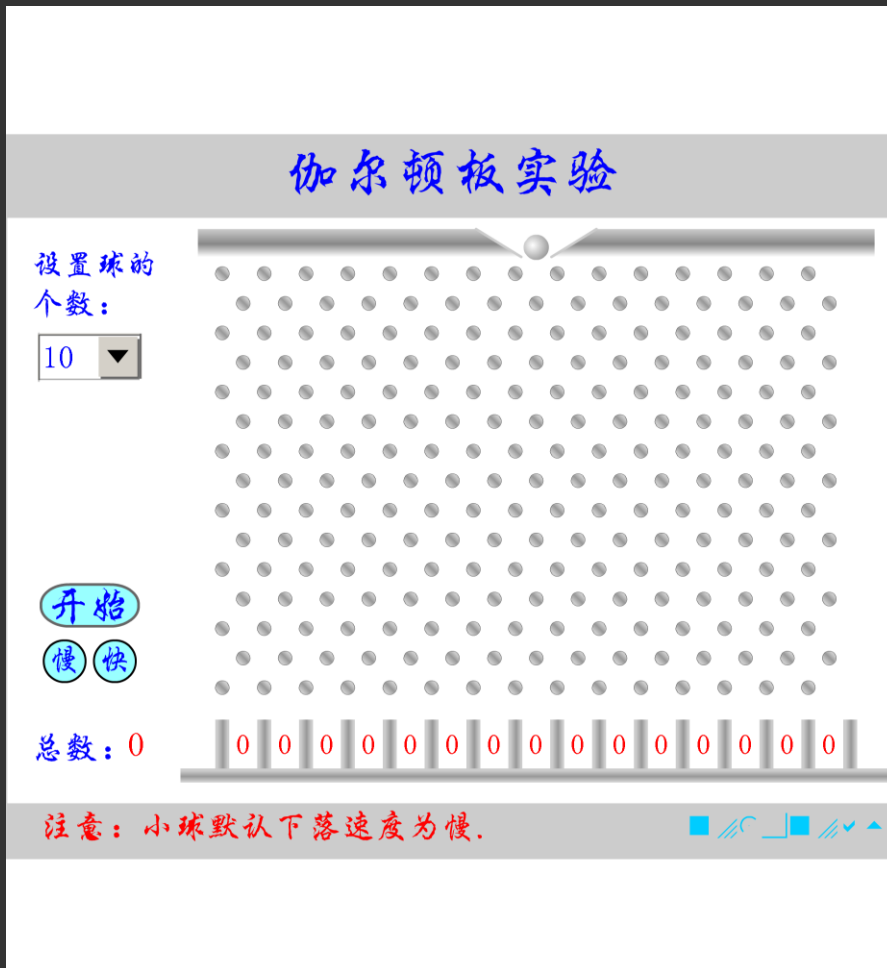
Probability distribution (概率分布)

Discrete distribution

$$P_i = \frac{N_i}{N}$$

Normalization condition (归一化条件)

