Chapter 11

Kinetic Theory of Gases (1)

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11.1 Basic Assumption

Basic assumptions of the kinetic theory

1) Large number of molecules

$$N_A = 6.02 \times 10^{26} \text{ molecules per kilomole}$$

2) Identical molecules which behave like hard spheres

3) No intermolecular forces except when in collision

Basic assumptions of the kinetic theory

4) Collisions are perfectly elastic

5) Uniform distribution throughout the container

$$n = \frac{N}{V} \qquad dN = n\,dV$$

Average # of molecules per unit volume

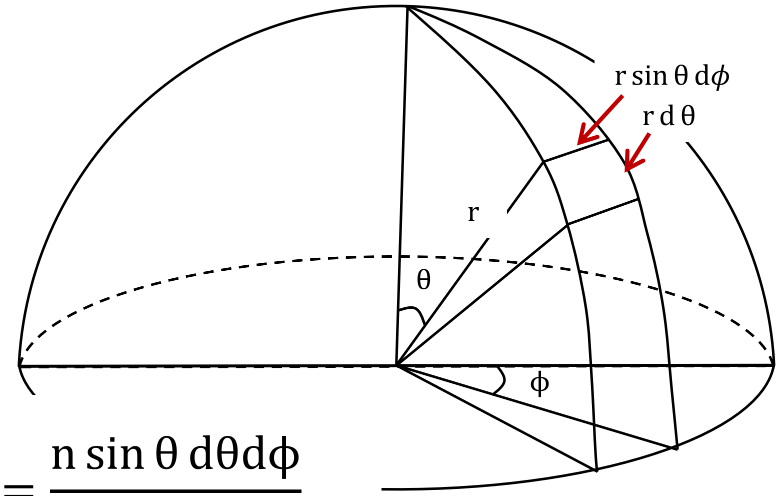
6) Equal probability on the direction of molecular velocity

average # of intersections of velocity vectors per unit area

$$\frac{N}{4\pi r^2}$$

the # of intersections in dA

$$\frac{N}{4\pi r^2}\,dA \leftarrow r^2 \sin\theta\, d\theta d\phi$$



$$= \underline{d^2N_{\theta\phi}} = \frac{N \sin\theta\, d\theta d\phi}{4\pi}, \qquad d^2n_{\theta\phi} = \frac{n \sin\theta\, d\theta d\phi}{4\pi}$$

# of molecules having velocities in a direction (θ< <θ+dθ)

(ϕ< <ϕ+dϕ)

11.1 Basic Assumption

7) Magnitude of molecular velocity : 0 ~ $\underline{\infty}$

$\uparrow$

c (speed of light)

dN_v : # of molecules with specified speed $(v < \quad < v+dv)$

11.1 Basic Assumption

- Let dN_v as # of molecules with specified speed (v<   <v+dv)
- $\int_0^\infty \mathrm{dN}_v = \mathrm{N}$
- Mean speed is $\bar{v} = \frac{1}{\mathrm{N}}\int_0^\infty v\mathrm{dN}_v$
- Mean square speed is $\overline{v^2} = \frac{1}{\mathrm{N}}\int_0^\infty v^2\mathrm{dN}_v$
- Square root of $\overline{v^2}$ is called the root mean square or rms speed:

$$v_{rms} = \sqrt{\overline{v^2}}$$

- The n-th moment of distribution is defined as

$$\overline{v^n} = \frac{1}{\mathrm{N}}\int_0^\infty v^n\mathrm{dN}_v$$

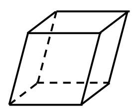
11.2 Molecular Flux

- # of molecules of a gas that strike a surface per unit area and unit time

- Molecules coming from particular direction θ, ϕ with specified speed v in time dt

  $\rightarrow \theta\phi v$ collision $\begin{cases} \theta < \quad < \theta + d\theta \\ \phi < \quad < \phi + d\phi \\ v < \quad < v + dv \end{cases}$

- # of $\theta\phi v$ collisions with dA dt

  $= \theta\phi v$ molecules in 

  $= \theta\phi$ molecules with speed v

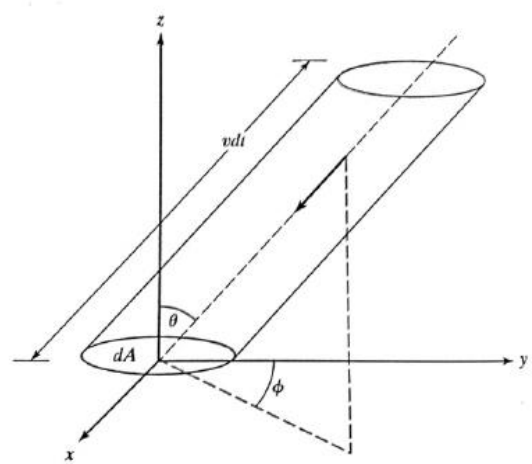
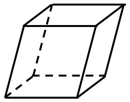


Fig. Slant cylinder geometry used to calculate
the number of molecules that strike the area dA in time dt.

