Chapter 11

Kinetic Theory of Gases (1)

Min Soo Kim

Seoul National University

11.1 Basic Assumption

Basic assumptions of the kinetic theory

1) Large number of molecules (Avogadro's number)

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

2) Identical molecules which behave like hard spheres

3) No intermolecular forces except when in collision

4) Collisions are perfectly elastic

5) Uniform distribution throughout the container

$$\mathrm{n} = \frac{\mathrm{N}}{\mathrm{V}} \qquad \mathrm{d}N = \mathrm{ndV}$$

n: The average number of molecules per unit volume

11.1 Basic Assumption

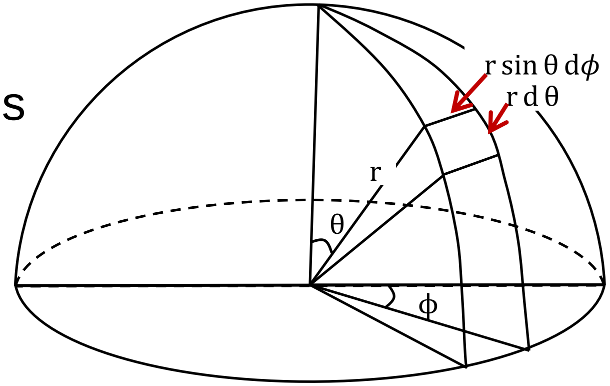
6) Equal probability on the direction of molecular velocity average number of intersections of velocity vectors per unit area; $\frac{\mathrm{N}}{4\pi \mathrm{r}^2}$

the number of intersections in dA

$$\mathrm{d}^2\mathrm{N}_{\theta\phi} = \frac{\mathrm{N}}{4\pi \mathrm{r}^2}\mathrm{d}A = \frac{\mathrm{N}\sin\theta\,\mathrm{d}\theta\mathrm{d}\phi}{4\pi} \qquad \text{Where } \mathrm{dA} = \mathrm{r}^2\sin\theta\,\mathrm{d}\theta\mathrm{d}\phi$$

$$\mathrm{d}^2\mathrm{n}_{\theta\phi} = \frac{\mathrm{n}\sin\theta\,\mathrm{d}\theta\mathrm{d}\phi}{4\pi}$$

$\mathrm{N}_{\theta\phi}$: The number of molecules having velocities in a direction ($\theta \sim \theta + \mathrm{d}\theta$) and ($\phi \sim \phi + \mathrm{d}\phi$)



11.1 Basic Assumption

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

↑

c (speed of light)

dN_v : The number of molecules with specified speed (v ~v+dv)

11.1 Basic Assumption

- Let dN_v as the number 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:

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{1}{\mathrm{N}}\int_0^\infty v^2\mathrm{dN}_v}$$

- The n-th moment of distribution is defined as

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

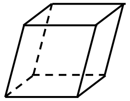
11.2 Molecular Flux

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

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

$$\rightarrow \theta\phi v \text{ collision } \begin{cases} \theta \sim \theta + d\theta \\ \phi \sim \phi + d\phi \\ v \sim v + dv \end{cases}$$

- The number of $\theta\phi v$ collisions with dA

= $\theta\phi v$ molecules in 

= $\theta\phi$ molecules with speed v

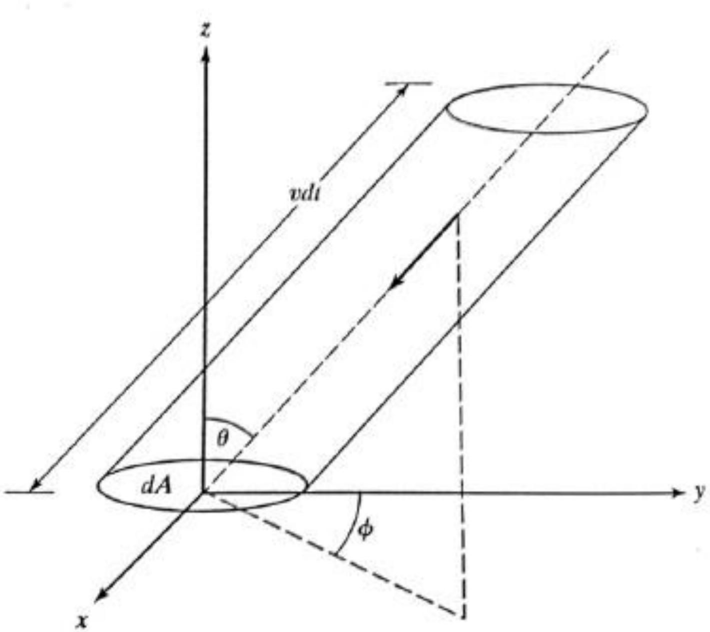
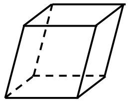


Fig. Slant cylinder geometry used to calculate the number of molecules that strike the area dA in time dt.