$$\sum_i P_i = 1$$



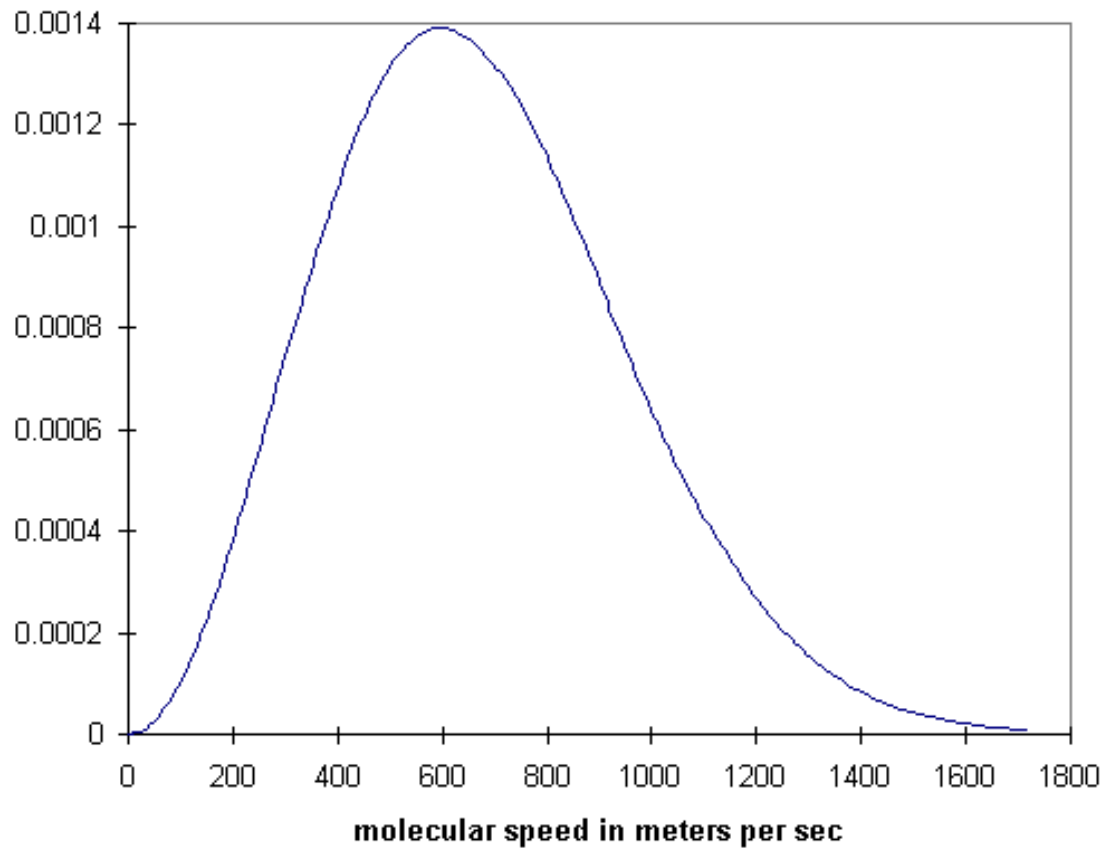
The average value

$$\bar{x} = \frac{1}{N} \sum_i x_i N = \sum_i x_i F_i$$

The average of square

$$\overline{x^2} = \frac{1}{N} \sum_i x_i^2 N = \sum_i x_i^2 F_i$$

Continuous distribution



Probability distribution function

$$f(v) = \lim_{\Delta v \rightarrow 0} \frac{\Delta N}{N \Delta v} = \frac{1}{N} \frac{dN}{dv}$$

$$f(v)dv = \frac{dN}{N}$$

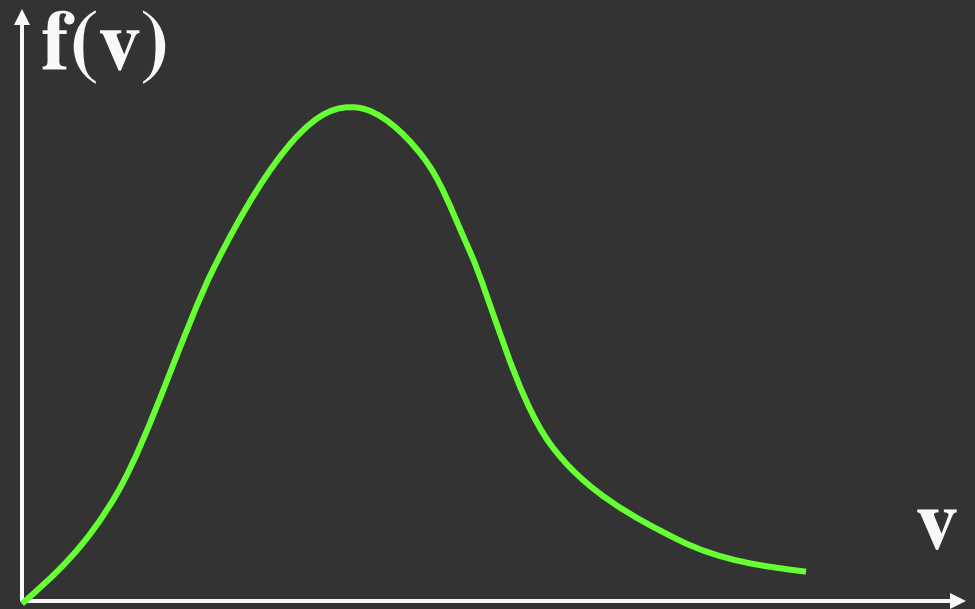
$F(v)dv$ stands for the probability of a molecule's speed is between v to $v+dv$

