Molecular Kinetic Energy and Potential Energy

(a) Translational motion (x, y, z)
(b) Rotational motion
(c) Vibrational motion
(d) Intramolecular potential
(e) Intermolecular potential

- Measured properties ⇒ [P, V, T]
- Fundamental to 1st & 2nd law [U, S]
- Derived [H, A, G]

Internal – stored within the molecules

Molecular interpretation of pressure

Temperature and internal energy are related
$\bar{e}$ molecular $KE \propto T$

① For each molecule, we can assign thermal energy as KT
② Each translational mode has ½ KT assigned or contributing to internal Energy.

For a monoatomic gas (like argon, Helium) ⇒ no vibration or rotation, only translational

$$U \approx \frac{3}{2}KT \left[3 \text{ dimensions of } \tfrac{1}{2}KT,\ x, y, z \right].$$

where K is Boltzman constant ⇒ $\frac{R}{M_{AV}} = \frac{\text{Universal gas constant}}{M_{\text{Avogadro}}}$

Refer to Fig 1.4
As we increased the temp, we have increased the distribution of the velocity of molecules. [Higher number of molecules with higher velocity than at a lower energy]

↑ Temp → ↑ energy

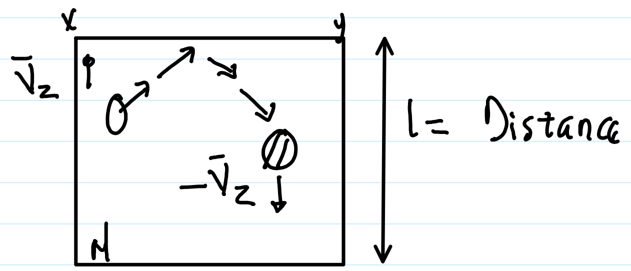
$$\frac{1}{2} m V_2^2 = U$$

if V is infinite, U should be infinite but it is not for a single molecule.

Molecular Interpretation of Pressure

Consider an ideal gas obtained in a constant volume container

$A \equiv$ Cross-sectional Area



Volume $= A \times l$

- Container has M no of Molecules
- pressure $= \frac{F}{Area} = \frac{Mass \times acceleration}{Area}$

$$= \underbrace{\frac{1}{A}\frac{d}{dt}\underbrace{(m\bar{V})}_{\text{Momentum}}}_{\text{Rate of Change of Momentum}} \quad + \text{rate of Change of Momentum}$$

Change in Momentum per collision of a molecule hitting the top Surface of Container

$$\left[(m\bar{V}_z) - (m(-\bar{V}_z))\right] = 2m\bar{V}_z$$

where 'm' is the mass of a Single Molecule

- Number of collision the molecule can have in a second

$$= \left(\frac{V_z}{l}\right)$$

- Total no of collision occuring in a second $\equiv M$

$$\sum_{i=1}^{M}(\text{event})$$

$$\frac{d}{dt}(mV_z) = \left[\begin{matrix}\text{Change in Momentum}\\ \text{per collision}\end{matrix}\right] \times \left[\begin{matrix}\text{No of collision}\\ \text{Per Second}\end{matrix}\right]$$

$$= \left[2m\bar{V}_z\right] \times \left[V_z/l\right]$$

rate of change of Momentum due to M molecules colliding with wall

$$M\frac{d}{dt}(mV_z) = \sum^{M} 2mV_z^2$$

rate of change of momentum due to N molecules colliding with wall

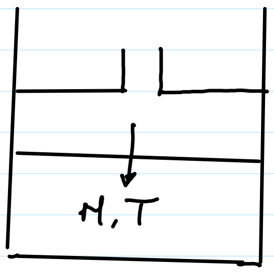
$$\sum_{i=1}^{N}\frac{d}{dt}(mV_z)=\sum_{i=1}^{N}\frac{2mV_z^2}{l}$$

Total force experienced = $\sum_{i=1}^{N}(2mV_z)\frac{V_z}{l}$

Pressure = $\frac{1}{A}\sum_{i=1}^{N}(2mV_z)\left(\frac{V_z}{l}\right)$

$$=\sum_{i=1}^{N}(2mV_z)\times\frac{V_z}{\forall}\longrightarrow \text{Volume}$$

(a) Isothermal Compression



Constant

N ✓

T ✓ ⇒ V_z is constant

but ∀ is changing (volume)

$$P=\underbrace{\sum_{i=1}^{N}(2m\bar{V}_z)}_{\text{Change in momentum per collision}}\underbrace{\left(\frac{\bar{V}_z}{A\times l}\right)}_{\text{No of collisions}}\longrightarrow\forall$$

Pressure is related to change in momentum per collision and number of collisions

$PV=nRT$

$P=\frac{nRT}{V}$ } This cannot help explain the molecular change

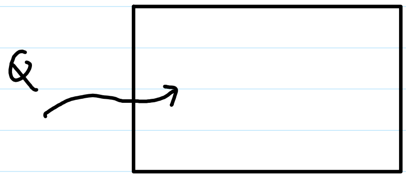
(b) Isochoric heat addition (constant volume)

Constant

∀ ✓

N ✓

but V_z is changing



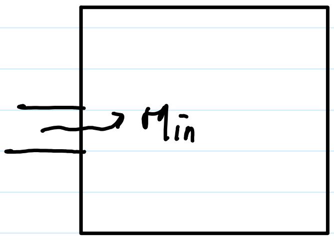
↑ V_z ⇒ momentum per collision ↑

⇒ Number of collision ↑

T ↑ V_z ↑ Change in Momentum ↑ Number of Collision ↑

per collision

(c) Isochoric, Isothermal mass addition



T is constant
$\forall_z$ is constant
m is constant (mass per molecule)
$\Rightarrow$ Increase in total number of molecules M

$$P = \boxed{\sum_{i=1}^{M}} (2mV_z) \times \left(\frac{V_z}{\forall}\right)$$

This is what leads to increase in pressure,
M↑, P↑