11.2 Molecular Flux

- How many molecules in unit volume



dn_v : Density between speed (v ~ v+dv)

dA : Surface of spherical shell of radius v and thickness dv (i.e., θ, ϕ molecules)

$$\mathrm{d}^3\mathrm{n}_{\theta\phi v} = \mathrm{dn}_v \cdot \frac{dA}{A} = \mathrm{dn}_v \frac{v^2 \sin\theta \, \mathrm{d}\theta \mathrm{d}\phi}{4\pi v^2}$$

- The number of $\theta\phi v$ molecules in the cylinder toward dA

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

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

11.2 Molecular Flux

- The number of collisions per unit area and time (i.e., particle flux)

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

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

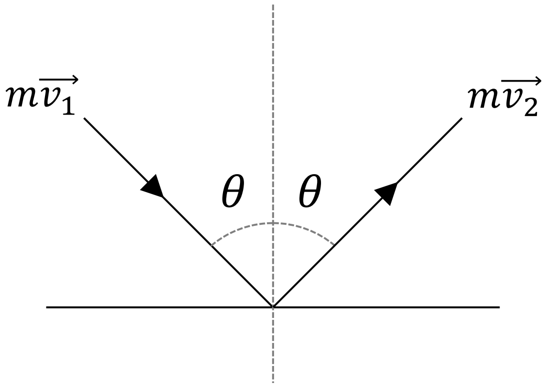
$$\int \frac{\mathrm{d^3 n_{\theta\phi\mathit{v}} dV}}{\mathrm{dA\ dt}} = \int_0^{2\pi} \mathrm{d\phi} \int_0^{\pi/2} \mathrm{sin\theta cos\theta d\theta} \ \cdot \frac{1}{4\pi} \int_0^{\infty} v\mathrm{dn}_v = \frac{\mathbf{1}}{\mathbf{4}} \boldsymbol{n\bar{v}} \quad \left(\int_0^{\infty} v\mathrm{dn}_v = n\bar{v}\right)$$

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

11.3 Gas Pressure and Ideal Gas Law

- Gas pressure in Kinetic theory

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



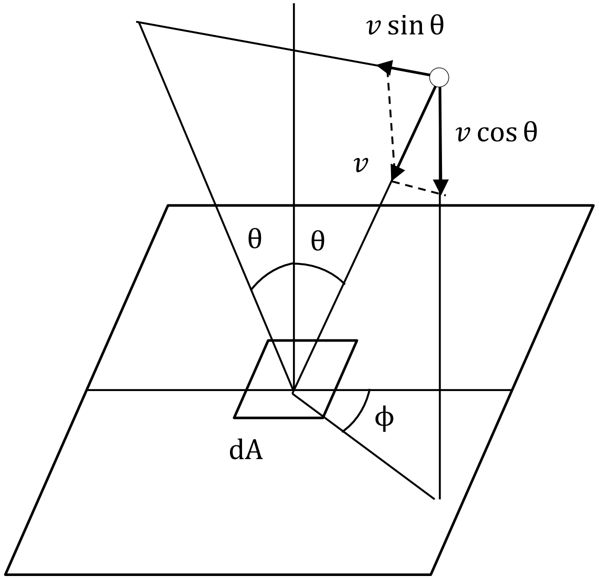
11.3 Gas Pressure and Ideal Gas Law

- Perfect elastic $v = v'$
- Average force exerted by molecules $\mathrm{F} = \dfrac{\mathrm{d}(m\vec{v})}{\mathrm{dt}} = m\vec{a} + \dot{m}\vec{v}$
- Momentum change of one molecule (normal component only)