The Maxwell distribution (麦克斯韦速率分布函数)

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

$$f(v)dv = \frac{dN}{N}$$

$$\int_0^{\infty} f(v)dv = 1$$



The average speed: (算术平均速率)

$$\bar{v} = \frac{\int v dN}{N} = \int v f(v) dv$$

$$\bar{v} = \sqrt{\frac{8kT}{\pi\mu}} = \sqrt{\frac{8RT}{\pi M}} \approx 1.60 \sqrt{\frac{RT}{M}}$$

The most likely speed (最可几速率):

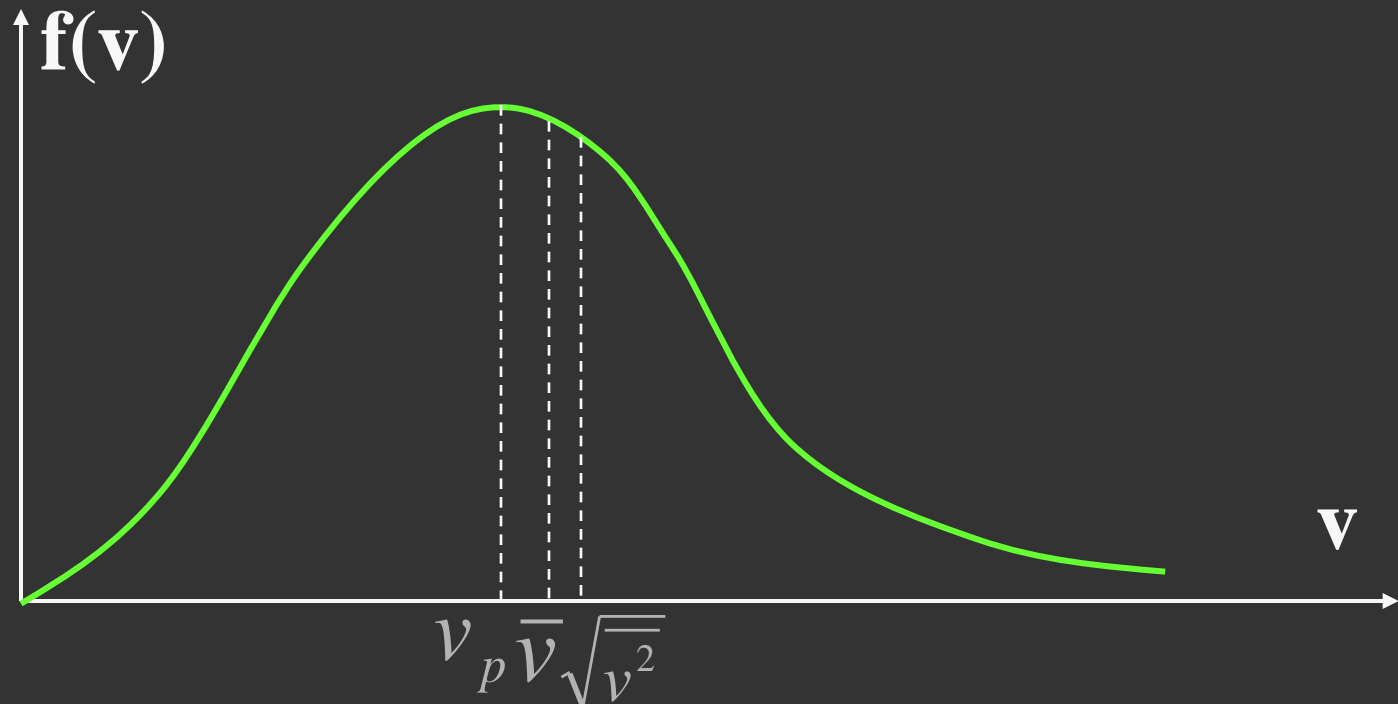
$$\frac{d}{dv} f(v) = 0$$

$$v_p = \sqrt{\frac{2kT}{\mu}} = \sqrt{\frac{2RT}{M}} \approx 1.41 \sqrt{\frac{RT}{M}}$$