11.2 Molecular Flux

- How many molecules in 

dn_v : # density between speed (v<   <v+dv)

$$\mathrm{d}^3\mathrm{n}_{\theta\phi v} = \mathrm{dn}_v \cdot \frac{dA}{A} = \mathrm{dn}_v \frac{\sin\theta \mathrm{d}\theta \mathrm{d}\phi}{4\pi}$$

$\mathrm{dV} = \mathrm{dA}\,(\mathrm{vdt}\cos\theta\,)$ ← Volume of cylinder

- # of $\theta\phi v$ molecules in the cylinder

$$\mathrm{d}^3\mathrm{n}_{\theta\phi v} dV = dA\,(v\mathrm{dt}\cos\theta\,)\mathrm{dn}_v \frac{\sin\theta \mathrm{d}\theta \mathrm{d}\phi}{4\pi}$$

- # of collisions per unit area and time

$$\frac{\mathrm{d}^3\mathrm{n}_{\theta\phi v}\mathrm{dV}}{\mathrm{dA\,dt}} = \frac{1}{4\pi} v\mathrm{dn}_v \sin\theta\cos\theta \mathrm{d}\theta \mathrm{d}\phi$$

- Total # of collisions per unit area and time

$$\frac{d^3 n_{\theta\phi v} dV}{dA\, dt} = \int_0^{2\pi} \int_0^{\pi/2} \sin\theta \cos\theta d\theta d\phi \cdot \frac{1}{4\pi} v dn_v = \frac{1}{4} v dn_v$$

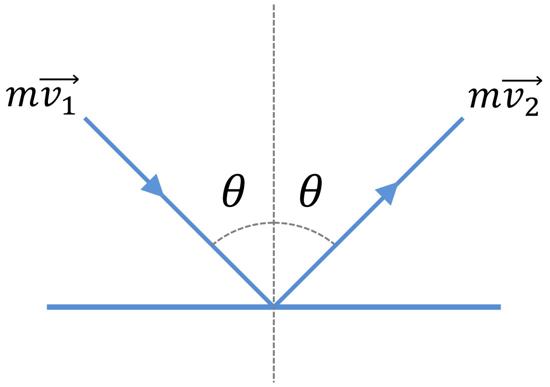
- Total # of collisions per unit area and time by molecules having all speed

$$\int_0^{\infty} \frac{1}{4} v dn_v = \frac{1}{4} n\bar{v}$$

Cf. average speed $\bar{v} = \frac{\sum \bar{v}}{N} = \frac{\sum N_i v_i}{N} = \frac{\sum n_i v_i}{\sum n_i} = \frac{\int v dn_v}{n}$

- Gas pressure in Kinetic theory

Gas pressure is interpreted as impulse flux of particles striking a surface



- Perfect elastic $v = v'$

- Average force exerted by molecules

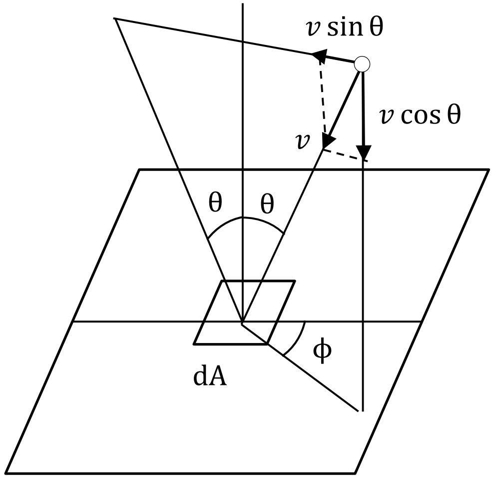
$$\mathrm{F} = \frac{\mathrm{d}(m\vec{v})}{\mathrm{dt}} = m\vec{a} + \dot{m}\vec{v}$$

- Momentum change of one molecule (normal component only)

$$mv\cos\theta - (-mv\cos\theta) = 2mv\cos\theta$$

- # of $\theta\phi v$ collisions for dA, dt

$$\frac{1}{4\pi} v \mathrm{d}n_v \sin\theta\cos\theta \mathrm{d}\theta \mathrm{d}\phi$$



- Change in momentum due to $\theta\phi v$ collisions in time dt

$$2mv\cos\theta \times \frac{1}{4\pi} v \mathrm{dn}_v \sin\theta\cos\theta \mathrm{d}\theta \mathrm{d}\phi$$

$$= \frac{1}{2\pi} mv^2 \mathrm{dn}_v \sin\theta\cos^2\theta \mathrm{d}\theta \mathrm{d}\phi \mathrm{dAdt}$$