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

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

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



11.3 Gas Pressure and Ideal Gas Law

- 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 p in all v collisions $0 < \theta \leq \frac{\pi}{2}, 0 < \phi \leq 2\pi$ at all speed

$$\mathrm{dp} = \int_0^\infty \int_0^{\pi/2} \int_0^{2\pi} \frac{1}{2\pi} \mathrm{mv}^2\mathrm{dn_v}\sin\theta\cos^2\theta\mathrm{d}\theta\mathrm{d}\phi \cdot \mathrm{dAdt} = \frac{1}{3} mn\overline{v^2}\mathrm{dAdt}$$

- Change in momentum from collisions of molecules with unit time

$$\frac{\mathrm{dp}}{\mathrm{dt}} = \mathrm{d}\vec{\mathrm{F}} = \frac{1}{3} mn\overline{v^2}\mathrm{dA}$$

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

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

$$\bar{P} = \frac{1}{3} mn\overline{v^2}$$

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11.3 Gas Pressure and Ideal Gas Law

Since $n = \frac{N}{V}$ then pressure $P = \frac{1}{3}\frac{N}{V}m\overline{v^2}$ $\therefore PV = \frac{1}{3}Nm\overline{v^2}$

EOS of an ideal gas: $\mathrm{PV} = \mathrm{n}\bar{R}T = \mathrm{mRT} = \frac{\mathrm{N}}{N_A}\bar{R}T = NkT$

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

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

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

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

The temperature is proportional to the average kinetic energy of molecule

11.4 Equipartition of Energy

- Equipartition of energy

Because of even distribution of velocity of particles,

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

By assumption, no preferred direction

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3}\overline{v^2} \quad \rightarrow \quad \frac{1}{2}m\overline{v_x^2} = \frac{1}{6}m\overline{v^2} = \frac{1}{2}kT$$

It can be interpreted that a degree of freedom allocate energy of $\frac{1}{2}kT$

11.5 Specific Heat

Total energy of a molecule in Cartesian coordinate

$$\overline{\varepsilon} = \overline{\varepsilon}_x + \overline{\varepsilon}_y + \overline{\varepsilon}_z = \frac{1}{2}m\overline{v_x^2} + \frac{1}{2}m\overline{v_y^2} + \frac{1}{2}m\overline{v_z^2} = \left(\frac{kT}{2} + \frac{kT}{2} + \frac{kT}{2}\right) = \frac{3}{2}kT$$

General expression of total energy of molecules for f –DOF (Degree of Freedom)

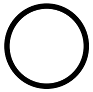
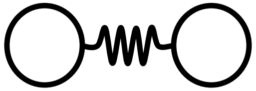
$$U = N\overline{\varepsilon} = \frac{f}{2}NkT = \frac{f}{2}nRT \quad \leftrightarrow \quad u = \frac{U}{n} = \frac{f}{2}RT$$

$c_v = \left.\frac{\partial u}{\partial T}\right)_v = \frac{f}{2}R$ from the above equation

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

The ratio of specific heat: $\gamma = \frac{c_p}{c_v} = \frac{f+2}{f}$

11.5 Specific Heat

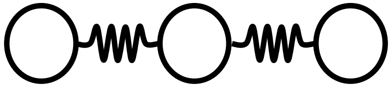
Monatomic **gas**		$\frac{1}{2}mv_x^2, \frac{1}{2}mv_y^2, \frac{1}{2}mv_z^2$ ③ **DOF**
Diatomic **gas**		$\frac{1}{2}mv_x^2, \frac{1}{2}mv_y^2, \frac{1}{2}mv_z^2$ Translational negligible $\frac{1}{2}Iw_x^2, \frac{1}{2}Iw_y^2, \cancel{\frac{1}{2}Iw_z^2}$ Rotational ⑤ **DOF** $\frac{1}{2}kx^2, \frac{1}{2}m\dot{x}^2$ 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. DOF: 7 → 5

11.5 Specific Heat

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

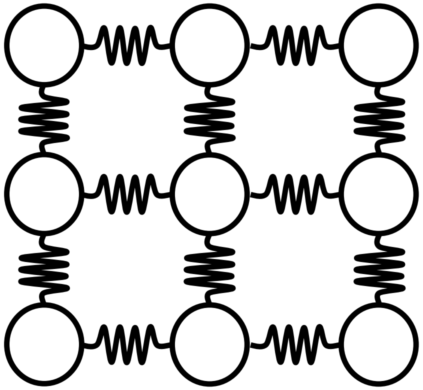
$$\frac{c_p}{c_v} = \frac{7+2}{7} = 1.28$$

- Vibration modes of CO_2

Stretch

Bending

11.5 Specific Heat

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