The root mean square speed (方均根速率)

$$\overline{v^2} = \int v^2 f(v) dv$$

$$\sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{\mu}} = \sqrt{\frac{3RT}{M}} \approx 1.73 \sqrt{\frac{RT}{M}}$$



With the conditions given, find the number of Nitrogen molecule whose speed is from 500 to 501ms⁻¹(V=1m³)

$$T = 273.15K \quad P = 1.013 \times 10^5 \text{ Pa}$$

$$M = 28 \times 10^{-3} \text{ kg} \cdot \text{mol}^{-1}$$

solution :

$$\mu = \frac{M}{N_A} = \frac{28 \times 10^{-3}}{6.022 \times 10^{23}} = 4.65 \times 10^{-26} \text{ kg}$$

$$n = \frac{P}{kT} = \frac{1.013 \times 10^5}{1.38 \times 10^{-23} \times 273.15} = 2.7 \times 10^{25} \text{ m}^{-3}$$

$$\frac{\Delta n}{n} = \frac{\Delta N}{N} = \left(\frac{\mu}{2\pi kT} \right)^{3/2} e^{-\frac{\mu v^2}{2kT}} \cdot 4\pi v^2 \Delta v$$

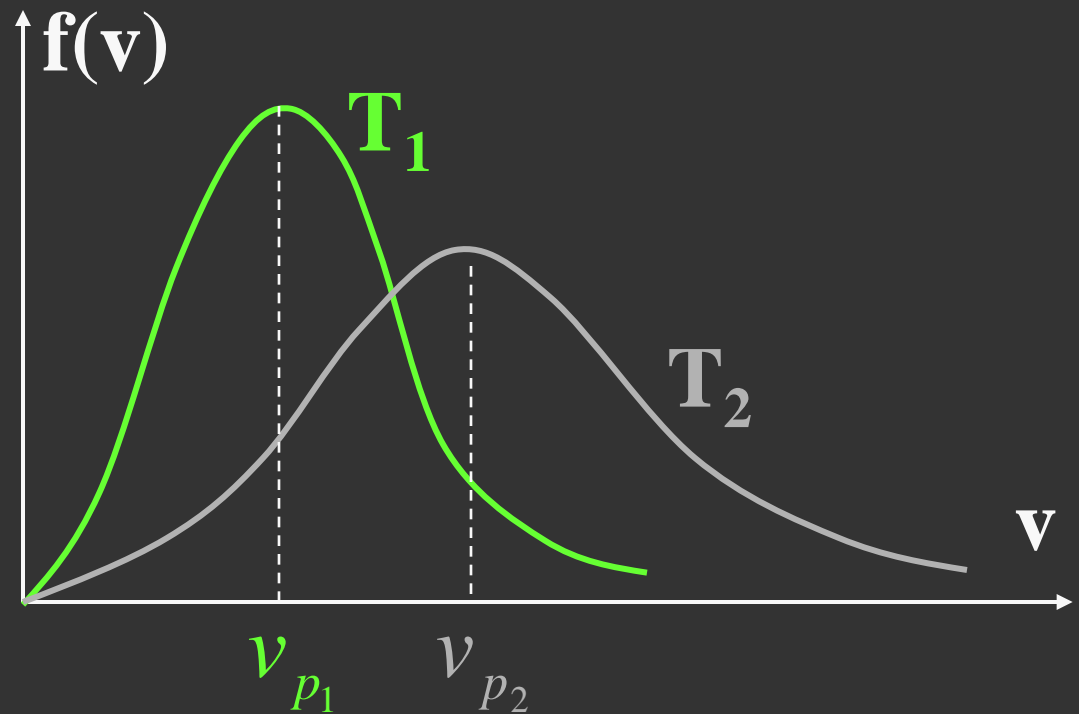
$$v = 500 \text{ m} \cdot \text{s}^{-1}, \Delta v = 1 \text{ m} \cdot \text{s}^{-1}$$

$$\frac{\Delta n}{n} = 1.85 \times 10^{-3}$$

$$\Delta n = 1.85 \times 10^{-3} \times 2.7 \times 10^{25} = 5.0 \times 10^{22} \text{ m}^{-3}$$

