Chapter 6

Thermal motion ⇒ diffusion
at $T > 0K$, kinetic energy ⇒ ∴ motion

Solids, Crystals ⇒ mostly vibration. Bonding too strong

Biased motion ⇐ Apply a force
e.g. gravity — sedimentation $\vec{E}$ field - electrophoresis

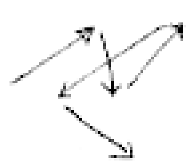
viscosity opposes motion (friction)

Why study?

1) Applications: centrifugation, electrophoresis
2) Diffusion: a) mixing, etc
b) reaction rates (!)

Back to GASES — Why? They're easy!
Billiard ball - like — ideally

Collisions re-direct.



Elementary Physics

mass ↘ velocity ↘

$$\text{Kinetic Energy (KE)} = U = \tfrac{1}{2} m \vec{u}^2$$

$$\text{Force} = \vec{f} = m\vec{a} = \frac{d(m\vec{u})}{dt}$$

mass ↗ acceleration ↑

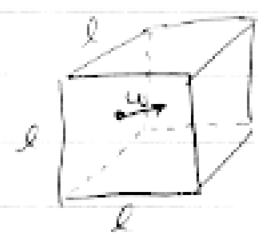
Vectors: f, a, u

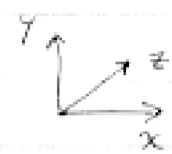
speed = | magnitude of velocity | $= \sqrt{\vec{u} \cdot \vec{u}}$

Back to Chemistry

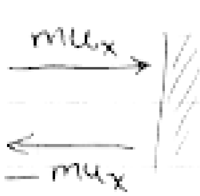
Pressure = collisional force / area $\quad A \sim l^2$

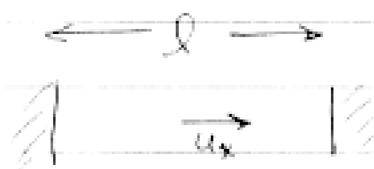
For one molecule in a cube of size l





$$f_x = \frac{\Delta(mu)}{\text{collision}} \times \frac{\text{collision}}{\text{sec}} \Leftarrow \frac{d(mu)}{dt}$$





Collisions/sec on one wall $= \dfrac{u_x}{2l}$

$$\frac{\Delta(mu)}{\text{collision}} = 2mu_x$$

$$\therefore \quad f_x = (2mu_x)\left(\frac{u_x}{2l}\right) = \frac{mu_x^2}{l}$$

$$\text{Pressure} = \frac{f}{A} = \frac{\frac{mu_x^2}{\ell}}{\ell^2} = \frac{mu_x^2}{\ell^3} \quad \text{for } \underline{\text{one}} \text{ molecule}$$

<u>Now, for N molecules</u>

$$F_x = \sum_{i=1}^{N} F_{x_i} = \sum_{i=1}^{N} \frac{m_i u_{x_i}^2}{\ell}$$

FOR <u>IDENTICAL</u> molecules

$$F_x = \frac{m}{\ell} \sum_{i=1}^{N} u_{x_i}^2$$

$$P = P_x = \frac{F_x}{\ell^2} = \frac{m}{\ell^3} \sum_{i=1}^{N} u_{x_i}^2 = \frac{m}{V} \sum_{i=1}^{N} u_{x_i}^2$$

<u>MEAN-SQUARE VELOCITY</u> (x-component)

$\langle \; \rangle \Leftarrow$ average

$$\langle u_x^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} u_{x_i}^2$$

$$\therefore \quad P_x = \frac{Nm}{V} \langle u_x^2 \rangle$$

FOR THE 3D <u>vector</u>

$$u_i^2 = u_{x_i}^2 + u_{y_i}^2 + u_{z_i}^2$$

$$\frac{1}{N} \sum u_i^2 = \frac{1}{N} \sum u_{x_i}^2 + \frac{1}{N} \sum u_{y_i}^2 + \frac{1}{N} \sum u_{z_i}^2$$

mean-squared speed

Define $\langle u^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} u_i^2$ ~~Pythag to each component~~

So $\langle u^2 \rangle = \langle u_x^2 \rangle + \langle u_y^2 \rangle + \langle u_z^2 \rangle$

For truely random motion,

$$\langle u_x^2 \rangle = \langle u_y^2 \rangle = \langle u_z^2 \rangle$$

$$\therefore \quad \langle u_x^2 \rangle = \frac{1}{3} \langle u^2 \rangle$$

Now $P = \frac{Nm}{V} \frac{1}{3} \langle u^2 \rangle \Leftarrow$ Cool P vs. $\langle u^2 \rangle$

IDEAL $\Rightarrow \quad PV = \underbrace{\frac{1}{3} N m \langle u^2 \rangle = nRT}$

$$RT = \frac{1}{3} \frac{N}{n} m \langle u^2 \rangle \qquad \frac{N}{n} = \frac{\#\text{ molec}}{\text{mole molec}} = N_0$$

$$= \frac{1}{3} N_0 m \langle u^2 \rangle$$

$$= \frac{2}{3} \Big(\underbrace{\frac{1}{2} (m N_0) \langle u^2 \rangle}_{\text{Kinetic Energy per mole}} \Big)$$

$$RT = \frac{2}{3} \underbrace{\langle U_{tr} \rangle}_{\text{average translational energy}}$$

$$\langle U_{tr} \rangle = \frac{3}{2} RT$$

Kinetic Energy of an Ideal Gas is a Function of Temperature only.