- Change in momentum in all v collisions $0 < \theta \le \frac{\pi}{2}, 0 < \phi \le 2\pi$

$$\int_0^{\frac{\pi}{2}} \int_0^{2\pi} \frac{1}{2\pi} mv^2 \mathrm{dn}_v \sin\theta\cos^2\theta \mathrm{d}\theta \mathrm{d}\phi \cdot \mathrm{dAdt}$$

$$= \frac{1}{3} mv^2 \mathrm{dn}_v \mathrm{dAdt}$$

11.3 Gas Pressure and Ideal Gas Law

- Change in momentum from collisions of molecules at all speed

$$\frac{1}{3} m \int v^2 \, \mathrm{dn}_v = d\vec{F} \cdot dt$$

- Average pressure $\bar{P} = \frac{d\vec{F}}{dA}$

$$\frac{1}{3} m \int v^2 \, \mathrm{dn}_v = \frac{1}{3} mn\overline{v^2}$$

cf. $\overline{v^2} = \frac{\sum v^2}{N} = \frac{\int v^2 \mathrm{d}n_v}{n}$

11.3 Gas Pressure and Ideal Gas Law

$$n = \frac{N}{V}, P = \frac{1}{3}\frac{N}{V}m\overline{v^2}$$

$PV = \frac{1}{3}Nm\overline{v^2}$ cf. EOS of an ideal gas $\mathrm{PV} = \mathrm{n}\bar{R}T = \mathrm{mRT} = \frac{\mathrm{N}}{N_A}\bar{R}T = NkT$

k: Boltzmann constant

N_A : Avogadro’s number : $6.02 \times 10^{26}\ number/kmole$

k_B : Boltzmann constant : $k_B = \frac{\bar{R}}{N_A} = 1.38 \times 10^{-23} J/K$

$$PV = \frac{1}{3}Nm\overline{v^2} = NkT$$

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$$

11.4 Equipartition of Energy

- Equipartition of energy

Because of even distribution of velocity of particles,

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}, \quad \overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3}\overline{v^2} \quad \rightarrow \quad \frac{1}{2}m\overline{v_x^2} = \frac{1}{2}kT$$

It can be interpreted that a degree of freedom allocate energy of 1/2 kT

11.4 Equipartition of Energy

$$\bar{E} = \bar{E}_x + \bar{E}_y + \bar{E}_z$$

energy

$$= \frac{1}{2}m\overline{v_x^2} + \frac{1}{2}m\overline{v_y^2} + \frac{1}{2}m\overline{v_z^2}$$

$$\bar{E}_x = \frac{kT}{2}, \bar{E}_y = \frac{kT}{2}, \bar{E}_z = \frac{kT}{2}$$

11.5 Specific Heat

$$\delta q = du + \delta W$$

$$U = f \cdot \frac{1}{2} NkT$$

f: number of degrees of freedom

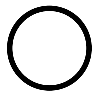
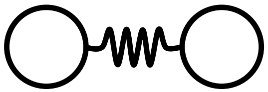
$$u = \frac{U}{N} = f \cdot \frac{1}{2} \bar{R}kT$$

$$c_v = \left.\frac{\partial u}{\partial T}\right)_v = f \cdot \frac{1}{2} \bar{R}$$

$$(n\bar{R} = Nk)$$

$$c_P = \left(\frac{\partial h}{\partial T}\right)_p = \frac{f}{2} \bar{R} + \bar{R} = \frac{(f+2)}{2} \bar{R}$$

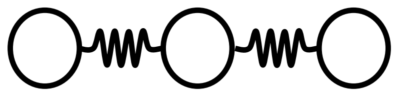
11.5 Specific Heat

Monatomic gas		$\frac{1}{2}mv_x^2, \frac{1}{2}mv_y^2, \frac{1}{2}mv_z^2$ 3
Diatomic gas		$\frac{1}{2}mv_x^2, \frac{1}{2}mv_y^2, \frac{1}{2}mv_z^2$ Translational negligible $\frac{1}{2}Iw_x^2, \frac{1}{2}Iw_y^2, \cancel{\frac{1}{2}Iw_z^2}$ 7 Rotational $\frac{1}{2}kx^2, \frac{1}{2}m\dot{x}^2$ no y,z vibration Vibrational

$$\frac{c_p}{c_v} = \frac{3+2}{3} = 1.67$$

$$\frac{c_p}{c_v} = \frac{5+2}{5} = 1.4$$

Near room temperature, rotational or vibrational DOF are excited, but not both.

Triatomic gas	**CO_2** 	translational 3 rotational 2 vibrational 4 9

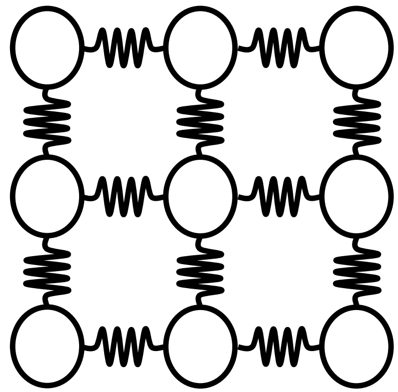
$$\frac{c_p}{c_v} = \frac{7+2}{7} = 1.28$$

- Vibration modes of CO_2

Stretch

Bending

11.5 Specific Heat

Solid		$\frac{kT}{2}$ (kinetic) $\frac{kT}{2}$ (potential) x,y,z direction $\mathrm{U} = 3NkT$ $\mathrm{c_v} = 3R$(Dulong-Petit Law)