The maxwell distribution function of oxygen and hydrogen are given below, which one is the function for hydrogen?

$$v_p = \sqrt{\frac{2RT}{M}}$$



Maxwell-Boltzmann distribution

$$f(v) = \frac{1}{Z} e^{-\frac{E_k + E_p}{kT}}$$

$$n = n_0 e^{-\frac{\mu g z}{kT}}$$

$$\therefore p = nkT, \quad p_0 = n_0 kT$$

$$p = p_0 e^{-\frac{\mu g z}{kT}} = p_0 e^{-\frac{M g z}{RT}}$$

Maxwell-Boltzmann distribution

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Why oxygen bottles is needed in maintain climbing?

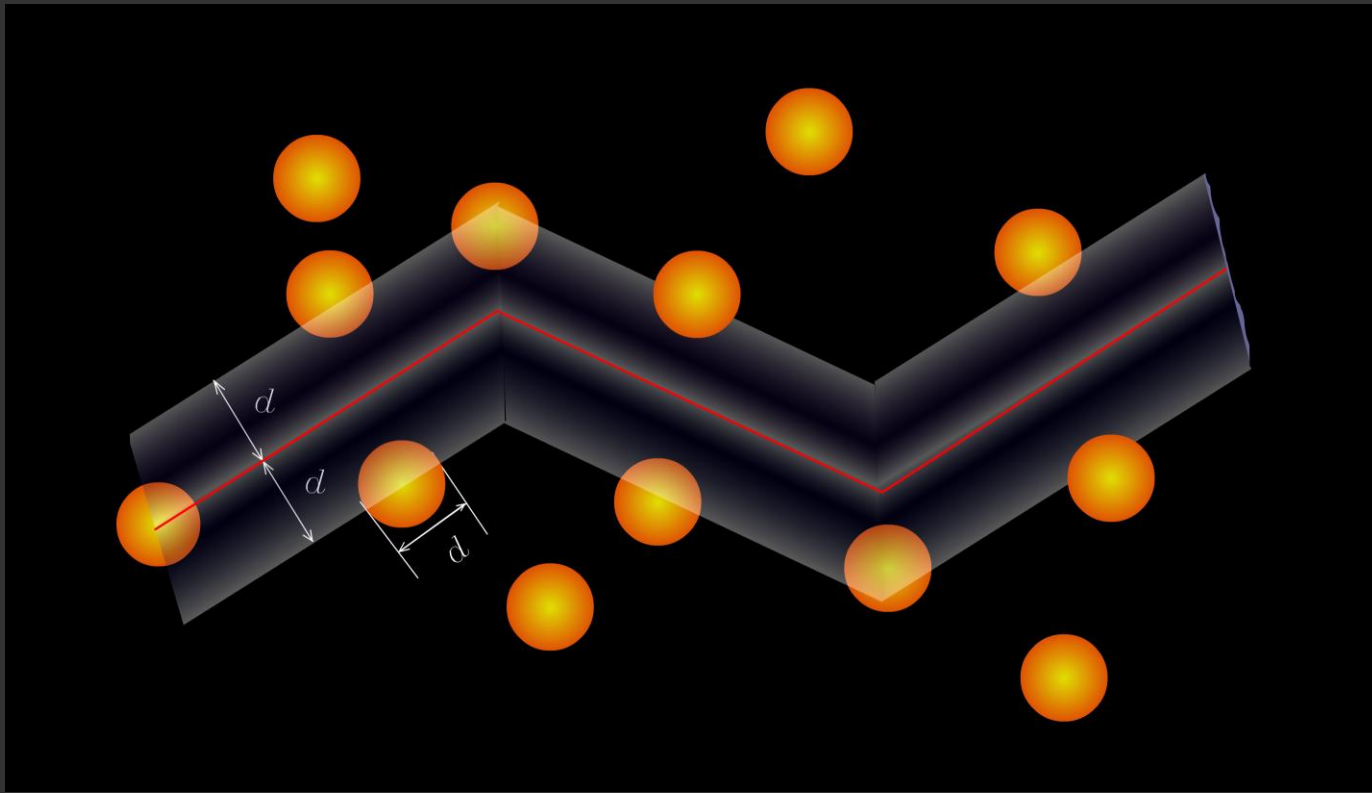
Transportation phenomena 输运现象

Mean free path (平均自由程)

The average distance a molecule may travel before the next collision

collision frequency(平均碰撞频率)

The number of collision in unit time



Diameter of molecule: d , density of molecule: n

Collision frequency: $\bar{z} = \sqrt{2\pi} d^2 n \bar{v}$

**Mean free
path:**

$$\bar{\lambda} = \frac{\bar{v}}{\bar{z}} = \frac{1}{\sqrt{2\pi} d^2 n}$$

$$\because p = nkT \quad \bar{\lambda} = \frac{kT}{\sqrt{2\pi} d^2 p}$$

**mean free path is proportional to the density of
the gas inversely**

Find the collision frequency of hydrogen gas at standard state. (the diameter of molecule $d = 2 \times 10^{-10} \text{m}$)

solution:
$$\bar{v} = \sqrt{\frac{8RT}{M\pi}} = \sqrt{\frac{8 \times 8.31 \times 273}{2 \times 10^{-3} \pi}} = 1.70 \times 10^3 \text{ m} \cdot \text{s}^{-1}$$

$$n = \frac{P}{kT} = \frac{1.013 \times 10^5}{1.38 \times 10^{-23} \times 273} = 2.69 \times 10^{25} \text{ m}^{-3}$$

$$\bar{\lambda} = \frac{1}{\sqrt{2\pi} d^2 n} = 2.14 \times 10^{-7} \text{ m}$$

$$\bar{z} = \frac{\bar{v}}{\bar{\lambda}} = 7.95 \times 10^9 \text{ s}^{-1}$$

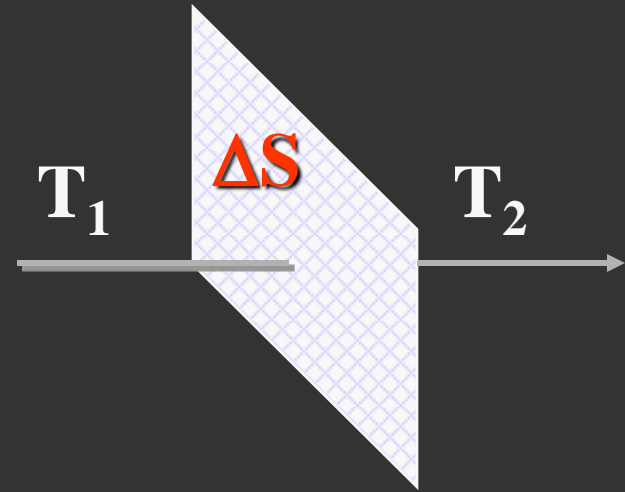
Heat conduction

The law of heat conduction (热传导方程)

$$\frac{\Delta Q}{\Delta t} = -K \frac{dT}{dx} \Delta S$$

Thermal conductivity (热导率)

$$k = \frac{1}{3} \rho \bar{v} \bar{\lambda} C_v$$

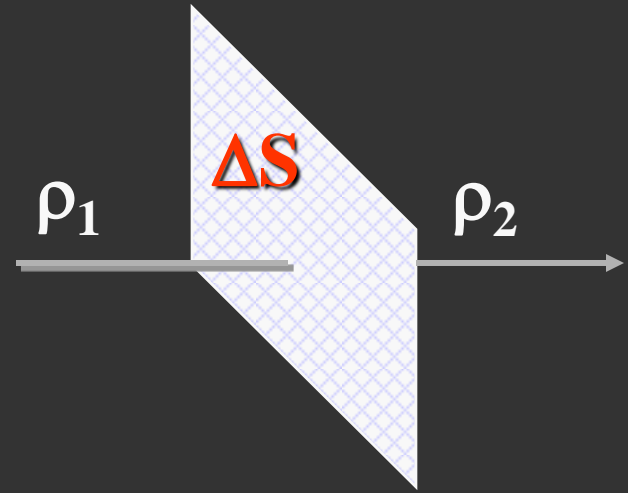


The diffusion of mass

Fick's Law

(菲克定律)

$$\frac{\Delta m}{\Delta t} = -D \frac{d\rho}{dx} \Delta S$$



Diffusion constant
扩散系数

$$D = \frac{1}{3} \bar{v} \bar{\lambda}$$